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Recent Advances in the Design and Coordination Chemistry of Heteroscorpionate Ligands Bearing Stereogenic Centres

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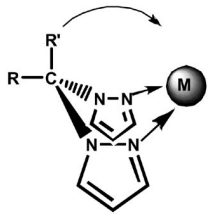
This review concerns the recent studies carried out by our research group and others aimed at the design of heteroscorpionate ligands based on bis(pyrazol-1-yl)methane-containing stereogenic centres. The capability of these systems to stabilize chiral complexes from early to late transition metals, through their behaviour as multidentate hybrid ligands, is also described.

1. Introduction

In the last few years the design of heteroscorpionate ligands derived from bis(pyrazol-1-yl)methane has been extended because these systems can be adapted to a range of metals, can be sterically and electronically tuned and constitute a useful type of multidentate hybrid ligand.[1] In this field, our research group and others have developed efficient synthetic methodologies for the synthesis of this type of ligand; for example our method consists of the deprotonation of bis(pyrazol-1-yl)methanes at the methylene group with *n*BuLi followed by an insertion reaction with different classes of heterocumulene molecules, such as carbon dioxide, carbon disulfide and fulvenes, into the lithium–carbon bond to yield lithium salts of these ligands. These lithium compounds are excellent reagents as precursors for the preparation of heteroscorpionate-containing metal complexes (Scheme 1).



Scheme 1.

These compounds have been widely employed with different metals to stabilize complexes where, in general, the metal centre is facially capped by the tridentate heteroscorpionate ligand. Furthermore, the synthesis of chiral ligands of high enantiopurity is an important goal in organometallic chemistry in order to prepare metal-based reagents from efficient asymmetric processes.[2] Unfortunately this aspect often proves arduous, severely hampering the optimization of the asymmetric processes.[3] Our group and others have recently undertaken the design of chiral heteroscorpionates based on bis(pyrazol-1-yl)methane and an in-depth account of these studies into the synthesis and characterization of metal complexes with this class of ligands is presented.

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2. Discussion

2.1. Synthetic Strategies Employed in the Preparation of the Different Classes of Heteroscorpionate Ligands Based on Bis(pyrazol-1-yl)methane-Containing Stereogenic Centres

Chiral heteroscorpionate ligands derived from bis(pyrazol-1-yl)methane have been prepared by three different methods: (a) The use of two different pyrazolyl donor groups bound to the carbon-bridge atom. This method leads to racemic mixtures of bis(pyrazol-1-yl)acetate tripod ligands. (b) The use of an enantiopure heterocycle to obtain a bis(pyrazol-1-yl)methane or a carbonyl- or sulfinylbis(pyrazole) and subsequent introduction of the third coordinating moiety at the methylene bridge. (c) The third method corresponds to the introduction of chirality in the substituent bound to the methyne bridge.

2.1.(a) Introduction of Chirality Through the Use of Two Different Pyrazole Rings

One of the first routes to synthesize new chiral heteroscorpionate ligands based on bis(pyrazol-1-yl)methane involved the design of new unsymmetrical bis(pyrazol-1-yl)-

methanes with different substituted pyrazole rings, which were subsequently used as the starting materials. Two different synthetic pathways to prepare this type of precursor have been reported. The first approach, which is the most convenient, is based on the synthesis of bis(3,5-dimethylpyrazol-1-yl)methane and was published by Elguero et al.[4] In this method the unsymmetrical (3,5-diphenylpyrazol-1-yl-3′,5′-dimethylpyrazol-1-yl)methane[5] (dpmpzm) and (3,5-di-*tert*-butylpyrazol-1-yl-3′,5′-dimethylpyrazol-1-yl)-methane[6] (bpm$^{t\mathrm{Bu2,Me2}}$) were obtained by a one-step phase-transfer-catalyzed reaction of 3,5-dimethylpyrazole with 3,5-diphenylpyrazole or 3,5-di-*tert*-butylpyrazole, dichloromethane, a base and tetrabutylammonium bromide (TBAB) (Scheme 2).

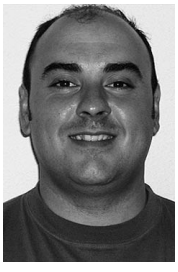
The compound dpmpzm was separated by exploiting differences in solubility between the three possible products and it could be isolated in up to 25% yield from the reaction mixture. However, the compound bpm$^{t\mathrm{Bu2,Me2}}$ was isolated by column chromatography on silica gel in up to 17% yield from the reaction mixture.

Antonio Otero was born in Minglanilla (Cuenca), Spain in 1949. He obtained his graduate degree in 1973 from the University of Murcia and his Doctorate in 1976 with Prof. Pascual Royo. From 1978–1979 he worked as a postdoctoral fellow at the University of Oxford with Prof. Malcolm Green researching C–H bond activation processes from cyclopentadienyl molybdenum and tungsten organometallic complexes. From 1979 to 1989 he was a lecturer at the University of Alcalá. In December 1989 he was appointed Full Professor in Inorganic Chemistry at the University of Castilla-La Mancha. He has authored more than 200 publications in reviewed journals. His current research interests include organometallic chemistry of early transition metals, particularly of group-3, -4 and -5 elements, homogeneous catalytic processes of olefin polymerization and ring-opening polymerization (ROP) of polar monomers.

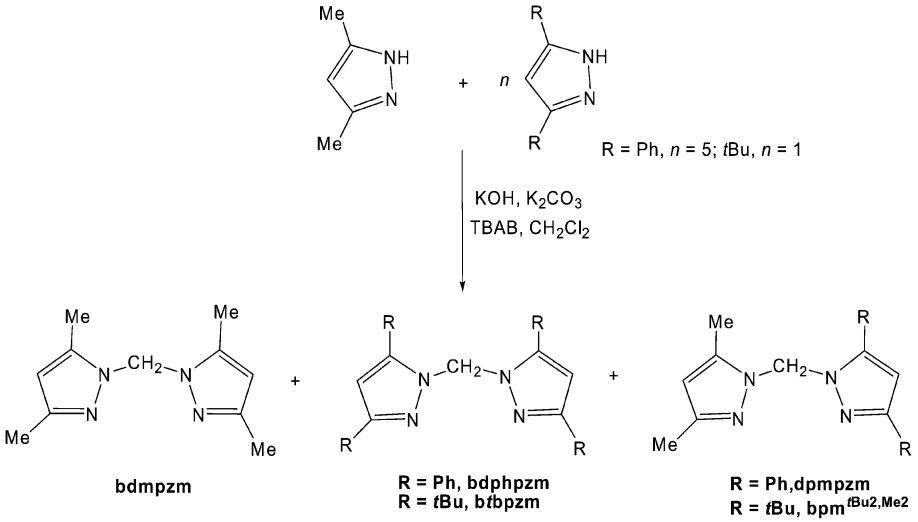
Juan Fernández-Baeza was born in 1961 in Molina de Segura (Murcia), Spain, and studied chemistry at the University of Murcia, where he obtained his graduate degree in 1984 and his Doctorate in 1989, both in organometallic chemistry under the supervision of Prof. Jose Vicente. After postdoctoral research on hydrides and C–H bond activation processes from ruthenium complexes with B. Chaudret at Laboratoire de Chimie de Coordination du CNRS he took up a lecture position at the University of Castilla-La Mancha in 1992. His research interests include the ligand design for reactive organometallic complexes.

Agustín Lara-Sanchez was born in La Solana, Spain in 1972, and studied chemistry at the University of Castilla-La Mancha, where he received his Diploma in 1995 and his doctoral degree in 1999, both in inorganic chemistry under the supervision of Prof. Antonio Otero and Dr. Juan Fernández-Baeza. He worked with Prof. Manfred Bochmann at the University of East Anglia, Norwich (UK), as a post-doctoral research Marie Curie Fellow (2001). He has been a Lecture Professor at the University of Castilla-La Mancha since 2004. His current research interests include the ligand design for reactive organometallic complexes of early transition metals, particularly of group-3 and lanthanide elements, homogeneous catalytic processes of olefin polymerization and ring-opening polymerization (ROP) of cyclic esters such as lactones and lactides to yield biodegradable and biocompatible polymers.

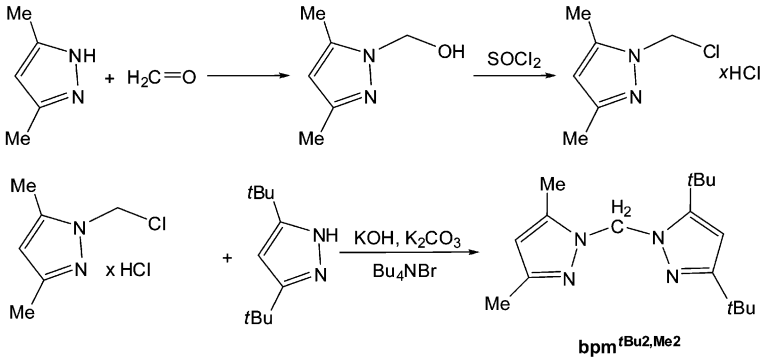
Juan Tejeda was born in Madrigalejo (Cáceres), Spain, in 1960. He obtained his graduate degree in 1984 from the University Complutense of Madrid, Spain, and his PhD. in 1992 from the University of Castilla-La Mancha, Spain, under the supervision of the Profs. Enrique Díez-Barra and Antonio de La Hoz. From 1992 to 1993 he worked as a postdoctoral application at the "Laboratoire de Chimie de Coordination", CNRS, in Toulouse, France, with Prof. Guy Bertrand studying the preparation of anti-aromatic derivatives bearing a phosphorus atom. From 1990 to 1997 he was a teaching assistant at the University of Castilla-La Mancha, Spain. In March 1997 he was appointed lecturer at the University of Castilla-La Mancha. His current research interests include the chemistry of metalodendrimers bearing 1,2,4-triazole rings on the periphery that can coordinate transition metals and the study of their catalytic properties.



Luis Fernando Sánchez-Barba was born in Valdepeñas (Spain) in 1975. From 1993 to 1997 he studied chemistry at the Facultad of Ciencias Químicas de Ciudad Real. Then he joined the group of Prof. Antonio Otero at the University of Castilla-La Mancha (Spain), where he received his MS in inorganic chemistry in 1998, and obtained his PhD in 2002 for his work on the studies of new group-4 and -5 complexes with heteroscorpionate systems. After working as an Assistant Lecturer at the University of Rey Juan Carlos (URJC, Madrid) with Prof. Mariano Fajardo in 2003, he moved as a Marie Curie fellow to the School of Chemical Sciences and Pharmacy in Norwich (England) with Prof. Manfred Bochmann, and worked on the production of advanced macromolecular architectures and functional materials via lanthanide catalysis. Since 2006 he has been working as a Lecture Professor at the Inorganic and Analytical Chemistry Department of the URJC. His main research interests are the design and synthesis of new group-2 (and analogous) complexes applied to the ring-opening polymerization of cyclic esters, and more recently he has focused on the development of polymeric biomaterials via group-2 heteroscorpionate catalysts.



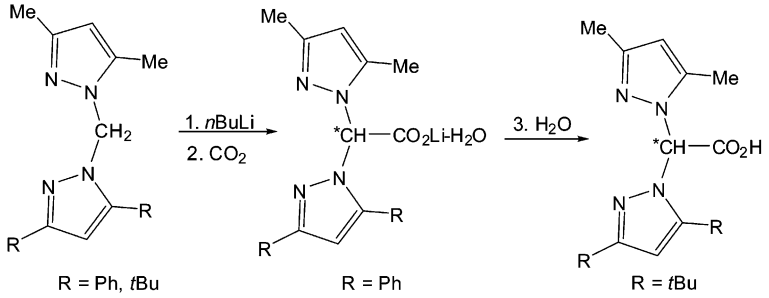
Scheme 2.



Scheme 3.

The second route is more challenging and has only been reported to prepare and isolate bpm^{tBu2,Me2}.[6] This method involves a phase-transfer-catalyzed reaction of 1-chloromethyl-3,5-dimethylpyrazole hydrochloride with 3,5-di-*tert*-butylpyrazole under basic conditions (Scheme 3).

On the basis of the early procedure published by us[7] for the synthesis of [{Li(bdmpza)(H_2O)}$_4$], the deprotonation process at the methylene group of dpmpzm and bpm^{tBu2,Me2} with *n*BuLi, followed by treatment with carbon dioxide, yielded a racemic mixture of the new chiral *NNO*-scorpionate ligands as a lithium salt for [{Li(dpmpza)(H_2O)}$_4$] [dpmpza = (3,5-diphenylpyrazol-1-yl-3′,5′-dimethylpyrazol-1-yl)acetate] in a yield of up to 96% and as a carboxylic acid for compound bpaH^{tBu2,Me2} [bpaH^{tBu2,Me2} = (3,5-di-*tert*-butylpyrazol-1-yl-3′,5′-dimethylpyrazol-1-yl)acetic acid] in a yield of up to 53% (Scheme 4).



Scheme 4.

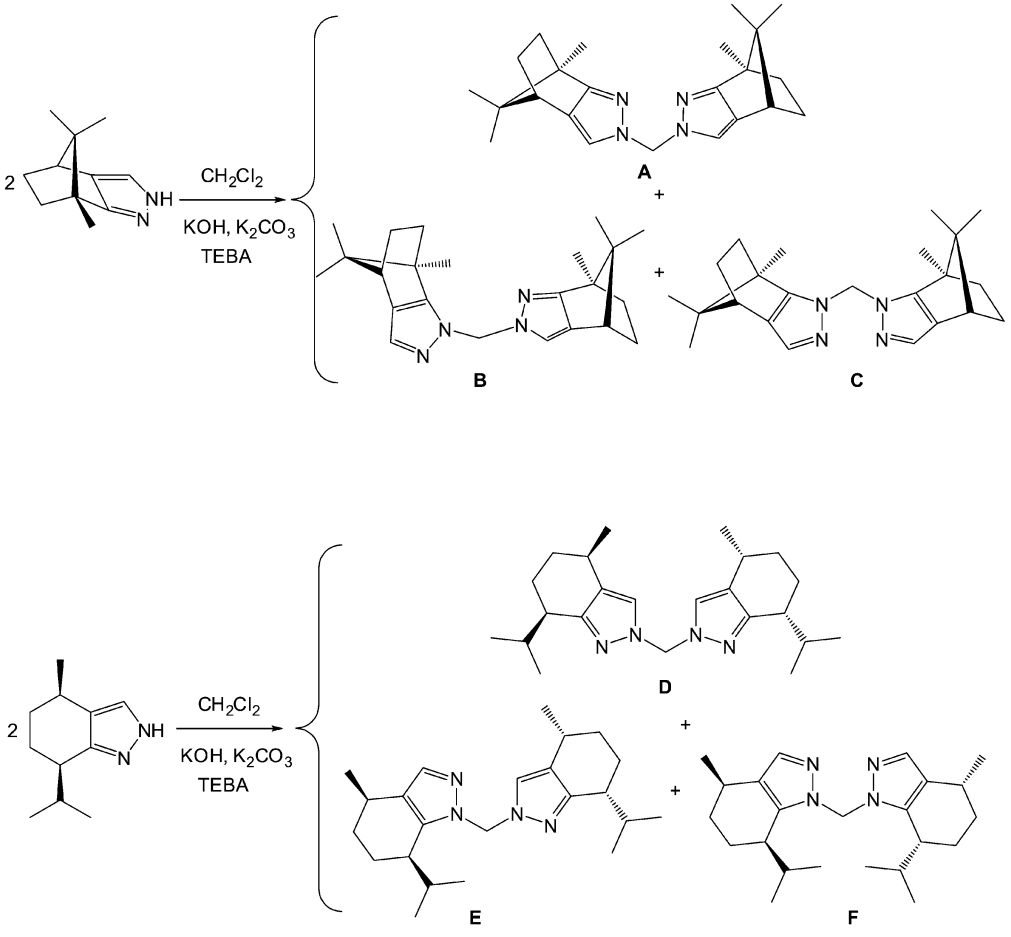
In these compounds the bridging carbon atom is a chiral centre and the presence of the corresponding two enantiomers has been confirmed in solution and in the solid state.

2.1.(b) Introduction of Chirality by the Use of Enantiopure Chiral Pyrazole Rings

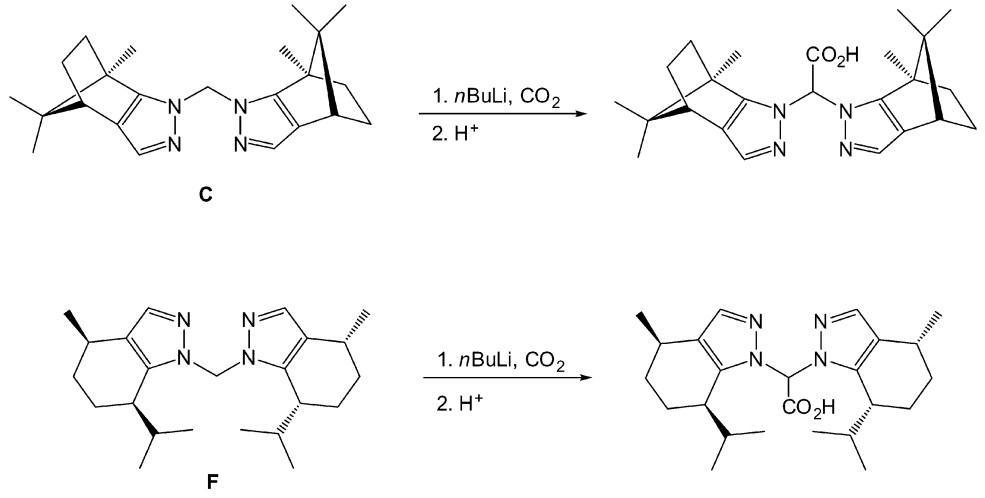
Burzlaff and Hegelmann reported a new approach to obtaining enantiopure facially-binding tripod ligands from C_2-symmetric precursors.[8] A chiral C_2-symmetric bidentate ligand results when two identical enantiopure donor groups Y* are connected by a tetrahedral bridging atom. If any additional donor group Z is attached to the tetrahedral bridging atom a homochiral tripod ligand can be obtained without any additional separation of enantiomers or diastereoisomers. Inversion of the configuration at the tetrahedral bridging atom yields identical compounds. This methodology was used to obtain a series of enantiopure chiral C_2-symmetric bis(pyrazol-1-yl)methane derivatives by the treatment of CH_2Cl_2 with a pyrazole ring fused to camphor[8] or menthone[9] in a two-phase system (Scheme 5). In both cases, the three possible structural isomers were obtained but only one isomer (C or F) could exclusively be deprotonated at the methylene bridge with *n*BuLi. The other isomers would also be deprotonated at the pyrazole C5 atom because of the absence of substituents on this carbon atom.[10] After isolation the compounds were deprotonated with *n*BuLi and the subsequent treatment with carbon dioxide and acidic workup yielded tripodal and enantiopure bis(pyrazol-1-yl)acetic acid derivatives in a yield of about 60% (Scheme 6).[8,9]

An enantiopure *NNO*-scorpionate ligand was recently synthesized by Burzlaff et al.[11] using the C_2-symmetric 2,2′-carbonyl(camphorpyrazole) or 2,2′-sulfinylbis(camphorpyrazole) compounds. The reaction of camphorpyrazole with triphosgene under reflux in toluene or benzene gave only the C_2-symmetrical compound in very high yield (Scheme 7). When the reaction was performed with triphosgene and triethylamine in diethyl ether the C_1-symmetrical isomer 1,2′-carbonyl(camphorpyrazole) was obtained first and this was then transformed into the C_2-symmetrical compound upon standing in solution for several days. The *NNO*-tripodal ligand (*o*-hydroxyphenyl)bis(camphorpyrazol-1-yl)methane was synthesized by treatment with salicylaldehyde and pyridine in reproducible yields of up to 70%. The cobalt-catalyzed ($CoCl_2$) reaction gave the same product but with quite erratic yields (ca. 30%).

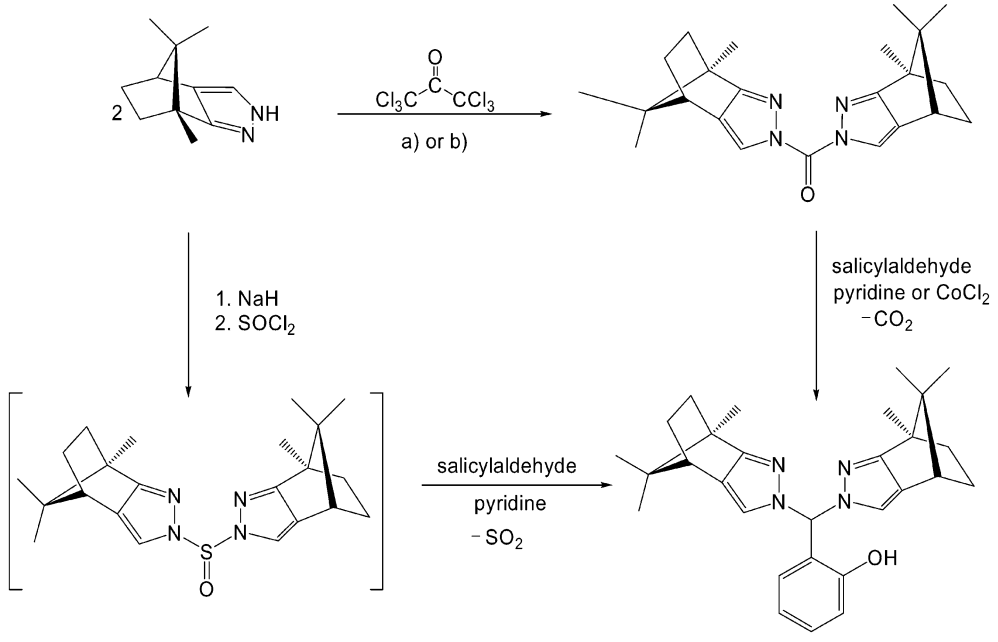
The 2,2′-sulfinylbis(camphorpyrazole) approach enabled the enantiopure ligand to be synthesized in a one-pot procedure on a multigram scale, starting with the reaction of



Scheme 5.



Scheme 6.

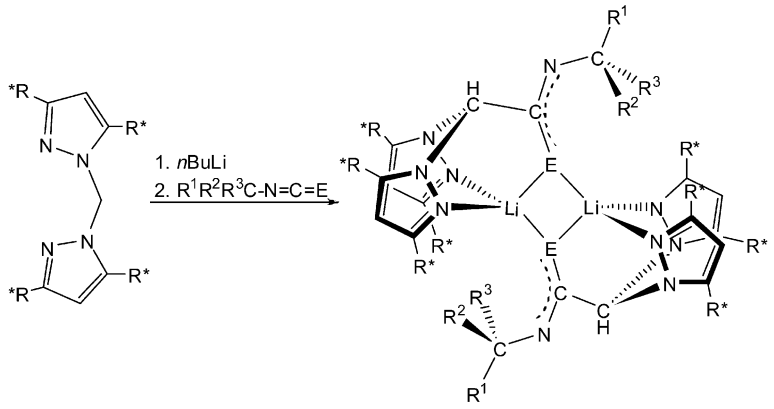


Scheme 7.

camphorpyrazole with sodium hydride and thionyl chloride. Pyridine and salicylaldehyde were added to the reaction mixture without purification of the resulting sulfinyl compound. This process gave ligands in yields of up to 60%.

2.1.(c) Introduction of Chirality in the Substituent Bound to the Methyne Bridge

We initially prepared[12] a series of new chiral heteroscorpionate ligands by following our previously described method[7] for the preparation of this type of system. Thus, deprotonation at the methylene group of bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm)[4] with *n*BuLi, followed by treatment with a series of chiral isocyanates [(*R*)-(+)- or (*S*)-(–)-α-methylbenzyl and (*S*)-(–)-1-phenylpropyl isocyanates] and isothiocyanates [(*S*)-(–)-1-phenylpropyl isothiocyanates] yielded the chiral lithium compounds (see Scheme 8), which were isolated as enantiopure ligands. This method constitutes a simple and efficient synthetic route for the preparation of acetamidate/thioacetamidate-containing enantiopure chiral, heteroscorpionate ligands. It was also interesting to assess the validity of the procedure with other types of substituted bis(pyrazol-1-yl)methanes. With this aim in mind, we also carried out the reactions with bis(3,5-diphenylpyrazol-1-yl)methane (bdphpzm)[4] and bis(3,5-di-*tert*-butylpyrazol-1-yl)methane (bdtbpzm)[13] and a chiral isocyanate [(*R*)-(+)-α-methylbenzyl isocyanate] to give the corresponding lithium compounds in yields of around 80% (Scheme 8) with an excellent enantiomeric excess (>99) established by adding a chiral shift reagent, namely, (*R*)-(–)-9-anthryl-2,2,2-trifluoroethanol. This process gave rise to two signals for each proton in the ^{1}H NMR spectrum resulting from the two diastereoisomers. A diastereoisomer ratio de-



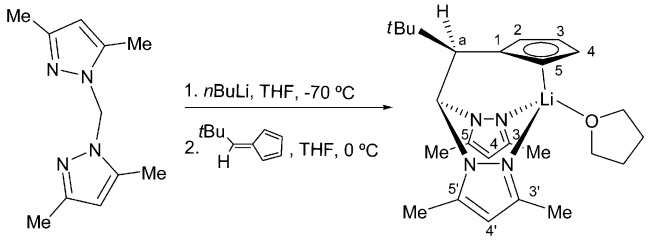
R* = Me; R^1 = Ph, R^2 = Me, R^3 = H; E = O (*R*-mbbpam)
R* = Me; R^1 = Me, R^2 = Ph, R^3 = H; E = O (*S*-mbbpam)
R* = Me; R^1 = Et, R^2 = Ph, R^3 = H; E = O (*S*-ppbpam)
R* = Me; R^1 = Et, R^2 = Ph, R^3 = H; E = S (*S*-ppbptam)
R* = Ph; R^1 = Ph, R^2 = Me, R^3 = H; E = O (*R*-mbbp^{Ph}am)
R* = *t*Bu; R^1 = Ph, R^2 = Me, R^3 = H; E = O (*R*-mbbp^{tBu}am)

Scheme 8.

noted as ">99:1" signifies that only the major diastereoisomer was detected. This methodology has been employed throughout our work to establish the values of enantiopurity of the different classes of compounds. These results confirm that the procedure can be applied to any type of substituted bis(pyrazol-1-yl)methane and it is worth noting the possibility of selecting the most appropriate pyrazole building block in the construction of the desired heteroscorpionate in order to tune both the electronic and steric effects in the subsequent coordination to a metal centre. The enantiopure lithium compounds can be seen in Scheme 8.

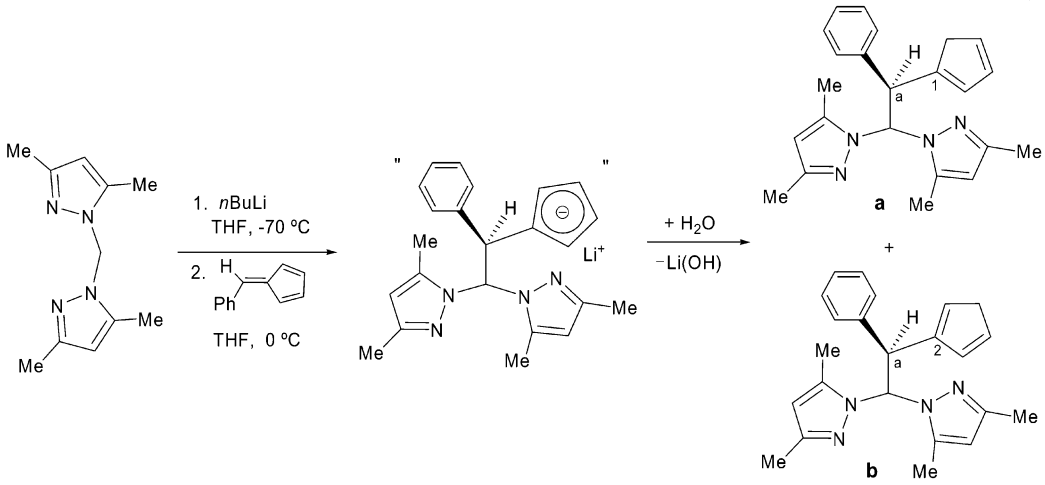
These compounds are dinuclear and the geometry around the Li atom can be described as a distorted tetrahedron with a "heteroscorpionate" ligand that acts in a tridentate fashion (two coordinated pyrazole rings and an oxygen/sulfur atom from the amidate/thioamidate fragment bridging the lithium atoms) (see Scheme 8). The dimeric aggregate is based on Li_2O_2 four-membered rings, which have previously been observed in other lithium compounds.[14]

The synthesis of hybrid chiral scorpionate/cyclopentadienyl ligands by a simple one-pot procedure has also been described.[15] Thus, deprotonation at the methylene group of bdmpzm followed by reaction with 6-*tert*-butylfulvene[16] yielded a chiral lithium compound in good yield (ca. 85%) (see Scheme 9). However, when the same reaction was carried out with 6-phenylfulvene[16] a mixture of two scorpionate/cyclopentadiene regioisomers was obtained in a yield of around 80% (see Scheme 10). Although the latter reaction was carried out in anhydrous THF, a hydrolysis process from the adventitious water in the workup occurred. It was established by DFT calculations[15b] that electronic effects due to the substituents on the fulvene carbon atom play an important role in the stabilization of the lithium scorpionate/cyclopentadienyl derivatives, meaning that the choice of substituents would be critical in designing a successful synthetic route. Deprotonation of these regioisomers with *n*BuLi was also carried out, but the expected lithium scorpionate/cyclopentadienyl compound was not isolated because an uncontrolled hydrolysis process occurred during the workup to give the starting material. Finally, treatment of a solution of the aforementioned chiral lithium complex with saturated aqueous ammonium chloride gave a mixture of two new scorpionate/cyclopentadiene regioisomers (see Scheme 11). This process gave ligands in yields of up to 90%. These compounds are the first examples of bis(pyrazol-1-yl)methanes to contain a cyclopentadiene moiety in the carbon bridge.

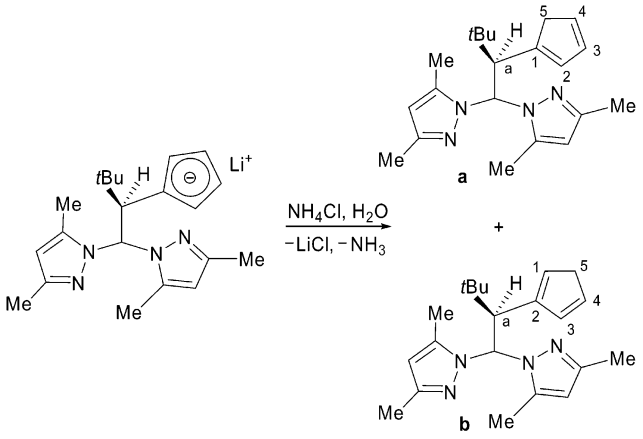


Scheme 9.

The lithium complexes have a monomeric structure and the geometry around the Li atom can be described as a distorted tetrahedron with a "heteroscorpionate" ligand, which acts in a tridentate fashion (two coordinated pyrazole rings and a cyclopentadienyl ring), and one molecule of THF. Furthermore, the C–C distances of the cyclopentadiene moiety found in the scorpionate/cyclopentadiene are comparable to those typically found for the classic cyclopentadiene.[17] The pyrazole rings of this compound are orientated in a quasi-antiparallel manner with respect to each other, presumably to minimize the intramolecular electronic repulsion of the nitrogen lone pairs of the two rings. This



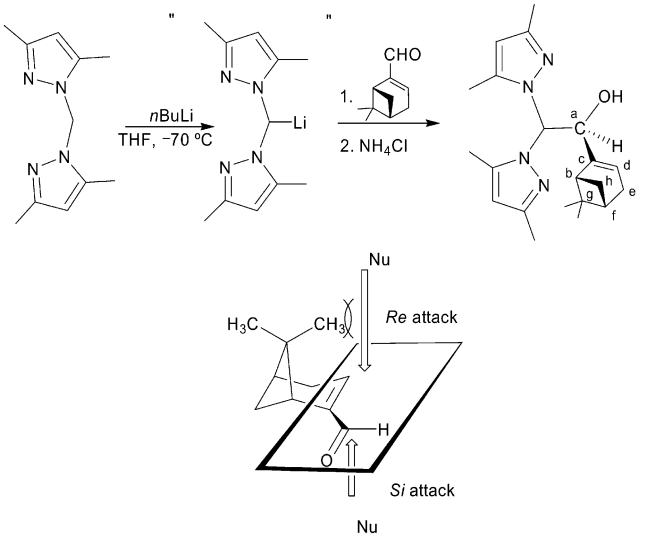
Scheme 10.



Scheme 11.

conformation is similar to that found in the (2-hydroxyphenyl)bis(pyrazolyl)methane derivative.[18] The cyclopentadiene and phenyl rings are probably in this quasi-antiparallel disposition to minimize steric interactions between the two rings. In addition, the structures of the lithium compounds were established on the basis of full-geometry optimizations at a DFT level and it was found that they agree very well with those determined by X-ray crystal structure studies.[15b]

An efficient and highly diastereoselective one-pot preparation of an enantiopure scorpionate ligand by means of a 1,2-addition of a lithium bis(pyrazol-1-yl)methane derivative to (1*R*)-(–)-myrtenal has recently been reported.[19] In this process a cold THF solution of lithium bis(3,5-dimethylpyrazol-1-yl)methide was added to a THF solution containing 1 equiv. of the commercially available (1*R*)-(–)-myrtenal and, after the appropriate workup, the enantiopure heteroscorpionate compound (*R*,*R*)-bpzmmH {(*R*,*R*)-bpzmmH = (1*R*)-1-[(1*R*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]-2,2-bis(3,5-dimethylpyrazol-1-yl)ethanol} was isolated in a good yield (83%) and with an excellent diastereomeric excess (>99% *de*) (Scheme 12). This procedure constitutes an efficient and highly diastereoselective method to prepare enantiopure scorpionate ligands in a one-pot process. Initial evidence for the stereochemical route was obtained from the X-ray molecular structure, which shows the *R* configuration for the newly formed chiral centre. This shows that the diastereofacial attack of the nucleophile proceeded through the *Si* face of the carbonyl group in an *s-trans* conformation. The steric effects from the methyl groups of the bicycle moiety are probably the main driving force for the diastereoselectivity observed in the process (Scheme 12).



Scheme 12.

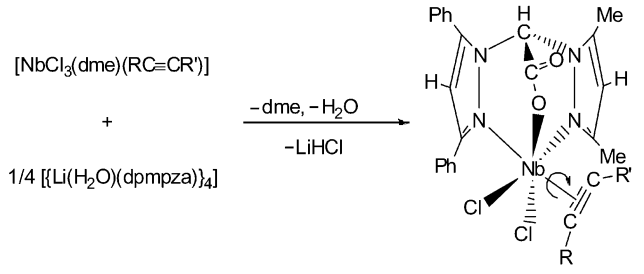
2.2. Coordination Chemistry with Heteroscorpionate Ligands Based on Bis(pyrazol-1-yl)methane-Containing Stereogenic Centres

2.2.(a) Complexes of Early Transition and Lanthanide Metals

The research into biodegradable polymers, which are not harmful to the environment, is an important task in the

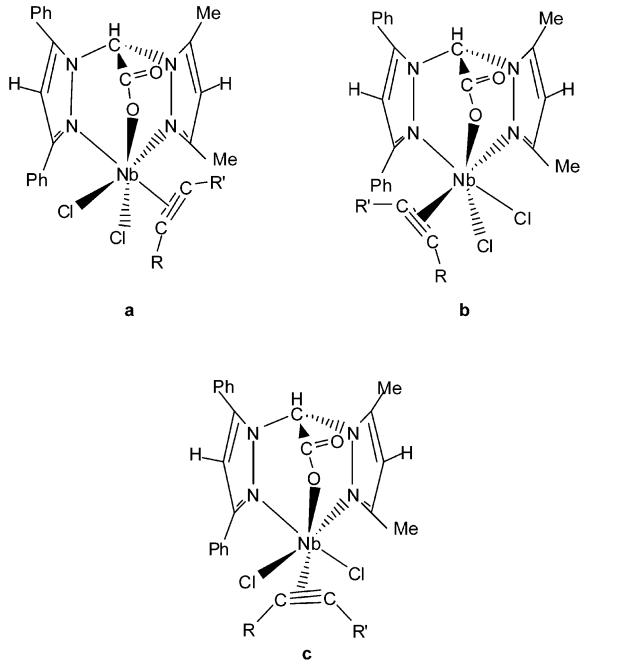
field of polymer catalysis. Some of the aliphatic polymers are currently commercially available as poly(ε-caprolactone) and poly(lactic acids). In the last few years the ring-opening polymerization (ROP) of cyclic esters with organometallic Lewis acid catalysts has emerged as an effective procedure of synthesis. In this field, we have recently described a series of efficient heteroscorpionate-containing organometallic initiators for this purpose; some bearing stereogenic centres are compiled in this review. They have been found to be excellent initiators in the well-controlled ROP processes of lactones and lactides.

The new chiral monoanionic *NNO*-tripod ligand [{Li(dpmpza)(H_2O)}$_4$], prepared as a racemic mixture, has proven to be a good precursor for the introduction of this scorpionate ligand into transition-metal complexes. For example, this ligand was used in the formation of a number of niobium complexes.[20] Previously we prepared and characterized a series of non-chiral scorpionate-containing niobium complexes.[5] It was found that the lithium compound reacted at room temperature in a 0.25:1 molar ratio with the precursors [$NbCl_3$(dme)(RC≡CR′)][21] (dme = 1,2-dimethoxyethane) to give the complexes [$NbCl_2$(dpmpza)(RC≡CR′)] in good yield (ca. 70%) after the appropriate workup (Scheme 13).



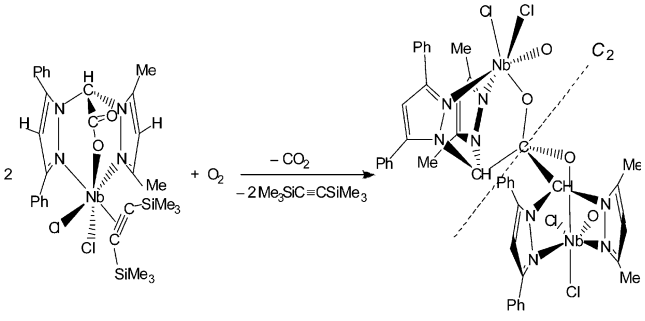
Scheme 13.

On the basis of spectroscopic data, an octahedral disposition was proposed in which the niobium atom is surrounded by an *NNO*-coordinated scorpionate ligand, an alkyne group and two chloride ligands. The proposed structures for the three possible diastereoisomers for these complexes are depicted in Scheme 14, where the alkyne ligand can be found in the *cis* disposition with respect to the 3,5-dimethylpyrazole ring (isomer a), in a *cis* disposition with respect to the 3,5-diphenylpyrazole ring (isomer b) or *trans* with respect to the oxygen atom (isomer c). On the basis of NOE experiments it has been established that diastereoisomer (a) is the only one present in the unsymmetrical alkyne complexes as well as being the major isomer of the two present in the symmetrical alkyne complexes. Diastereoisomer (c) is the minor isomer and has a *trans* disposition of alkyne ligands with respect to the oxygen atom. The ^{13}C NMR spectroscopic data indicate that in this type of complex the alkyne ligand behaves as a four-electron donor.[22] It is also noteworthy that in solution these complexes show a rotation of the alkyne ligand around the bisector of the metal–alkyne isosceles triangle. Free energy values, $\Delta G^{\ddagger}$, were calculated from variable-temperature NMR spectroscopic studies. Additionally, the calculated values allowed us to establish a relationship between the steric demand of the alkyne and the rotation phenomenon, in such a way that the higher $\Delta G^{\ddagger}$ values and coalescence temperatures were found in the cases with the bulkier alkyne substituents.



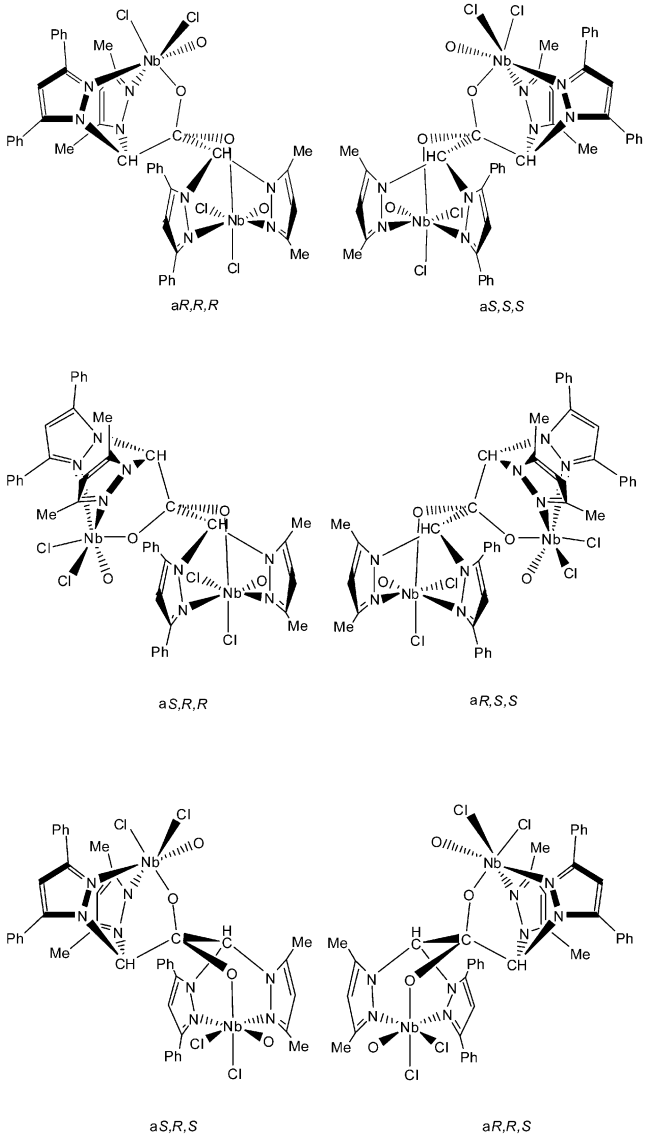
Scheme 14.

The reactivity of [$NbCl_2$(dpmpza)($Me_3SiC{\equiv}CSiMe_3$)] towards oxygen was particularly notable since it led to the formation of the first gem-diolate niobium species, [($NbCl_2O$)$_2$(μ-η^1-*O*,*O*′-tpzpdo)] [tpzpdo = 1,3-bis(3,5-diphenylpyrazol-1-yl)-1,3-bis(3′,5′-dimethylpyrazol-1-yl)-2,2′-propanediolate] (Scheme 15). A novel anionic gem-diolate bridging two niobium centres is present in this complex.



Scheme 15.

In addition, this unusual ligand contains two chiral carbon centres as well as two bis(pyrazol-1-yl) moieties, which are also coordinated to both metals in such a way that the ligand behaves as a tripod in its coordination to each metal atom. For this complex the presence of three diastereoisomers is possible, each as a racemic mixture (Scheme 16), namely [*rac*(a*R*,*R*,*R* + a*S*,*S*,*S*)], [*rac*(a*S*,*R*,*R* + a*R*,*S*,*S*)] and [*rac*(a*S*,*R*,*S* + a*R*,*R*,*S*)].[23]

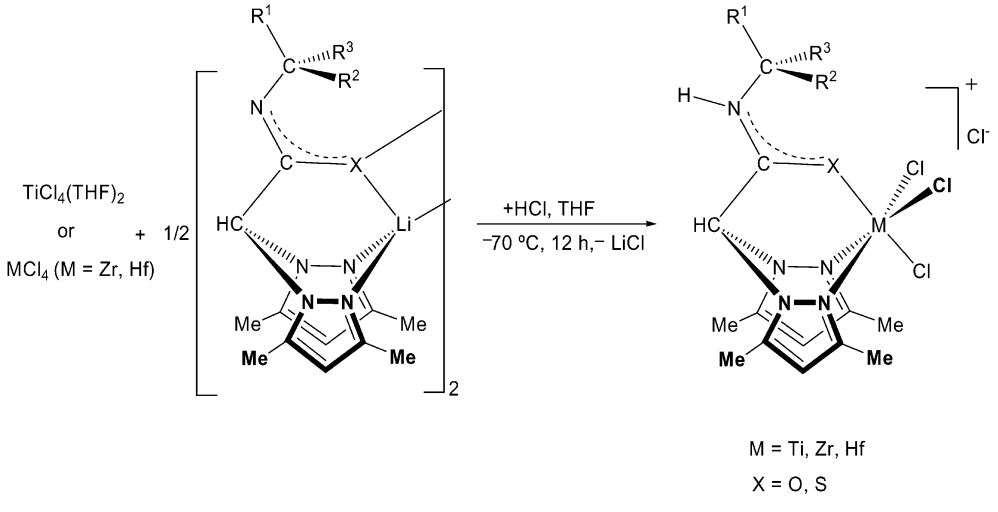


Scheme 16.

The X-ray crystal data and the NMR spectroscopic results indicate the presence of only one diastereoisomer [*rac*(a*R*,*R*,*R* + a*S*,*S*,*S*)].

The aforementioned enantiopure ligands [Li(*R*-mbbpam)]$_2$ [*R*-mbbpam = (*R*)-(+)-*N*-α-methylbenzyl-2,2-bis(3,5-dimethylpyrazol-1-yl)acetamidate], [Li(*S*-mbbpam)]$_2$ [*S*-mbbpam = (*S*)-(–)-*N*-α-methylbenzyl-2,2-bis(3,5-dimethyl-pyrazol-1-yl)acetamidate], [Li(*S*-ppbpam)] [*S*-ppbpam = (*S*)(–)-*N*-1-phenylpropyl-2,2-bis(3,5-dimethylpyrazol-1-yl)acetamidate and [Li(*S*-ppbptam)]$_2$] [*S*-ppbptam = (*S*)-(–)-*N*-1-phenylpropyl-2,2-bis(3,5-dimethylpyrazol-1-yl)-thioacetamide], prepared in one step by a simple, versatile and efficient synthetic path involving an insertion reaction of commercial, enantiopure isocyanates or isothiocyanates into bis(3,5-dimethylpyrazol-1-yl)methane,[12] were used to prepare new scorpionate-containing titanium, zirconium and hafnium complexes. The lithium precursors reacted with [$TiCl_4(THF)_2$]$_2$ or [MCl_4] (M = Zr, Hf) to give the complexes [MCl_3{κ^3-NNE(H)}]Cl in moderate yield (ca. 60%) (Scheme 17).[12] The reactions were carried out under rigorously anhydrous experimental conditions, but the presence of adventitious HCl arising from MCl_4 in the reaction mixture during the workup procedure was probably responsible for the protonation of the acetamidate or thioacetamidate moieties and their transformation into acetamide or thioacetamide units, respectively. The complexes have an octahedral geometry and were isolated in an enantiopure form.

In order to avoid the presence of adventitious HCl arising from the MCl_4 precursors an alternative reaction with another reagent, namely $Ti(NMe_2)_4$, was considered. Treatment of a THF solution of $Ti(NMe_2)_4$ with [Li(*S*-mbbpam)]$_2$ afforded the triamido-derivative [$Ti(NMe_2)_3$(*S*-mbbpam)] in moderate yield (60%) (Scheme 18). Additionally, the reactivity of this complex with Me_3SiCl in different molar ratios and under different experimental conditions led to the preparation of the halide-amide-containing complexes [$TiCl(NMe_2)_2$(*S*-mbbpam)] and [$TiCl_2(NMe_2)$(*S*-mbbpam)]

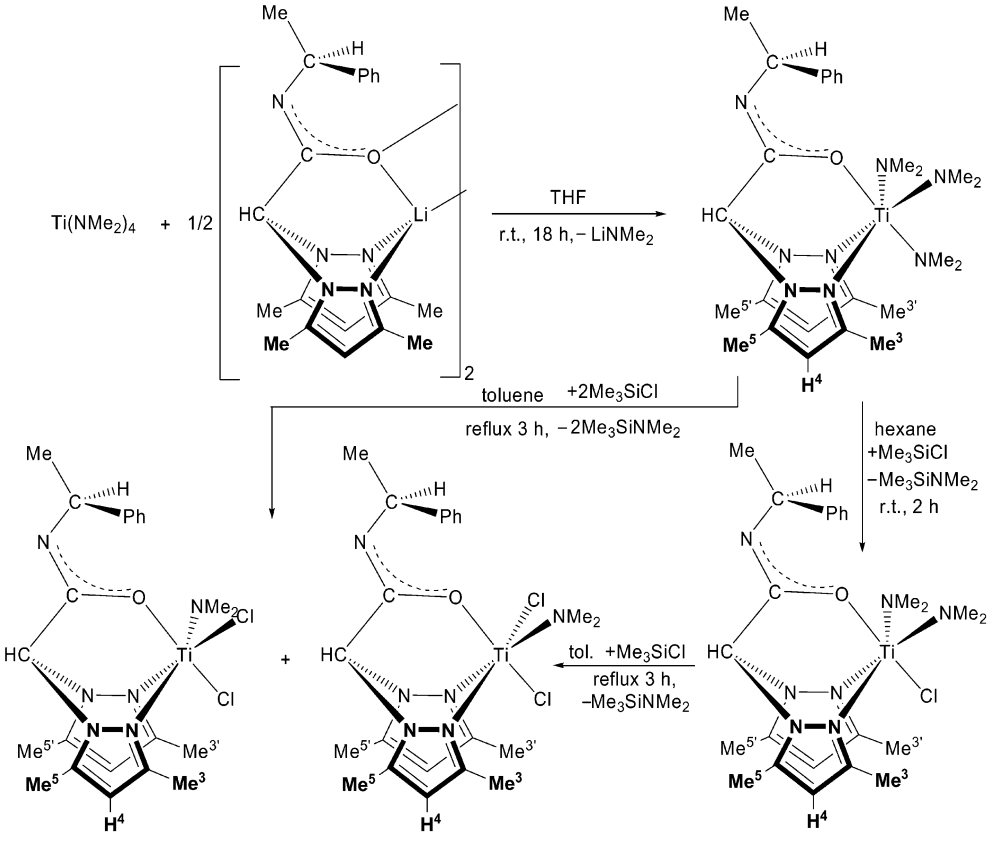


Scheme 17.

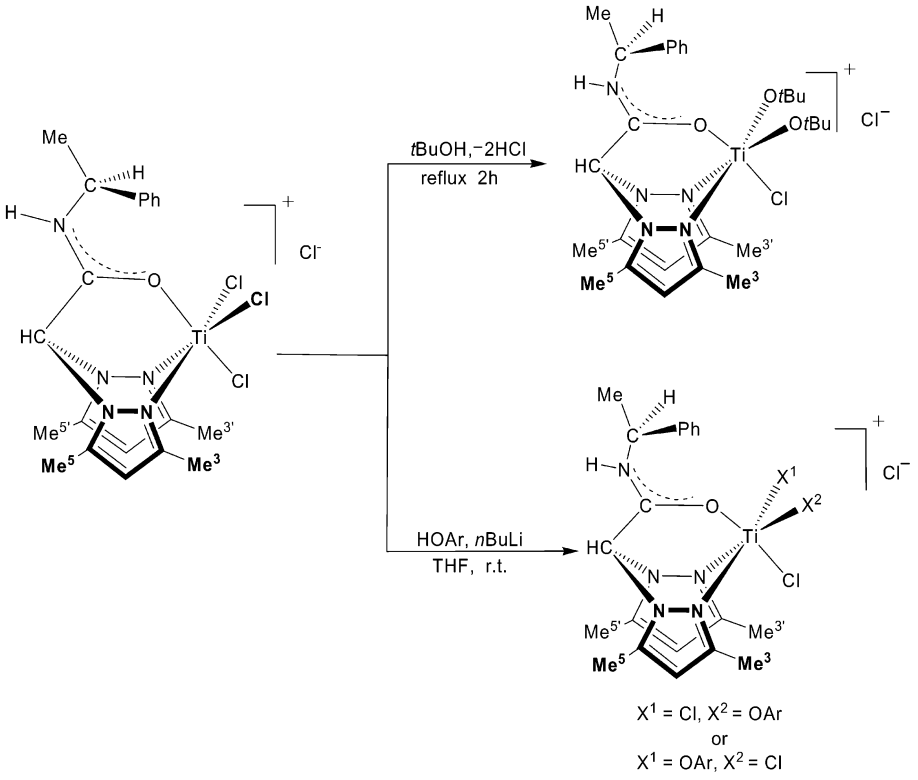
in good yield (ca. 70%) (Scheme 18). On the basis of ^{1}H NOESY-1D experiments the structure suggested for [TiCl(NMe$_2$)$_2$(*S*-mbbpam)] is that depicted for the isomer in which the chloride ligand is *trans* to the oxygen atom. In the case of complex [TiCl$_2$(NMe$_2$)(*S*-mbbpam)] it was proposed that both of the isomers depicted in Scheme 18 are present. Furthermore, a number of enantiopure derivatives of [TiCl$_3$(*S*-mbbpamH)]Cl containing alkoxide ancillary ligands were prepared using two different experimental methods. The first approach involved the direct reaction of this complex with a series of alcohols, thus allowing the isolation of only one alkoxide complex with the *tert*-butoxide moiety (Scheme 19). The second method involved deprotonation of the alcohol group of 2,6-dimethylphenol with *n*BuLi, followed by treatment with [TiCl$_3$(*S*-mbbpamH)]Cl to give the complex [TiCl$_2$(OC$_6$H$_3$-2,6-Me$_2$)(*S*-mbbpamH)]Cl (Scheme 19). Additionally, ^{1}H NOESY-1D experiments for the *tert*-butoxide-containing complex indicate the presence of the isomer in which the chloride ligand is *trans* to the oxygen of the acetamide group, but for the second derivative the aforementioned experiments suggest a *cis* or *trans* disposition of the aryloxide ligand with respect to one of the pyrazolyl rings, i.e. two isomers.

Hybrid scorpionate/cyclopentadienyl ligands have been successfully employed in the stabilization of group-4 and lanthanide metal complexes. This class of ligand was first described by us[15] and we have developed a well-established synthetic methodology to prepare a wide variety of these kinds of ligands. Among them, as outlined in Section 2.1, two classes of ligands containing stereogenic centres have been described. These are lithium derivatives [Li(bpztcp)(THF)] [bpztcp = 2,2-bis(3,5-dimethylpyrazol-1-yl)-1-*tert*-butylethylcyclopentadienyl], which exist as a mixture of the two enantiomers in the solid state and in solution, and scorpionate/cyclopentadienes [2,2-bis(3,5-dimethylpyrazol-1-yl)-1-phenylethyl]-1,3-cyclopentadiene (bpzpcpH) and [2,2-bis(3,5-dimethylpyrazol-1-yl)-1-*tert*-butylethyl]-1,3-cyclopentadiene (bpztcpH), which in solution are present as a mixture of tautomers (Scheme 20).

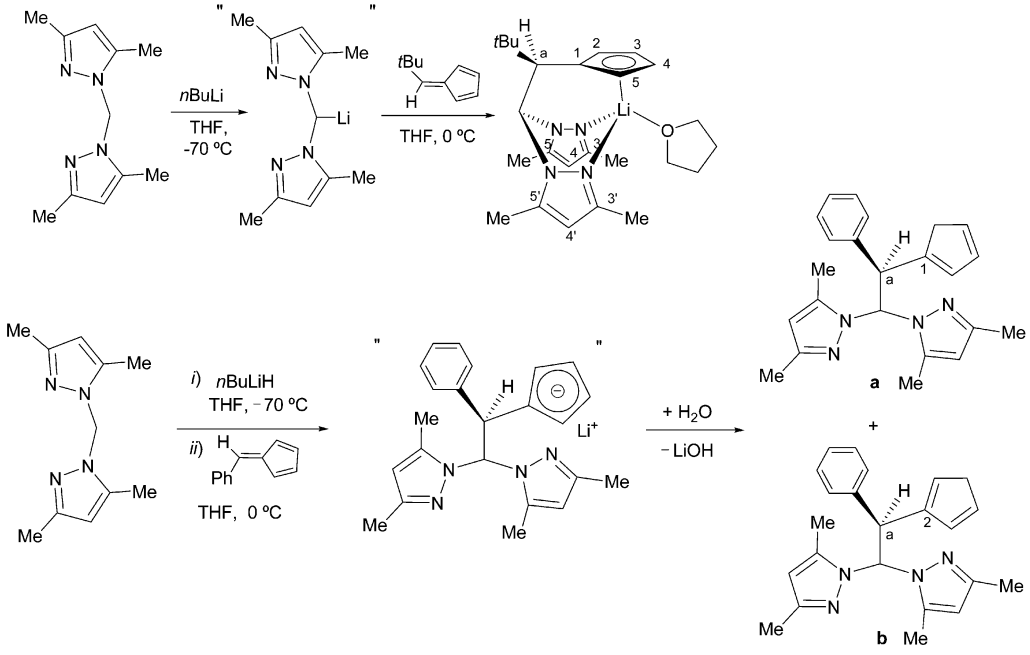
Having prepared this new class of hybrid scorpionate/cyclopentadienyl precursors we explored their potential utility as tridentate ligands in the preparation of new group-4 metal complexes.[15] Thus, [Li(bpztcp)(THF)] reacted with [TiCl$_4$(THF)$_2$] or [MCl$_4$] (M = Zr, Hf) in a 1:1 molar ratio to give the complexes [MCl$_3$(bpztcp)] (M = Ti, Zr, Hf) (Scheme 21). An interesting reaction was observed when a mixture of the precursors [MCl$_4$] (M = Zr, Hf) and bpzpcpH was heated under reflux to give the new complexes [MCl$_3$(bpzpcp)] (Scheme 22). These processes gave complexes in yields of up to 90%. The analogous reaction with TiCl$_4$(THF)$_2$ gave a complex mixture of products that could not be separated. This process involved an unusual deprotonation of the cyclopentadiene moiety with the formation of hydrogen chloride. The deprotonation of cyclopentadiene is a well-known process and it normally proceeds by either acid–base or protonolysis processes.[24] The



Scheme 18.

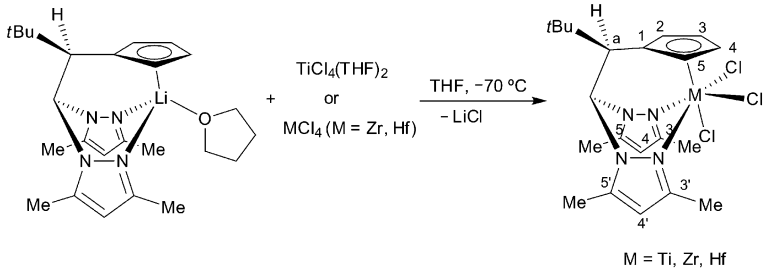


Scheme 19.

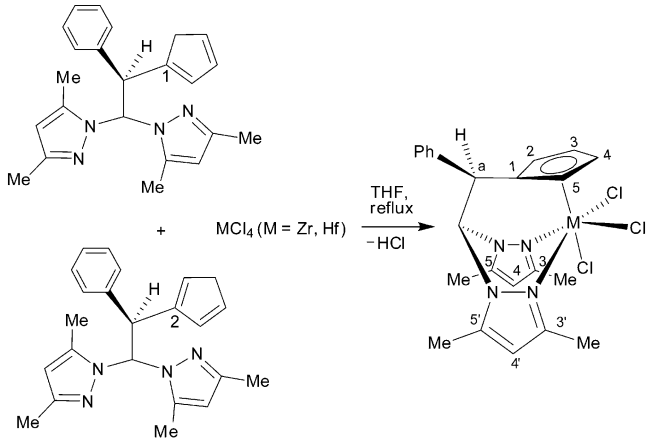


Scheme 20.

process described here represents the second example[25] of a novel and direct one-pot procedure for the synthesis of monocyclopentadienyl group-4 metal trichloride complexes with a side chain containing a group, in our case two pyrazoles, that is able to coordinate to the metal centre by the reaction of the appropriate MCl_4 precursor and cyclopentadienes. The different complexes were found to have an octahedral geometry, as depicted in Schemes 21 and 22, and their structures contain a heteroscorpionate ligand bonded to the metal centre though the two nitrogen atoms and the cyclopentadienyl ring in a κ^2-NNη^5-Cp coordination mode. These complexes were isolated as a mixture of enantiomers.



Scheme 21.

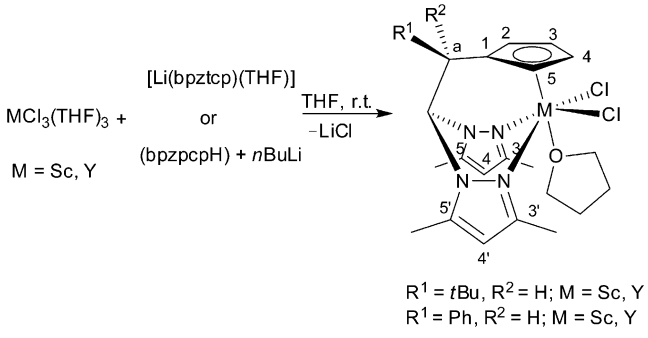


Scheme 22.

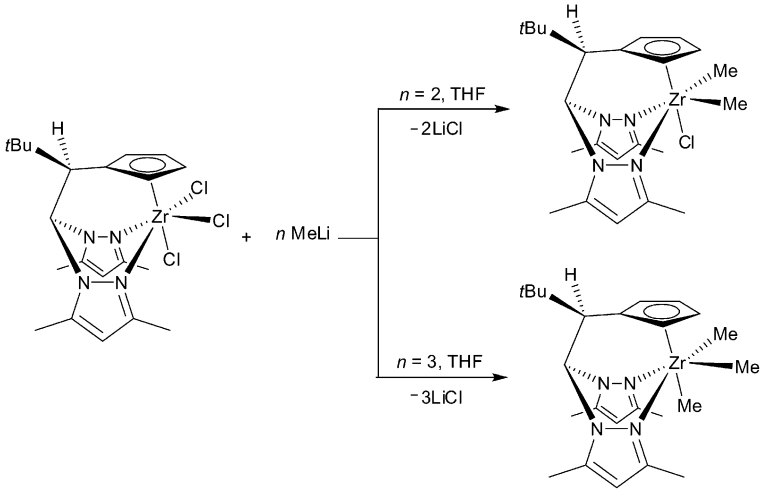
In addition, the structures of some of these complexes were obtained by full-geometry optimizations at the DFT level.

We also proceeded to explore the synthesis of alkyl derivatives starting from the complex [$ZrCl_3$(bpztcp)] by treatment with MeLi in different molar ratios. In this way the dialkyl and the trialkyl complexes [$ZrClMe_2$(bpztcp)] and [$ZrMe_3$(bpztcp)], respectively, were prepared (Scheme 23).

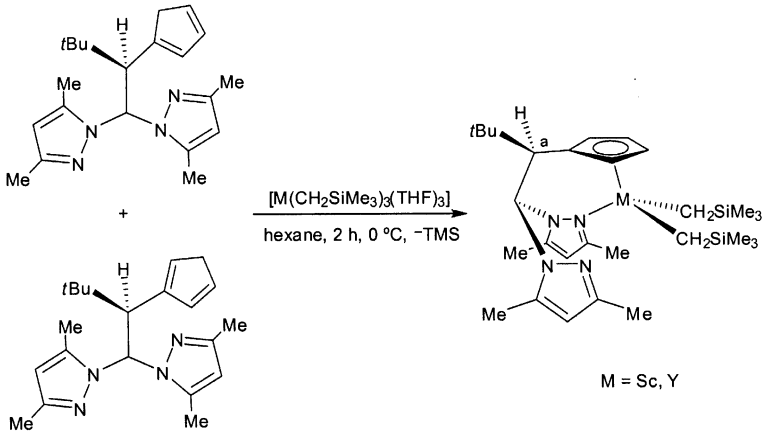
The first examples of group-3 metal halide complexes bearing a hybrid scorpionate/cyclopentadienyl ligand have also been described.[26] The reagents [Li(bpztcp)(THF)] and bpzpcpH/*n*BuLi reacted with $MCl_3(THF)_3$ (M = Sc, Y) to give a series of new complexes, namely [MCl_2(bpztcp)-(THF)] and [MCl_2(bpzpcp)] (Scheme 24). These processes gave complexes in yields of up to 80%. The complexes have an octahedral arrangement in which a κ^2-NNη^5-Cp coordination is present. In these asymmetric complexes the carbon atom (C^a) is a stereogenic centre and we found evidence for the presence in solution of the two corresponding enantiomers by adding a chiral shift reagent, namely (*R*)-(–)-9-anthryl-2,2,2-trifluoroethanol. This process gave rise to two signals for each proton in the ^{1}H NMR spectrum resulting from the two diastereoisomers of the corresponding two enantiomers. However, it is worth noting that the complex crystallized to give an enantiopure product.



Scheme 24.



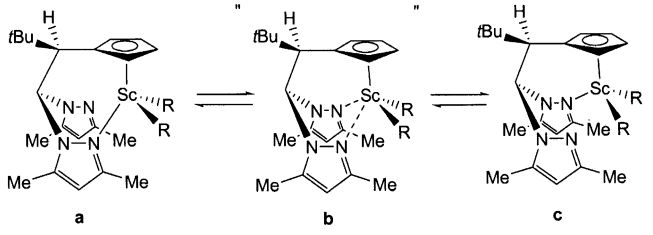
Scheme 23.



Scheme 25.

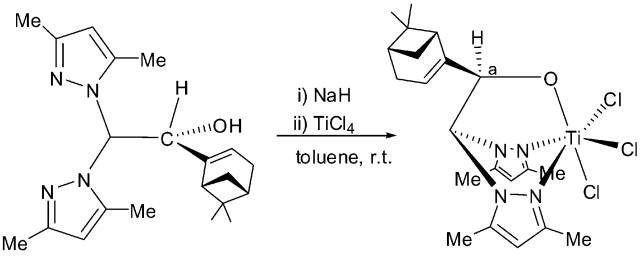
Group-3 alkyl compounds were also prepared.[27] Indeed, having prepared the reagent bpztcpH we explored its potential utility as a ligand in the preparation of new alkyl group-3 metal complexes. It is well known that the alkane elimination reaction is frequently the route of choice to prepare early transition-metal organometallics as the precursors are readily available and "ate" complex formation is avoided. As mentioned above, deprotonation of the cyclopentadiene moiety is a well-known procedure that normally proceeds by either acid–base or protonolysis processes.[24] Thus, the reaction of bpztcpH with $[M(CH_2SiMe_3)_3(THF)_3]$[28] (M = Sc, Y) yielded the THF-free scandium and yttrium alkyl complexes $[M(CH_2SiMe_3)_2(bpztcp)]$ bearing a hybrid scorpionate/cyclopentadienyl ligand with a stereogenic centre (Scheme 25). This process gave complexes in yields of up to 70%.

In these complexes the heteroscorpionate ligand is κ^1-NNη^5-Cp coordinated and they exhibit a pseudo-four-coordinate tetrahedral structure with C_1 symmetry. However, in solution a dynamic behaviour was found and this was studied by means of VT NMR spectroscopy. The dynamic behaviour was found to be due to an exchange process between the coordinated and the noncoordinated pyrazole rings, a process that results in the interconversion from one stereoisomer to the other (Scheme 26).



Scheme 26.

An enantiopure scorpionate ligand, namely (*R*,*R*)-bpzmmH [(*R*,*R*)-bpzmmH = (1*R*)-1-[(1*R*)-6,6-dimethylbicyclo[3.1.1]2-hepten-2-yl]-2,2-bis(3,5-dimethylpyrazol-1-yl)ethanol], has been prepared through a highly diastereoslective nucleophilic 1,2-addition of a lithium bis(pyrazol-1-yl)-methane derivative to (1*R*)-(–)-myrtenal, as mentioned in Section 2.1. In a preliminary study we explored the potential utility of this compound as a tridentate ligand in the preparation of chiral group-4 metal complexes.[19] Deprotonation of the alcohol group of this ligand with NaH followed by treatment with $TiCl_4$ in a 1:1 molar ratio yielded the enantiopure titanium complex $[TiCl_3\{(R,R)$-bpzmm$\}]$ in good yield (ca. 70%). In addition, treatment of $Ti(NMe_2)_4$ with the same ligand afforded the enantiopure triamido derivative $[Ti(NMe_2)_3\{(R,R)$-bpzmm$\}]$ (Scheme 27). The titanium centre has a distorted octahedral geometry in which the heteroscorpionate ligand is coordinated by two nitrogen atoms of the pyrazole rings and the oxygen atom of the alkoxide group. The scorpionate ligand maintains the *R* configuration at the C^a atom. It is worth noting the close proximity of the stereogenic carbon C^a to the metal, an arrangement that is able to create an effective chiral pocket around the Ti centre. This characteristic may be very useful in subsequent studies on the reactivity of this complex in enantioselective processes.

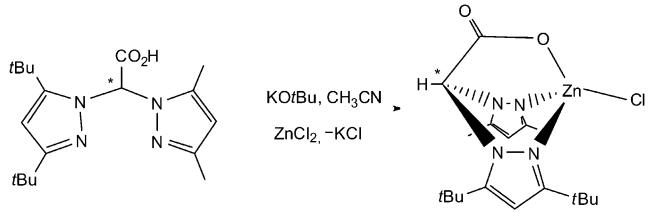


Scheme 27.

2.2.(b) Complexes of Late Transition Metals and Zn

Enzymes are chiral compounds and, as a result, there has been a major effort in bioinorganic chemistry to supply chiral models for the active sites of metalloenzymes. In this sense, Burzlaff et al.[6] developed zinc complexes with *NNO* ligands that can serve as models for the active site of zinc-containing enzymes that bind the metal ion with two histidine groups and one aspartate or glutamate group. Exam-

ples include carboxypeptidase A, thermolysin and other proteases.[29] In this way, the aforementioned novel chiral ligand (3,5-di-*tert*-butylpyrazol-1-yl)(3′,5′-dimethylpyrazol-1-yl)acetic acid (bpaH$^{t\mathrm{Bu2,Me2}}$) was transferred to zinc to yield the complex [Zn(bpa$^{t\mathrm{Bu2,Me2}}$)Cl] in good yield (ca. 70%) (Scheme 28).



Scheme 28.

The analogous reaction of (3,5-di-*tert*-butylpyrazol-1-yl)(3′,5′-dimethylpyrazol-1-yl)acetic acid (bpaH$^{t\mathrm{Bu2,Me2}}$) with dimethylzinc gave the chiral methylzinc complex [Zn(bpa$^{t\mathrm{Bu2,Me2}}$)(CH$_3$)] in very good yield (ca. 93%). The reactivity of this complex towards acetic acid was examined and led to an acetate complex [Zn(bpa$^{t\mathrm{Bu2,Me2}}$)(OAc)] as a useful precursor to enzyme models (Scheme 29).

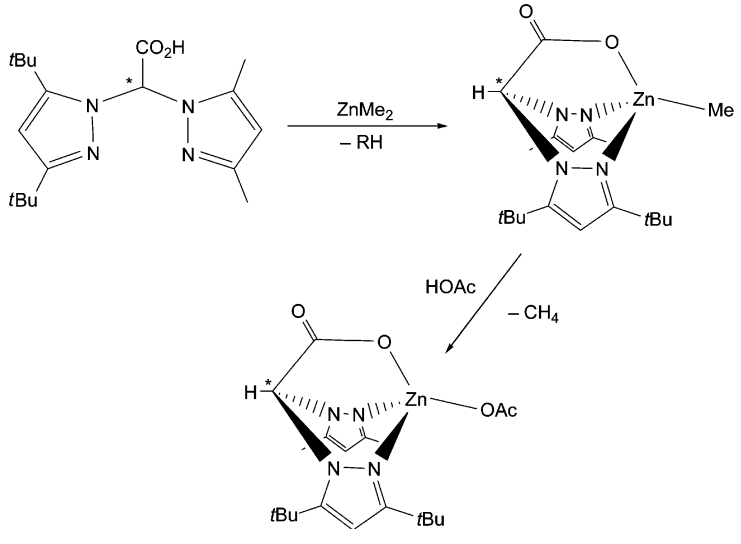
The synthesis of this complex was carried out in acetonitrile solution and the sandwich complex [Zn(bpa$^{t\mathrm{Bu2,Me2}}$)$_2$] was formed as a byproduct during this process. The facile formation of the related six-coordinate complexes [Zn(Tp^R)$_2$] in the reactions of [Zn(Tp^R)X] (X = OH, CH$_3$, Cl) has already been reported by Vahrenkamp et al.,[30] Parkin et al.[31] and Kläui et al.[32] with either octahedral[31] or tetrahedral[32] structures for the complexes [Zn(Tp^R)$_2$]. This redistribution seems to be favoured by polar solvents and sterically less demanding ligands. In contrast, we recently proved[33] that sandwich heteroscorpionate complexes were not formed from alkylzinc complexes of the type [Zn(NNN)(*R*)] [where NNN = *N*-ethyl-*N*′-*tert*-butylbis(3,5-dimethylpyrazol-1-yl)acetamidinate (tbpamd) and *N*,*N*′-diisopropylbis(3,5-dimethylpyrazol-1-yl)acetamidinate (pbpamd)],[34] even in refluxing toluene over several days. Furthermore, when the reaction was carried out with 2 equiv. of ligand with respect to Zn, even under reflux in toluene, formation of the sandwich species was not detected. In contrast, related monoalkyl heteroscorpionate magnesium complexes[35] readily give the corresponding sandwich units.

Burzlaff and Hegelmann also described the preparation of a series of ruthenium complexes by using the aforementioned enantiopure facially-binding tripod *NNO*-ligands bis(camphorpyrazol-1-yl)acetic acid (Hbpa$^{4\mathrm{cam}}$) and bis(menthylpyrazol-1-yl)acetic acid (Hbpz$^{4\mathrm{meth}}$). Thus, the ruthenium complex [Ru(bpa$^{4\mathrm{cam}}$)Cl(PPh$_3$)$_2$] was prepared in moderate yield (ca. 51%) by the treatment of the potassium carboxylate with [RuCl$_2$(PPh$_3$)$_3$][8] (Scheme 30).

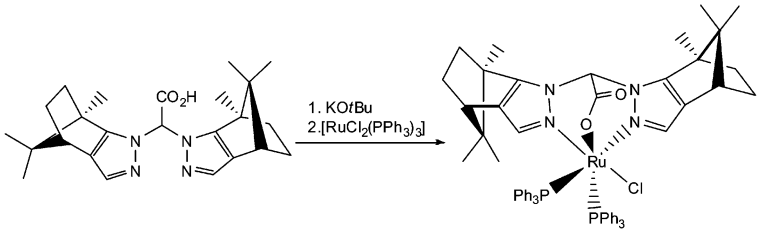
A similar reaction of the potassium salt of Hbpz$^{4\mathrm{meth}}$ with [RuCl$_2$(PPh$_3$)$_3$] yielded [Ru(bpa$^{4\mathrm{menth}}$)Cl(PPh$_3$)$_2$][9] (Scheme 31). Furthermore, treatment of the pentacarbonyl complexes [MnBr(CO)$_5$] and [ReBr(CO)$_5$] with the potassium bis(menthylpyrazol-1-yl)acetate K[bpa$^{4\mathrm{menth}}$] afforded the chiral bis(menthylpyrazol-1-yl)acetate tricarbonyl complexes [Mn(bpa$^{4\mathrm{menth}}$)(CO)$_3$][9] and [Re(bpa$^{4\mathrm{menth}}$)(CO)$_3$] (Scheme 31).[9] These processes gave complexes in yields of around 70%.

The synthesis of rhenium and zinc complexes using the enantiopure *NNO*-scorpionate ligand HOPhbpm$^{3\mathrm{cam}}$ derived from (+)-camphor[11] has also been described (Scheme 32).

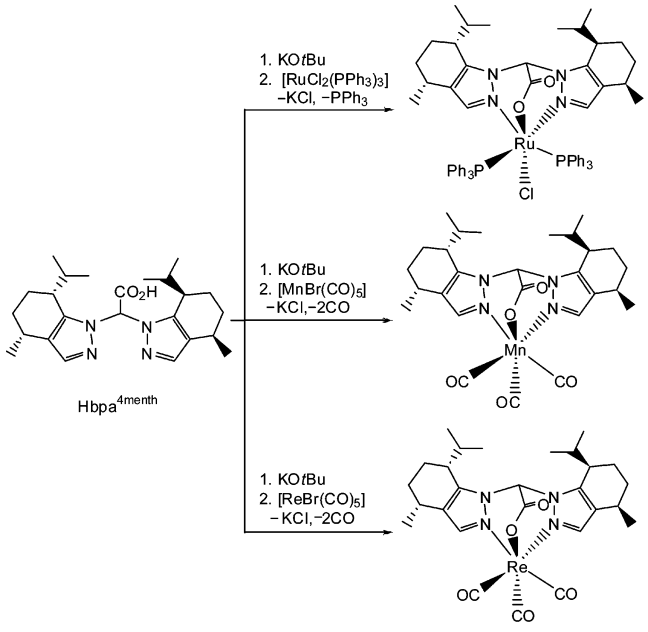
The reaction of the analogous *NNO*-scorpionate ligand 2,2-bis(3,5-dimethylpyrazol-1-yl)-3-acetatopropionic acid,[36] which is suitable for solid-phase immobilization, with [MBr(CO)$_5$] yielded the chiral complexes [Mn(bdmpzap)(CO)$_3$] and [Re(bdmpzap)(CO)$_3$] (Scheme 33). In both complexes the acetyl fragment remains uncoordinated indicating its ability to act as a linking group to solid phases.



Scheme 29.



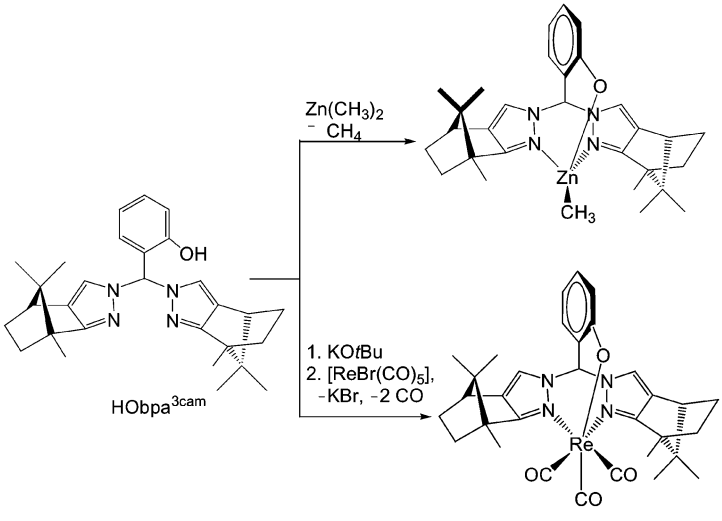
Scheme 30.



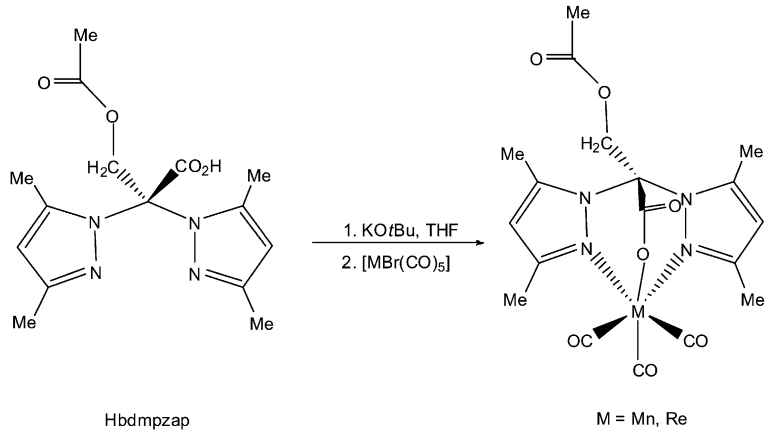
Scheme 31.

Marchiò et al.[37] recently reported the high yielding synthesis of a new chiral pyrazole–pyridine-based *NN′O*-scorpionate ligand, namely 1-(4-methoxy-3,5-dimethylpyridin-2-yl)-2-methyl-1-(pyrazol-1-yl)propan-2-ol (LOH). The coordination properties of LOH were explored and the ligand exhibits a κ^3-*N*,*N*′,*O* coordination mode towards late transition divalent ions (M^{2+} = Ni^{2+}, Cu^{2+} and Zn^{2+}), as evidenced by X-ray structures of the resulting complexes. Interestingly, in the solid state only octahedral centrosymmetric $[M(LOH)_2]^{2+}$ complexes can be isolated, with the $[MCl_4]^{-}$ anionic species as the counterion: a similar situation is also found for a 1:1 M^{2+}/LOH ratio (Scheme 34). The speciation of the M^{2+}/LOH systems in methanol/water (95:5) was investigated by UV/Vis (Ni^{2+} and Cu^{2+}) and ^{1}H NMR (Zn^{2+}) spectroscopic titrations. The structural description of the Zn^{2+}/LOH system in solution was performed in detail by means of ESI-MS, ^{1}H-^{1}H EXSY NMR spectroscopy and DFT calculations. The results revealed the occurrence of equilibria between different $[Zn(LOH)_2]^{2+}$ octahedral isomers and the $[Zn(LOH)Cl]^{2+}$ tetrahedral species.

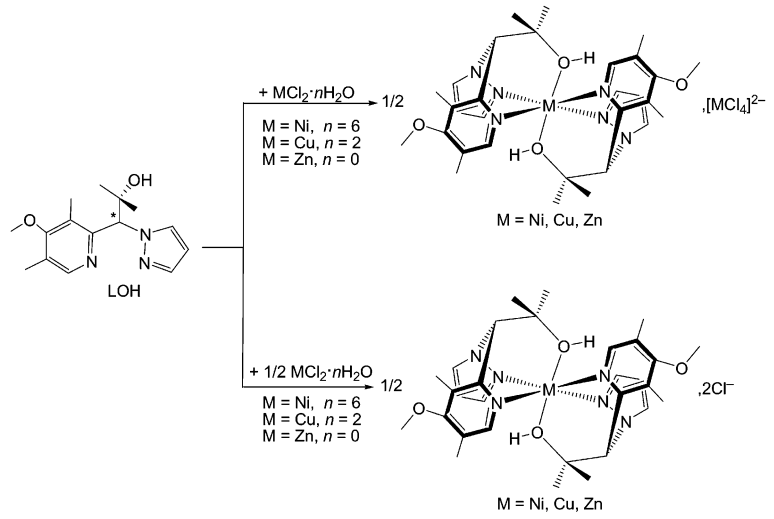
The same group is currently exploring the coordination properties of N_xS_y polydentate ligands derived from the pyrazole–pyridine moiety.[38] They are studying the coordination properties of two C-centred tetradentate *NN′SS′* donor ligands (L^a and L^b, Scheme 35) with Cu^I. L^a and L^b are based on an *NN′S*-donor-substituted pyrazole–pyridine platform, with an alkylthioether group as the fourth coordination site. These compounds were designed with the aim of obtaining geometrically preorganized ligands with a suitable donor set that satisfies the electronic and steric require-



Scheme 32.

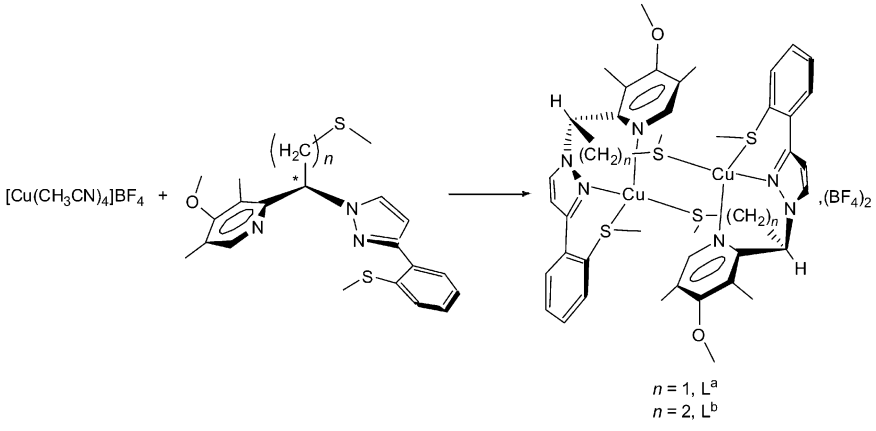


Scheme 33.



Scheme 34.

ments of Cu^{I} to yield mononuclear tetrahedral complexes. However, the Cu^{I} complexes synthesized, $[Cu(L^{a})]_2(BF_4)_2$ and $[Cu(L^{b})]_2(BF_4)_2$, are dinuclear in the solid state, where each copper centre exhibits a distorted tetrahedral *NN′SS′*-coordination environment. However, the solution properties, particularly in acetonitrile, show evidence for the formation of mononuclear species in equilibrium with the dimers.



Scheme 35.

3. Concluding Remarks

The different synthetic methodologies that we, and others, have described for a type of heteroscorpionate ligand based on bis(pyrazol-1-yl)methane containing stereogenic centres have been discussed. The coordinative ability of these ligands to stabilize chiral complexes from early to late transition metals has also been described. This chemistry opens new avenues to a promising research area focused on the synthesis of enantiopure ligands that can be used in the preparation of useful chiral complexes. Further studies focused on the design of new strategies to prepare enantiopure ligands as well as on the efficient chirality transfer to different types of metal centres will be welcome, for example to prepare alternative highly effective single-component living initiators for the well-controlled ring-opening polymerization of cyclic esters.

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