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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 C_5 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.

Keywords: *ansa*-Metallocene; Titanium; Zirconium; Hafnium; Vanadium; Niobium; Tantalum

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{$H_2C(\eta^5$-$C_5H_4)_2$}Cl_2], 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].

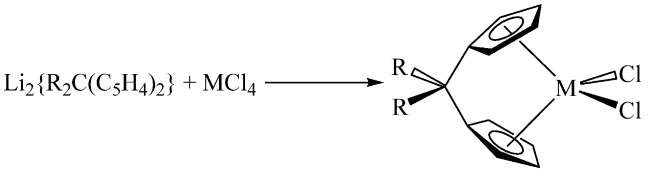
Apart from changing the group 14 bridging heteroatom, the *ansa*-bis(cyclopentadienyl) system can be varied by substitution at the C_5 ring or the bridging atom. This substitution can be designed to modify electronic and/or steric effects which may influence catalytic activity and selectivity.

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 η^5:η^5 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 derivativization (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.

2. *ansa*-Metallocene complexes without ring substituents

2.1. Carbon atom ansa-bridge

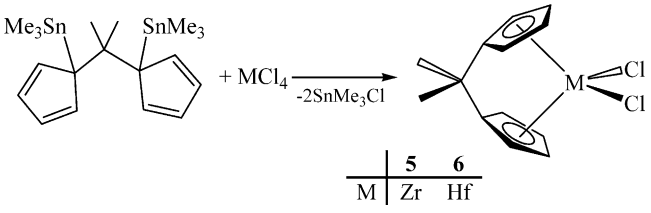
The synthesis of the CH_2 bridged *ansa* complexes, $[M\{H_2C(\eta^5\text{-}C_5H_4)_2\}Cl_2]$ (M = Ti (**1**), Zr (**2**)), in 30 and 17% yield, respectively, was achieved by the reaction of bis(cyclopentadienyl)methane with *n*-butyllithium and subsequent addition of the metal tetrachloride (Eq. (1)) [5e,8,19]. The *ansa*-metallocene complexes, $[M\{R_2C(\eta^5\text{-}C_5H_4)_2\}Cl_2]$ (M = Ti, R = Me (**3**); M = Ti, R = Et (**4**); M = Zr, R = Me (**5**); M = Hf, R = Me (**6**)), were prepared in an identical manner although in very poor yields (ca. 10%) (Eq. (1)) [9,20]. The same reaction carried out by Nifant'ev et al. gave superior yields for **3** (46%) and **5** (35%) [21].



	1	2	3	4	5	6
M	Ti	Zr	Ti	Ti	Zr	Hf
R	H	H	Me	Et	Me	Me

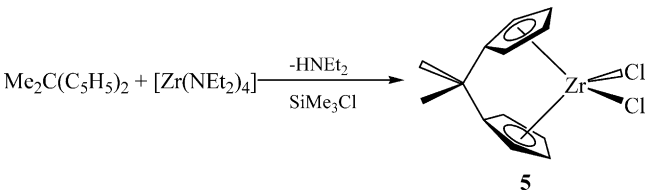
(1)

The yields of these compounds were greatly improved (95%) by the reaction, in toluene, of the metal tetrachlorides with distannylated *ansa*-bis(cyclopentadiene) (Eq. (2)) [22]. The preparation of **5**, in 84% yield, was also reported via amine elimination in the reaction between $[Zr(NEt_2)_4]$ and the organic compound $Me_2C(C_5H_5)_2$ followed by chloride/amide exchange on the addition of trimethylsilylchloride (Eq. (3)) [23].



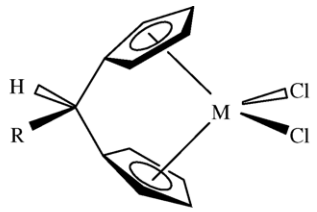
	5	6
M	Zr	Hf

(2)



5

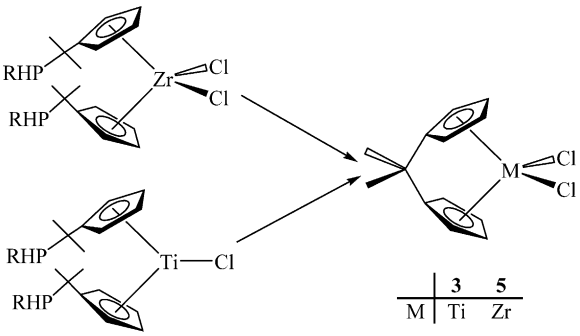
(3)



	7	8	9	10
M	Ti	Ti	Zr	Zr
R	Me	Bu^t	Me	Bu^t

Fig. 1. Compounds **7**–**10**.

Hey-Hawkins and co-workers serendipitously isolated **3** and **5** as the decomposition products of phosphine substituted metallocene complexes (Eq. (4)) [24].



	3	5
M	Ti	Zr

R = Ph, Bu^t

(4)

The molecular structures of **1**–**3**, **5** and **6** were determined by single crystal X-ray diffraction studies and show the typical bent metallocene complexes associated with group 4 compounds [5e,10,24,25]. The introduction of the single-atom inter-annular bridge affects the geometry of the *ansa* complex compared with its non-*ansa* analogue making it a more rigid system which translates to higher selectivity in the complex's chemical behaviour. Comparative structural data for the compounds discussed in this review can be found in Table 1.

The asymmetrically substituted *ansa*-bridge complexes, $[M\{R(H)C(\eta^5\text{-}C_5H_4)_2\}Cl_2]$ (M = Ti, R = Me (**7**), Bu^t (**8**); M = Zr, R = Me (**9**), Bu^t (**10**)), were prepared, in very low yields, by the reaction of MCl_4 with $Li_2\{R(H)C(\eta^5\text{-}C_5H_4)_2\}$ [9a,26] (Fig. 1).

The synthesis of cycloalkylidene-bridged *ansa*-metallocene complexes $[M\{(CH_2)_n(\eta^5\text{-}C_5H_4)_2\}Cl_2]$ (M = Ti, *n* = 4 (**11**), 5 (**12**), 6 (**13**); M = Zr, *n* = 4 (**14**), 5 (**15**), 6 (**16**); M = Hf, *n* = 4 (**17**), 5 (**18**), 6 (**19**)) has been reported [27] (Eq. (5)). The catalytic activity of **11**–**19**, in the polymerization of ethylene, was tested and the highest activities were surprisingly observed for the titanium complexes.

Table 1
Selected structural data of *ansa*-metallocene complexes[a]

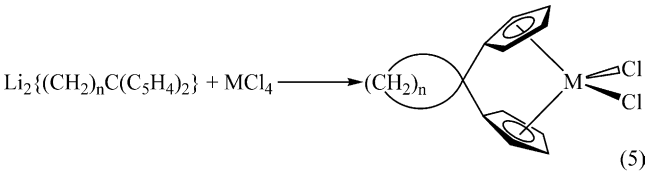
Complex	M–Cp (Å)	M–Cl (Å)	Cp–M–Cp (°)	Cl–M–Cl (°)	$C_{(cp)}$–E–$C_{(cp)}$ (°)	Reference
[Ti{$H_2C(\eta^5$-$C_5H_4)_2$}Cl_2] (**1**)[b]	2.06 2.04	2.34 2.35	121(1) 122(1)	97.2(3) 97.0(3)	99 (2) 96(2)	[10]
[Ti{$Me_2C(\eta^5$-$C_5H_4)_2$}Cl_2] (**3**)	2.056	2.343	121.6	98.04(4)	96.6(2)	[24,25]
[Ti{$(CH_2)_4C(\eta^5$-$C_5H_4)_2$}Cl_2] (**11**)	2.051	2.342	121.1	96.98(3)	96.9(2)	[27b]
[Ti{$(CH_2)_5C(\eta^5$-$C_5H_4)_2$}Cl_2] (**12**)	2.052	2.346	121.1	97.41(4)	96.6(2)	[27b]
[Ti{$(CH_2)_6C(\eta^5$-$C_5H_4)_2$}Cl_2] (**13**)	2.043	2.348	121.4	97.54(5)	96.6(3)	[27b]
meso-[Ti{$Me_2C(\eta^5$-$C_5H_3Pr^i)_2$}Cl_2] (**67**)		2.339		96.37(6)		[43b]
rac-[Ti{$Me_2C(\eta^5$-$C_5H_3Bu^t)_2$}Cl_2] (**68**)		2.330 2.35		96.6(1) 98(1)	98.3(8) 96(1)	[43a]
[Ti{$Me_2Si(\eta^5$-$C_5H_4)_2$}Cl_2] (**30**)	2.075(5)	2.356(1)	128.7(1)	95.75(4)	89.5(1)	[11]
[Ti{$(CH_2)_4Si(\eta^5$-$C_5H_4)_2$}Cl_2] (**47**)[b]	2.069	2.349 2.347	129.12	96.32(8) 96.03(8)	90.4(3) 91.0(3)	[40]
[Ti{$(CH_2)_5Si(\eta^5$-$C_5H_4)_2$}Cl_2] (**49**)[b]	2.072	2.343 2.342	129.43	97.4(2) 98.2(2)	89.8(6) 90.4(5)	[40]
rac-[Ti{$Me_2Si(\eta^5$-$C_5H_2[SiMe_3]Bu^t$-2,4)$_2$}Cl_2] (**101**)	2.111	2.339	130.5	95.8(0.2)	90.8(1)	[56b]
[Ti{$Me_2Si(\eta^5$-$C_5H_2(SiMe_3)_2$-3,4)$_2$}Cl_2] (**113**)	2.100	2.3372	129.61	97.40(3)	90.76(10)	[63]
[Ti{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}Cl_2] (**146**)		2.343		97.33	90.3(1)	[71b]
R-[Ti{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-C_5H_3(menthyl))}Cl_2] (**196**)		2.328		95.3(2)	90.8(6)	[77a]
S-[Ti{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-C_5H_3(menthyl))}Cl_2] (**196**)[b]		2.326 2.328		97.75(8) 97.86(8)	91.3(3) 91.1(3)	[77a]
[Ti{$Me_2Si(\eta^5$-$C_5H_4)(\eta^5$-$C_5H_3SiMe_3$)}Cl_2] (**201**)	2.078 Cp^R 2.068 Cp	2.345	128.8	97.4(1)	90.1(1)	[47]
[Ti{$Me_2Ge(\eta^5$-$C_5Me_4)_2$}Cl_2] (**143**)		2.331		96.01(1)	89.7(2)	[54]
[Zr{$H_2C(\eta^5$-$C_5H_4)_2$}Cl_2] (**2**)			116.4			[5e]
[Zr{$Me_2C(\eta^5$-$C_5H_4)_2$}Cl_2] (**5**)	2.213	2.4364	116.7	100.25(3)	99.5(2)	[24]
[Zr{$(CH_2)_4C(\eta^5$-$C_5H_4)_2$}Cl_2] (**14**)	2.191	2.433	116.6	100.51(7)	99.8(5)	[27b]
[Zr{$(CH_2)_5C(\eta^5$-$C_5H_4)_2$}Cl_2] (**15**)	2.192	2.445	116.4	99.48(7)	99.7(5)	[27b]
[Zr{$(CH_2)_6C(\eta^5$-$C_5H_4)_2$}Cl_2] (**16**)	2.178	2.437	116.3	100.0(1)	99.1(2)	[27b]
[Zr{CH_2CH_2(Me)$NCH_2CH_2C(\eta^5$-$C_5H_4)_2$}Cl_2] (**20**)		2.432		100.6(3)	99.7	[28]
[Zr{$C_{12}H_8C(\eta^5$-$C_5H_4)_2$}Cl_2] (**21**)		2.427		100.92(8)	99.2(4)	[29]
rac-[Zr{$Me_2C(\eta^5$-$C_5H_3Bu^t)_2$}Cl_2] (**69**)		2.427		99.17(9)	99.2(6)	[43a]
meso-[Zr{$Me_2C(\eta^5$-$C_5H_3Bu^t)_2$}Cl_2] (**69**)		2.432		98.5(2)	99(1)	[43a]
[Zr{$H_2C(\eta^5$-$C_5H_2Me_2$-2,5)$_2$}Cl_2] (**92**)[b]	2.202 2.198	2.4386 2.4379	117.13 117.60	102.46(4) 102.98(4)	102.7(2) 102.9(2)	[55a]
[Zr{Me(H)$C(\eta^5$-$C_5H_2Me_2$-2,5)$_2$}Cl_2] (**93**)[b]	2.198 2.205	2.4404 2.4357	117.64 117.59	100.69(4) 101.73(5)	102.2(3) 101.7(3)	[55b]
[Zr{Ph(H)$C(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}Cl_2] (**158**)	2.495 Cp 2.502 Cp^*	2.434	117.1(1)	99.40(2)	100.9(2)	[73]
[Zr{Me(H)$C(\eta^5$-$C_5H_4)(\eta^5$-$C_5H_2Me_2$-2,5)}Cl_2] (**159**)	2.188 Cp 2.186 Cp^R	2.4353(10)	117.00	102.11(7)	100.7(4)	[55b]
[Zr{$Me_2Si(\eta^5$-$C_5H_4)_2$}Cl_2] (**32**)	2.197(6)	2.435(1)	125.4(3)	97.98(4)	93.2(2)	[11]
[Zr{Me(CH_2=$CHCH_2$)$Si(\eta^5$-$C_5H_4)_2$}Cl_2] (**41**)	2.205	2.437	125.40	98.09(7)	94.0(3)	[39a,b]
[Zr{$(CH_2)_3Si(\eta^5$-$C_5H_4)_2$}Cl_2] (**50**)		2.4381	126.2(2)	100.01(3)	94.68(9)	[41]
[Zr{$(CH_2)_4Si(\eta^5$-$C_5H_4)_2$}Cl_2] (**51**)	2.201	2.434	125.57	99.36(9)	94.3(3)	[40]
[Zr{$(CH_2)_5Si(\eta^5$-$C_5H_4)_2$}Cl_2] (**53**)	2.205	2.438	125.48	97.71(5)	94.0(2)	[40]
meso-[Zr{$Me_2Si(\eta^5$-C_5H_3(neomenthyl))$_2$}Cl_2] (**80**)[b]		2.427 2.425	126.8 126.9	102.77(10) 102.62(10)	94.2(3) 94.2(3)	[45d]
meso-[Zr{$Me_2Si(\eta^5$-$C_5H_2MeBu^t$-2,4)$_2$}Cl_2] (**96**)	2.231	2.420(1)	126.7	97.6(1)	94.3(1)	[13]
rac-[Zr{$Me_2Si(\eta^5$-C_5H_2MePh-2,4)$_2$}Cl_2] (**97**)	2.225	2.428	126.0	98.6(1)	93.3(1)	[56a]
rac-[Zr{$Me_2Si(\eta^5$-$C_5H_2[SiMe_3]Bu^t$-2,4)$_2$}Cl_2] (**98**)	2.233	2.429	126.7	97.6(0.3)	94.0(1)	[56b]
meso-[Zr{$Me_2Si(\eta^5$-C_5H_2MePh-2,4)$(\eta^5$-C_5H_2PhMe-2,4)$_2$}Cl_2] (**100**)		2.4257		97.86(2)	94.43(7)	[57]
rac-[Zr{Me(CH_2=$CHCH_2$)$Si(\eta^5$-$C_5H_2Me_2$-2,4)$_2$}Cl_2] (**102**)	2.211	2.433	126.6	99.5(1)	94.0(2)	[59]
rac-[Zr{(CH_2=CH)$_2Si(\eta^5$-$C_5H_2Me_2$-2,4)$_2$}Cl_2] (**105**)	2.218	2.4330	126.5	99.49(3)	94.98(9)	[60]
rac-[$(\eta^5$-$C_5H_5)Rh(\eta^2$-CH_2=CH)$_2Si(\eta^5$-$C_5H_2Me_2$-2,4)$_2ZrCl_2$] (**108**)	2.215	2.420	127.3	98.47(6)	95.6(1)	[60]

Table 1 (*Continued*)

Complex	M–Cp (Å)	M–Cl (Å)	Cp–M–Cp (°)	Cl–M–Cl (°)	$C_{(cp)}$–E–$C_{(cp)}$ (°)	Reference
[Zr{$Me_2Si(\eta^5$-$C_5H_2(SiMe_3)_2$-3,4)$_2$}Cl_2] (**114**)	2.231	2.432	124.72	98.32(11)	93.73(35)	[63]
rac-[Zr{$Me_2Si(\eta^5$-C_5HMe_2-3,5-(furyl)-2)$_2$}Cl_2] (**125**)	2.23	2.435	128.1	98.63(8)	94.6(3)	[66]
[Zr{$Me_2Si(\eta^5$-$C_5Me_4)_2$}Cl_2] (**127**)	2.329	2.4334(7)	128.6	99.28(3)	95.7(1)	[24,67b]
[Zr{$(CH_2{=}CH)_2Si(\eta^5$-$C_5Me_4)_2$}Cl_2] (**129**)	2.235	2.4333	128.7	99.24(3)	96.3(1)	[61]
[$(\eta^5$-$C_9H_7)Rh(\eta^2$-$CH_2{=}CH)_2Si(\eta^5$-$C_5Me_4)_2ZrCl_2$] (**132**)	2.240	2.441	129.0	100.3(1)	96.7(3)	[61]
[Zr{$Me(H)Si(\eta^5$-$C_5Me_4)_2$}Cl_2] (**134**)	2.230	2.427	128.5	98.85(6)	96.15(19)	[68]
[Zr{$Me(CH_2{=}CH)Si(\eta^5$-$C_5Me_4)_2$}Cl_2] (**138**)	2.220	2.418	128.76	99.32(7)	95.8(2)	[39a]
[Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}Cl_2] (**147**)	2.202 Cp 2.198 Cp^*	2.451(1)	128.10	104.60(7)	95.2(2)	[71a,b]
[Zr{$Me_2Si(\eta^5$-$C_5H_4)(\eta^5$-$C_5H_2Bu^t_2$-3, 4)}Cl_2] (**149**)	2.209 Cp 2.236 Cp^R	2.442	125.2	97.11(3)	94.5(1)	[71c]
[Zr{$Me(Et)(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}Cl_2] (**161**)	2.219(2) Cp 2.218(2) Cp^*	2.4336(8)	126.70(4)	101.17(5)	93.82(14)	[74]
[Zr{$Me(CH_2{=}CHCH_2)Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}$Cl_2$] (**166**)	2.207 Cp 2.220 Cp^*	2.428	126.67	100.9(1)	95.0(3)	[39a]
[Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3Me)$}Cl_2] (**185**)	2.194 Cp^R 2.184 Cp^*	2.414(4)	126.25	101.1(2)	92.4(8)	[71a]
[Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3Et)$}Cl_2] (**186**)	2.214 Cp^R 2.207 Cp^*	2.429(4)	126.5	100.4(2)	93.3(7)	[75]
[Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3Pr^i)$}Cl_2] (**187**)	2.223 Cp^R 2.230 Cp^*	2.429	126.9	98.2(1)	94.2(2)	[75]
R-[Zr{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-C_5H_3(menthyl))}Cl_2] (**198**)		2.419	126.6	98.6(2)	93.6(4)	[77c,d]
[Zr{$Me_2Si(\eta^5$-$C_5H_4)(\eta^5$-$C_5H_3CH_2CH{=}CH_2$)}Cl_2] (**207**)		2.4290		98.74(3)	94.0(1)	[78]
[Zr{$Me_2Si(\eta^5$-$C_5H_4)(\eta^5$-$C_5H_3CH_2CH_2CH_2B(C_8H_{14})$)}$Cl_2$] (**216**)		2.431	126.0	99.60(4)	93.6(1)	[80b]
[Zr{$Me_2Si(\eta^5$-$C_5H_4)(\eta^5$-$C_5H_3CH_2CH_2CH_2B(C_6F_5)_2$)(2-methyl-4,5-dihydrooxazole)}Cl_2] (**218**)		2.443		95.56(3)	93.8(1)	[80b]
[Zr{$Me_2Si(\eta^5$-$C_5H_4)(\eta^5$-$C_5H_3CH_2CH_2CH_2B(C_6F_5)_2$)(*N*-methylbenzimidazole)}Cl_2] (**219**)		2.432		98.93(3)	93.7(1)	[80a]
[Zr{$Me_2Ge(\eta^5$-$C_5Me_4)_2$}Cl_2] (**144**)	2.235	2.437	129.39	98.35(7)	92.7(3)	[54,70]
[Zr{$Me_2Ge(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}Cl_2] (**153**)	2.213 Cp 2.217 Cp^*	2.404(9)	127.5	99.3(5)	91.01(1)	[70,71b]
[Hf{$Me_2C(\eta^5$-$C_5H_4)_2$}Cl_2] (**6**)	2.174	2.409	117.1	98.9(1)	99.4(3)	[25]
[Hf{$Me_2Si(\eta^5$-$C_5H_4)_2$}Cl_2] (**33**)	2.191	2.424	126.8			[37]
[Hf{$Me_2Si(\eta^5$-$C_5Me_4)_2$}Cl_2] (**128**)	2.223	2.407(2)	129.2	98.0(1)	95.1(3)	[67b]
[Hf{$Et_2Si(\eta^5$-$C_5Me_4)_2$}Cl_2] (**131**)	2.224	2.407		98.75(8)	95.3(2)	[67b]
[Hf{$(CH_2{=}CH)_2Si(\eta^5$-$C_5Me_4)_2$}Cl_2] (**130**)	2.217	2.405	129.2	97.98(7)	96.5(2)	[67b]
[Hf{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}Cl_2] (**148**)		2.413		99.96	94.1(2)	[71b]
[Hf{$Me_2Ge(\eta^5$-$C_5Me_4)_2$}Cl_2] (**145**)	2.227	2.409(2)	129.8	97.9(1)	92.8(4)	[67b]
[Hf{$Me_2Ge(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_4)$}Cl_2] (**154**)	2.193 Cp 2.210 Cp^*	2.409	127.74	98.6(1)	91.2(3)	[70]
				Cl–M–N (°)		
[Nb(=$NSiMe_3$){$Me_2C(\eta^5$-$C_5H_4)_2$}Cl] (**22**)	2.181	2.4387(4)	114.2	98.21(4)	98.89(9)	[30]
[Nb(=NBu^t){$Me_2C(\eta^5$-$C_5H_4)_2$}Cl] (**23**)	2.189	2.446(1)	113.3	95.3(1)	99.3(3)	[30]
[Nb(=$NC_6H_3Pr^i_2$-2, 6){$Me_2C(\eta^5$-$C_5H_4)_2$}Cl] (**26**)	2.167	2.433(1)		98.3(1)	99.4(2)	[32]
[Nb(=NBu^t){$Me_2Si(\eta^5$-$C_5H_4)_2$}Cl] (**58**)	2.110(2)	2.448(1)	121.21	95.15(9)	94.17(6)	[42a]
[Nb(=NBu^t){$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3Me)$}Cl] (**221**)[b]	2.225 Cp^R 2.249 Cp^* 2.2275 Cp^R 2.250 Cp^*	2.458(1) 2.460(1)	122.7 122.3	97.0(1) 96.2(1)	93.7(2) 94.4(2)	[71a]
[Nb(=NBu^t){$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3Pr^i)$}Cl] (**222**)	2.228 Cp^R 2.245 Cp^*	2.4372(6)	122.1	96.33(7)	93.3(1)	[71a]
[Ta(=$NC_6H_3Pr^i_2$-2, 6){$Me_2C(\eta^5$-$C_5H_4)_2$}Cl] (**27**)	2.154	2.404(1)		98.1(1)	99.0(2)	[32]

[a] Blank spaces in this table indicate that these data were not reported; ESD values are given when reported.

[b] There are two independent molecules in the asymmetric cell.

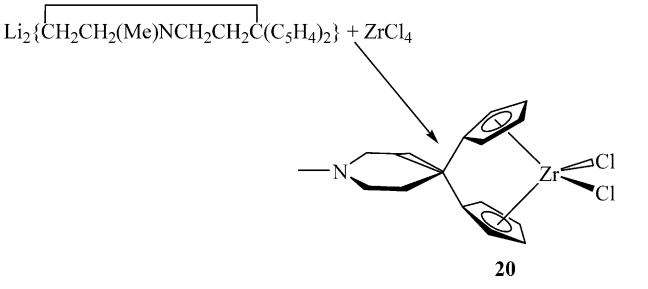


(5)

	11	12	13	14	15	16	17	18	19
M	Ti	Ti	Ti	Zr	Zr	Zr	Hf	Hf	Hf
n	4	5	6	4	5	6	4	5	6

(5)

An *ansa*-zirconocene complex with an *N*-methylpiperdine bridge has been prepared and characterized by single crystal X-ray diffraction studies (Eq. (6)) [28]. The synthesis and molecular structure of an *ansa*-zirconocene complex with a fluorenylidene bridge were reported by Nifant'ev and co-workers (Eq. (7)) [29].



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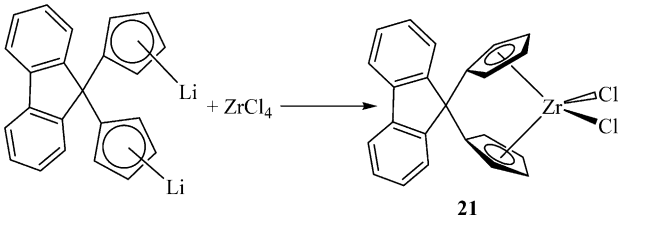
(6)



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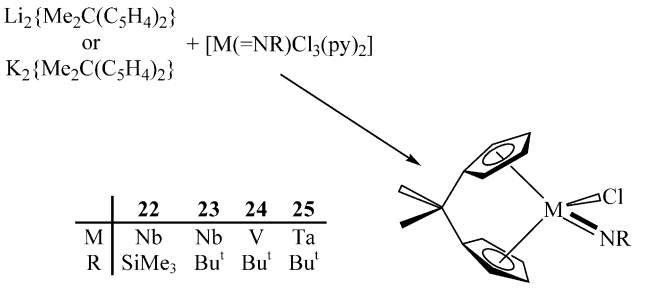
(7)

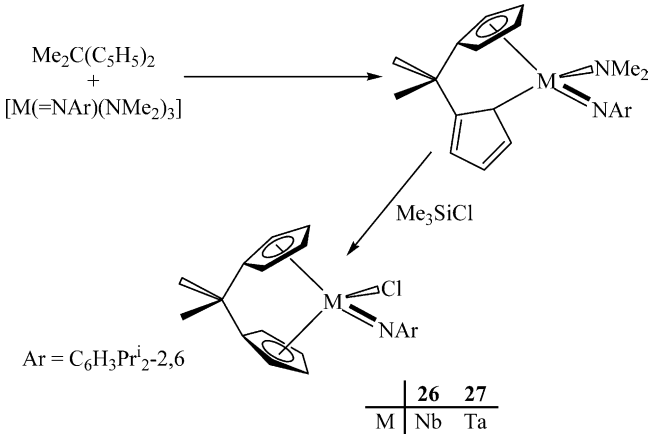
For the group 5 compounds, the inclusion of an imido ligand appears to provide the stability needed to isolate the *ansa*-metallocene(V) complexes, [M(=NR){$Me_2C(\eta^5$-$C_5H_4)_2$}Cl] (M = Nb, R = $SiMe_3$ (**22**), Bu^t (**23**); M = V, R = Bu^t (**24**); M = Ta, R = Bu^t (**25**)) (Eq. (8)) [30]. **22**–**25** were readily converted to their bromide, iodide, methyl or cationic derivatives [30,31]. The molecular structures of **22** and **23** were established [30].



	22	23	24	25
M	Nb	Nb	V	Ta
R	$SiMe_3$	Bu^t	Bu^t	Bu^t

(8)

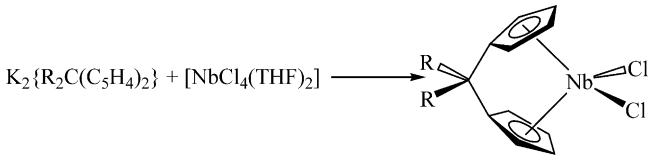
An alternative method was employed by Herrmann and co-workers in the preparation of the group 5 *ansa*-metallocene imido compounds [M(=$NC_6H_3Pr^i_2$-2, 6){$Me_2C(\eta^5$-$C_5H_4)_2$}Cl] (M = Nb (**26**), Ta = (**27**)) (Eq. (9)). With an amide ancillary ligand, the *ansa*-ligand adopted a chelating η^5:η^1 arrangement. Nevertheless, an η^5:η^5 arrangement was observed in the X-ray crystal structure of the chloride derivative [15a,32].



	26	27
M	Nb	Ta

(9)

The niobocene(IV) dichloride complexes, [Nb{$R_2C(\eta^5$-$C_5H_4)_2$}Cl_2] (R = Me (**28**), Et (**29**)) were prepared by the reaction of the corresponding di-potassium *ansa*-derivative reagent with [$NbCl_4(THF)_2$] (Eq. (10)) [33]. Tetrahydroborate and hydride derivatives were obtained by reaction of **28** and **29** with the appropriate reagents [33].



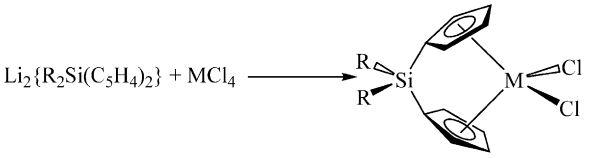
	28	29
M	Me	Et

(10)

2.2. Silicon atom ansa-bridge

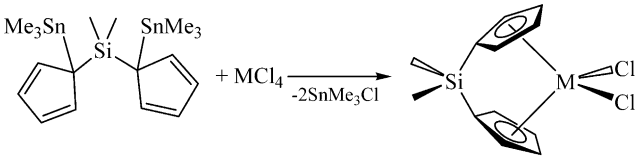
The first reported silylene bridged group 4 *ansa*-metallocene complexes described the synthesis of [M{$R_2Si(\eta^5$-$C_5H_4)_2$}Cl_2] (M = Ti, R = Me (**30**), Et (**31**); M = Zr, R = Me (**32**); M = Hf, R = Me (**33**)) in yields of ca. 10% (Eq. (11)) [9]. The same synthetic route was employed by Petersen and co-workers in the preparation of **30**, **32** and [Zr{$R_2Si(\eta^5$-$C_5H_4)_2$}Cl_2] (Et (**34**), Pr^n (**35**)) but with yields of approximately 70 and 50% for the titanocene and zirconocene derivatives, respectively [11]. Royo and co-workers using the same reaction scheme reported yields of 51 and 87% for **32** and **33**, respectively [34]. Alt and co-workers observed a yield for **32** of 50–70% [35] and similarly Yasuda

et al. reported a yield of 48% [36]. **32** and **33** were also prepared, in yields of over 90%, via the transmetalation of the distannylated *ansa*-bis(cyclopentadiene) with the metal tetrachlorides (Eq. (12)) [22]. The molecular structures of **30**, **32** and **33** were determined by X-ray diffraction studies [11,37]. In general, the centroid–metal–centroid angles of the silicon *ansa*-bridge compounds are 10° larger than their carbon *ansa*-bridge analogues (see Table 1).



	30	31	32	33	34	35
M	Ti	Ti	Zr	Hf	Zr	Zr
R	Me	Et	Me	Me	Et	Pr^n

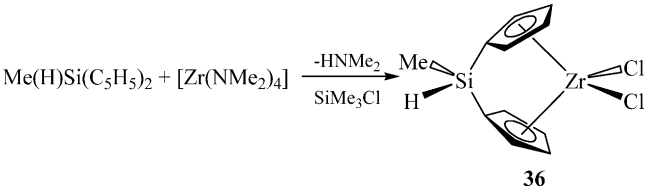
(11)



	32	33
M	Zr	Hf

(12)

The *ansa*-metallocene complex bearing a MeSiH bridge, [Zr{Me(H)Si(η^5-C_5H_4)$_2$}Cl_2] (**36**), was prepared by the amine elimination reaction between [Zr(NMe_2)$_4$] and bis(cyclopentadienyl)methylsilane followed by metathesis with Me_3SiCl (Eq. (13)) [38]. The titanium analogue, [Ti{Me(H)Si(η^5-C_5H_4)$_2$}Cl_2] (**37**), has been reported but its synthesis from the dilithium *ansa*-cyclopentadienyl derivative was only achieved in a 5% yield [9a,c]. **36** was immobilized on silica via hydrosilylation of a vinyl functionalized surface by the *ansa*-metallocene complex [38].

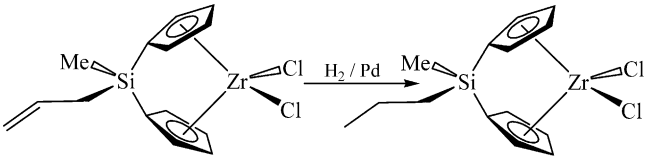


36

(13)

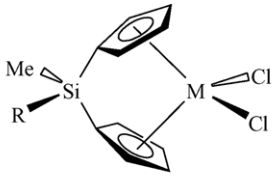
Group 4 *ansa*-metallocene complexes with vinyl or allyl substituents at the silicon bridge, [M{Me(R)Si(η^5-C_5H_4)$_2$}Cl_2] (M = Ti, R = CH=CH_2 (**38**), CH_2CH=CH_2 (**39**); M = Zr, R = CH=CH_2 (**40**), CH_2CH=CH_2 (**41**); M = Hf, R = CH=CH_2 (**42**), CH_2CH=CH_2 (**43**)), were prepared via the reaction of the dilithium derivative and the metal tetrachloride (Fig. 2) [39]. **40** was also synthesized in a similar manner to **36** by amine elimination [38]. Using a Me_2SiHCl treated hydroxylated silica, the hydrosilylation of **40** gave the *ansa*-metallocene complex supported on silica [38]. When **39** was used as the catalyst in the polymerization of styrene, the allyl group of the *ansa*-ligand co-polymerized with the olefin monomer producing the immobilization of the metallocene complex on the polymer chain [39b]. The molecular structure of **39** was determined by X-ray diffraction studies [39a,b].

The hydrogenation of the C=C double bond of the allyl group of **41** gave the saturated *ansa*-metallocene complex [Zr{Me(Pr^n)Si(η^5-C_5H_4)$_2$}Cl_2] (**44**) (Eq. (14)) [39a]. Likewise, the hydroboration of the vinylic double bond of **40** by 9-BBN gave [Zr{Me((BC_8H_{14})CH_2CH_2)Si(η^5-C_5H_4)$_2$}Cl_2] (**45**), resulting from anti-Markonikoff addition (Eq. (15)) [39a].



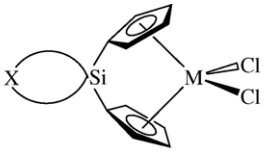
41 **44**

(14)



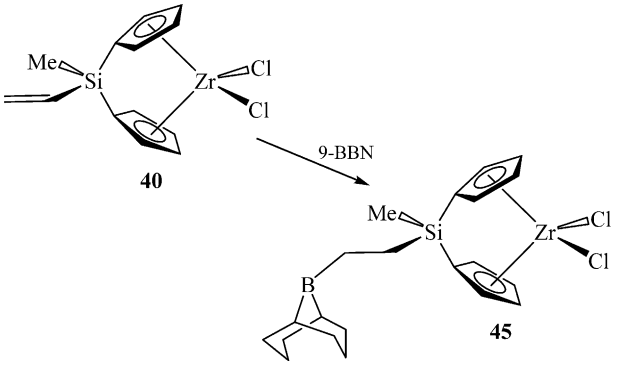
	38	39	40	41	42	43
M	Ti	Ti	Zr	Zr	Hf	Hf
R	CH=CH_2	CH_2CH=CH_2	CH=CH_2	CH_2CH=CH_2	CH=CH_2	CH_2CH=CH_2

Fig. 2. Compounds **38**–**43**.



	Si	Si	Si	Si
Ti	**46**	**47**	**48**	**49**
Zr	**50**	**51**	**52**	**53**
Hf	**54**	**55**	**56**	**57**

Fig. 3. Compounds **46**–**57**.

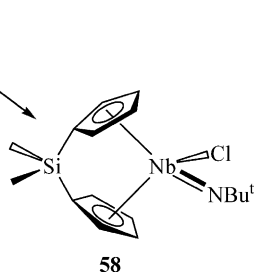


(15)

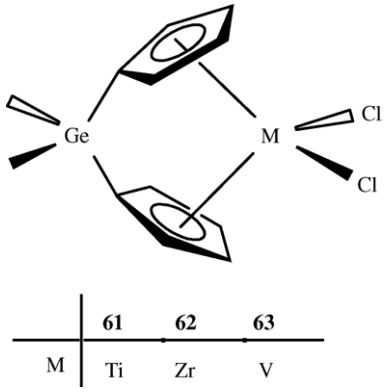
Silacycloalkane *ansa*-bridged compounds formed by the reaction of the lithium derivative of the *ansa*-ligand with the metal tetrachloride have been described (Fig. 3) [27b,40]. The spirocyclic *ansa*-zirconocene complex $[Zr\{CH_2CH_2CH_2Si(\eta^5\text{-}C_5H_4)_2\}Cl_2]$ (**50**) was also prepared by the amine elimination reaction of the spiro-*ansa*-bis(cyclopentadiene) with $[Zr(NMe_2)_4]$ and posterior treatment with Me_3SiCl [41]. The transition metal catalyzed ring-opening polymerization of **50** was studied [41].

The *ansa*-niobocene imido compound $[Nb(=NBu^t)\{Me_2Si(\eta^5\text{-}C_5H_4)_2\}Cl]$ (**58**) and its alkyl and alkynyl derivatives have been reported (Eq. (16)) [42]. The molecular structure of **58** was determined.

$Li_2\{Me_2Si(C_5H_4)_2\} + [Nb(=NBu^t)Cl_3(py)_2]$



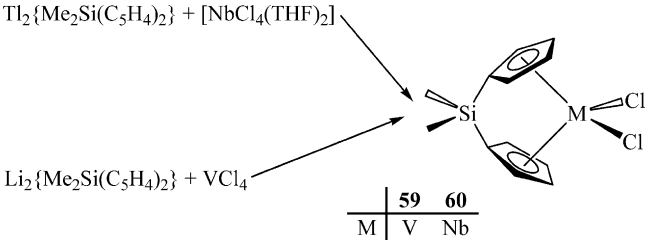
(16)



	61	62	63
M	Ti	Zr	V

Fig. 4. Compounds **61**–**63**.

The vanadocene and niobocene(IV) dichloride complexes have also been prepared $[M\{Me_2Si(\eta^5\text{-}C_5H_4)_2\}Cl_2]$ (M = V (**59**), Nb (**60**)) (Eq. (17)) [14,15b]. The tetrahydroborate derivative of **60** was obtained by its reaction with $Li(BH_4)$ [33b].



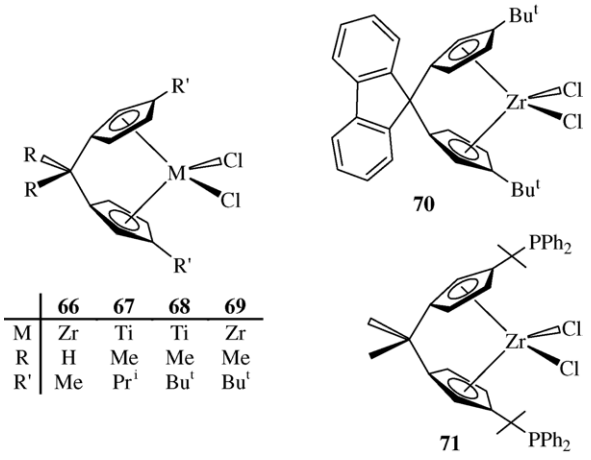
(17)

2.3. Germanium atom ansa-bridge

The germanium bridged group 4 *ansa*-metallocene complexes, $[M\{Me_2Ge(\eta^5\text{-}C_5H_4)_2\}Cl_2]$ (M = Ti (**61**), Zr (**62**)), were prepared in yields of only 2% by the reaction of the lithium *ansa*-bis(cyclopentadienyl) derivative with the metal tetrachloride (Fig. 4) [9a]. The vanadium complex $[V\{Me_2Ge(\eta^5\text{-}C_5H_4)_2\}Cl_2]$ (**63**) was prepared in a similar manner to its silicon bridged analogue **59** (Fig. 4) [14].

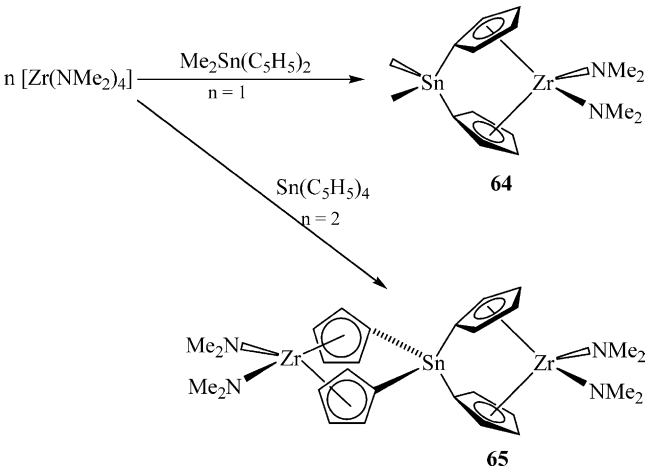
2.4. Tin atom ansa-bridge

The instability of the Sn–C bond has meant that only two tin bridged *ansa*-metallocene complexes, $[Zr\{Me_2Sn(\eta^5\text{-}C_5H_4)_2\}(NMe_2)_2]$ (**64**) and $[Zr_2\{Sn(\eta^5\text{-}C_5H_4)_4(NMe_2)_4]$ (**65**), have been reported (Eq. (18)) [17]. The lithiation of the *ansa*-ligand precursor is not possible due to the rupture of the Sn–C bond of the cyclopentadienyl moiety. Compounds **64** and **65** gave higher catalytic activities in the polymerization of ethylene compared with the silicon bridged *ansa*-complex $[Zr\{Me_2Si(\eta^5\text{-}C_5H_4)_2\}(NMe_2)_2]$ [17]. Dichloride derivatives of **64** and **65** have not been reported.

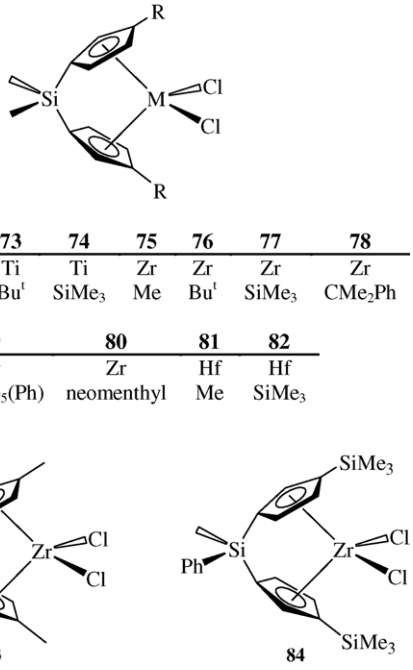


	66	67	68	69
M	Zr	Ti	Ti	Zr
R	H	Me	Me	Me
R'	Me	Pr^i	Bu^t	Bu^t

Fig. 5. Compounds **66**–**71**.



(18)



	72	73	74	75	76	77	78
M	Ti	Ti	Ti	Zr	Zr	Zr	Zr
R	Me	Bu^t	SiMe$_3$	Me	Bu^t	SiMe$_3$	CMe$_2$Ph

	79	80	81	82
M	Zr	Zr	Hf	Hf
R	C(CH$_2$)$_5$(Ph)	neomenthyl	Me	SiMe$_3$

Fig. 6. Compounds **72**–**84**.

3. *ansa*-Metallocene complexes with symmetric ring mono-substitution

The inclusion of ring substituents in symmetric *ansa* systems presents the possibility of the formation of *meso* and *rac* isomers of the *ansa*-metallocene complex. However, only the *rac* isomer is isospecific in the polymerization of α-olefins and therefore, great importance has been placed in the stereoselective synthesis of this diastereomer.

3.1. Carbon atom ansa-bridge

The *ansa*-metallocene complex, [Zr{$H_2C(\eta^5$-$C_5H_3Me)_2$}Cl_2] (**66**), was prepared via the reaction of the lithium derivative of the ligand and $ZrCl_4$ (Fig. 5) [20] with the *rac* isomer being isolated by crystallization. [M{$Me_2C(\eta^5$-$C_5H_3R)_2$}Cl_2] (M = Ti, R = Pr^i (**67**), Bu^t (**68**); M = Zr, R = Bu^t (**69**)) were synthesized as 1:1 mixtures of the *rac* and *meso* isomers which were separated by fractional recrystallization (Fig. 5) [43]. The titanium complexes **67** and **68** were prepared using [$TiCl_3(THF)_3$] and subsequent oxidation of the *ansa*-titanocene(III) intermediate by HCl [43]. The molecular structures of **67**–**69** were determined by X-ray diffraction (see Table 1) [43].

The *ansa*-zirconocene complex with a fluorenylidene bridge **70** was prepared as a 1:1 mixture of its *meso* and *rac* isomers via reaction of the lithium *ansa*-derivative and $ZrCl_4$ (Fig. 5) [29]. In a similar manner, the phosphine containing complex, [Zr{$Me_2C(\eta^5$-$C_5H_3(CMe_2PPh_2))_2$}Cl_2] (**71**), was obtained in a 2.8:1 *rac*:*meso* ratio (Fig. 5), although by recrystallization the *rac* isomer could be separated [44].

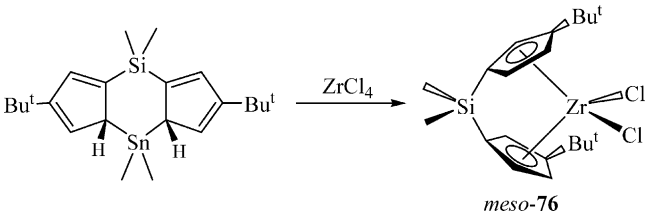
3.2. Silicon atom ansa-bridge

The discovery that the C_2 symmetric *ansa*-metallocene complexes are isospecific in the polymerization of α-olefins has led to the preparation of a variety of compounds with special interest being paid to synthetic routes that produce preferentially the catalytically stereoselective *rac* isomer.

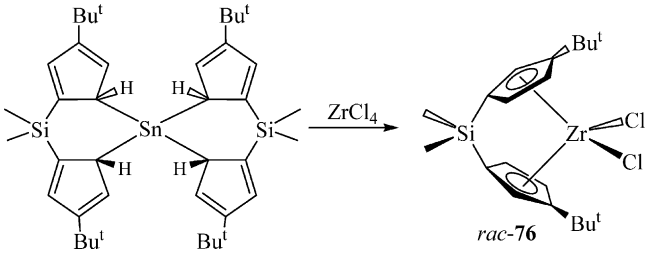
The *ansa*-metallocene complexes, [M{$Me_2Si(\eta^5$-$C_5H_3R)_2$}Cl_2] (M = Ti, R = Me (**72**), Bu^t (**73**), $SiMe_3$ (**74**); M = Zr, R = Me (**75**), Bu^t (**76**), $SiMe_3$ (**77**), CMe_2Ph (**78**), $C(CH_2)_5$(Ph) (**79**), neomenthyl (**80**); M = Hf, R = Me (**81**), $SiMe_3$ (**82**)), were prepared by the reaction of the dilithium or dipotassium derivative with the metal tetrachloride or in the case of **73** and **74** with [$TiCl_3(THF)_3$] (Fig. 6) [13,45]. **76** and **77** were also prepared using the magnesium *ansa*-derivative [13]. The synthesis of **72**–**82** was normally achieved in 1:1 *rac*:*meso* ratios. By fractional recrystallization it was possible, in most cases, to separate

the diastereomers. In a similar manner, Ewen et al. prepared $[Zr\{Et_2Si(\eta^5\text{-}C_5H_3Me)_2\}Cl_2]$ (**83**), again as a 1:1 mixture of the *rac* and *meso* isomers (Fig. 6) [46]. Lang et al. have reported the asymmetrically substituted *ansa*-bridge compound $[Zr\{Me(Ph)Si(\eta^5\text{-}C_5H_3SiMe_3)_2\}Cl_2]$ (**84**) (Fig. 6) [47].

Transmetalation reactions of tin derivatives have been employed in the stereoselective synthesis of **76**. The *meso* isomer of the tin bis(cyclopentadiene) compound gave exclusively the *meso*-configured *ansa*-zirconocene complex (Eq. (19)) [48]. The *rac* isomer was stereoselectively obtained using the spiro tin tetra(cyclopentadiene) derivative (Eq. (20)) [49].

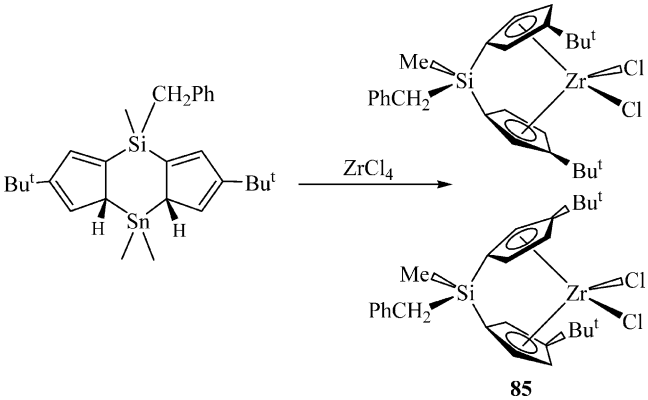


(19)



(20)

The asymmetrically substituted *ansa*-bridge complex, $[Zr\{Me(PhCH_2)Si(\eta^5\text{-}C_5H_3Bu^t)_2\}Cl_2]$ (**85**), was prepared exclusively in its *meso* configurations via transmetalation of the *meso* isomer of the tin derivative (Eq. (21)) [50].



(21)

Nifant'ev and co-workers prepared the adamantyl substituted *ansa*-zirconocene complex, $[Zr\{Me_2Si(\eta^5\text{-}C_5H_3[adamantyl])_2\}Cl_2]$ (**86**), via transmetalation of the

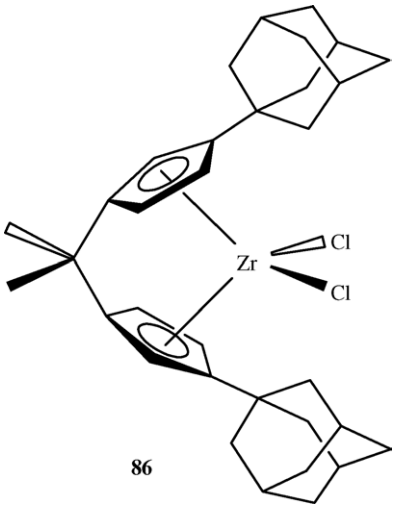
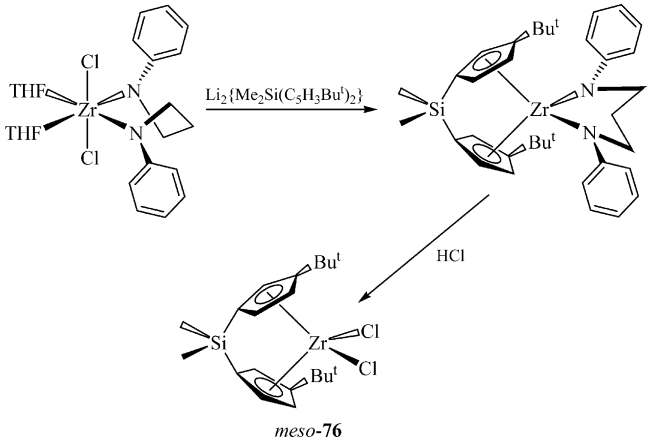


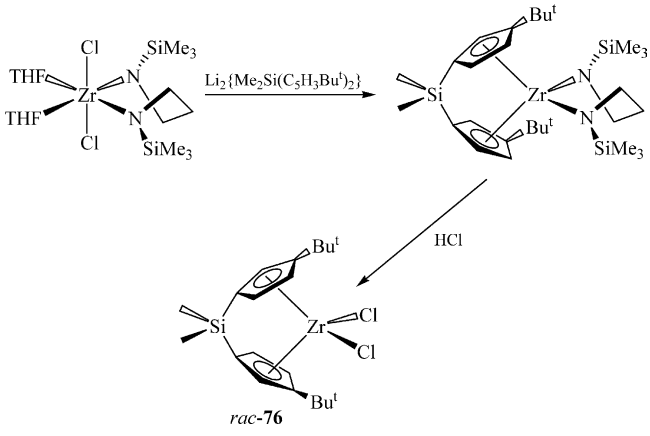
Fig. 7. Compound **86**.

corresponding tin derivative (Fig. 7) [51]. The *rac* and *meso* isomers were separated by crystallization.

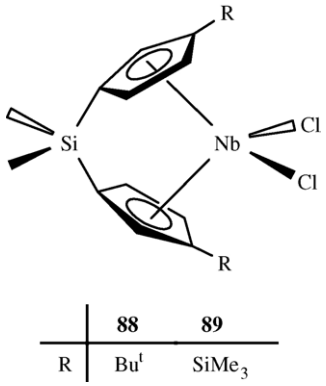
LoCoco and Jordan have also reported the stereoselective synthesis of **76** using chelating bis-amide ligands coordinated to the zirconium precursor giving high stereocontrol in the reaction with the dilithium *ansa*-derivative (Eqs. (22) and (23)) [52].



(22)



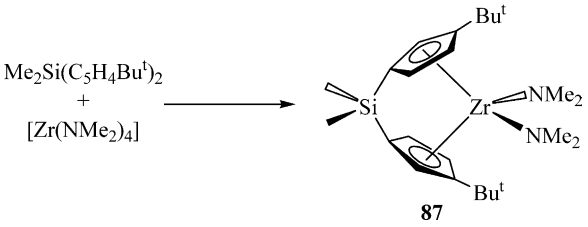
(23)



	88	89
R	Bu^t	$SiMe_3$

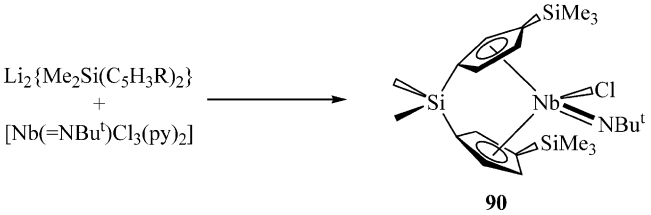
Fig. 8. Compounds **88** and **89**.

The preparation of the amide derivative of **76**, $[Zr\{Me_2Si(\eta^5\text{-}C_5H_3Bu^t)_2\}(NMe_2)_2]$ (**87**), was achieved by amine elimination in the reaction between $[Zr(NMe_2)_4]$ and the organic compound $Me_2Si(C_5H_4Bu^t)_2$; however, its conversion to the dichloride compound was not reported (Eq. (24)) [53]. **87** was initially obtained in a *rac*:*meso* ratio of 1:2 with the *meso* isomer being subsequently isolated by fractional crystallization.



(24)

The *ansa*-niobocene dichloride complexes, $[Nb\{Me_2Si(\eta^5\text{-}C_5H_3R)_2\}Cl_2]$ (R = Bu^t (**88**), $SiMe_3$ (**89**)), were prepared by the reaction of $Li_2\{Me_2Si(\eta^5\text{-}C_5H_3R)_2\}$ with $[NbCl_4(THF)_2]$ and isolated as a mixture of the *rac* and *meso* isomers (Fig. 8) [16a,42a]. The reactivity of these complexes in reduction and alkylation processes was reported [16a,42a]. The niobium imido complex, $[Nb(=NBu^t)\{Me_2Si(\eta^5\text{-}C_5H_3SiMe_3)_2\}Cl_2]$ (**90**), was prepared stereoselectively as its *meso* isomer (Eq. (25)) [42a].



(25)

3.3. Germanium atom ansa-bridge

$[Zr\{Me_2Ge(\eta^5\text{-}C_5H_3Bu^t)_2\}Cl_2]$ (**91**) was prepared via the reaction of $ZrCl_4$ and the lithium *ansa* precursor (Fig. 9)

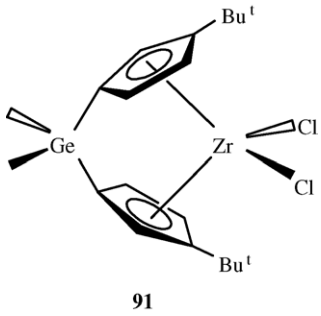
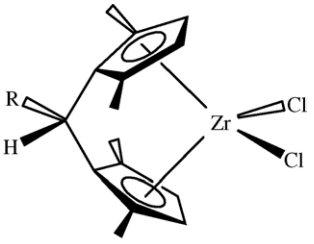


Fig. 9. Compound **91**.



	92	93
R	H	Me

Fig. 10. Compounds **92** and **93**.

and isolated as a mixture of its *meso* and *rac* isomers [54].

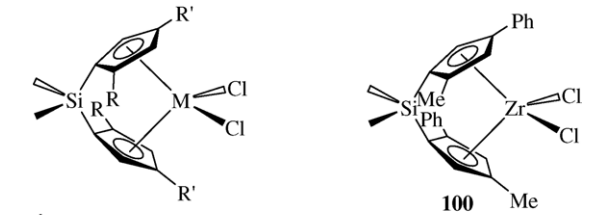
4. *ansa*-Metallocene complexes with symmetric ring di-substitution

4.1. Carbon atom ansa-bridge

The complexes $[Zr\{R(H)C(\eta^5\text{-}C_5H_2Me_2\text{-}2,5)_2\}Cl_2]$ (R = H (**92**), Me (**93**)) were prepared by the reaction of the dilithium *ansa*-precursors with $ZrCl_4$ (Fig. 10) [55]. The molecular structures of **92** and **93** were reported (see Table 1) [55].

4.2. Silicon atom ansa-bridge

The *ansa*-metallocene complexes, $[M\{Me_2Si(\eta^5\text{-}C_5H_2RR'\text{-}2,4)_2\}Cl_2]$ (M = Zr, R = Me, R′ = Me (**94**), Pr^i (**95**), Bu^t (**96**), Ph (**97**); R = $SiMe_3$, R′ = Bu^t (**98**); M = Hf, R = Me, R′ = Me (**99**)), were prepared by the reaction of the corresponding dilithium or dipotassium derivative with the metal tetrachloride (Fig. 11) [13,45b,c,56]. The compounds were generally obtained as mixtures of their *rac* and *meso* isomers which in many cases were separated by fractional recrystallization. However, **121** was obtained exclusively as the *rac* isomer [56b]. Royo and co-workers recently observed during the preparation of **97**, the pres-

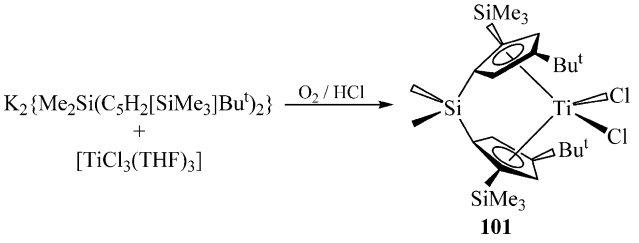


	94	95	96	97	98	99
M	Zr	Zr	Zr	Zr	Zr	Hf
R	Me	Me	Me	Me	$SiMe_3$	Me
R'	Me	Pr^i	Bu^t	Ph	Bu^t	Me

Fig. 11. Compounds **94**–**100**.

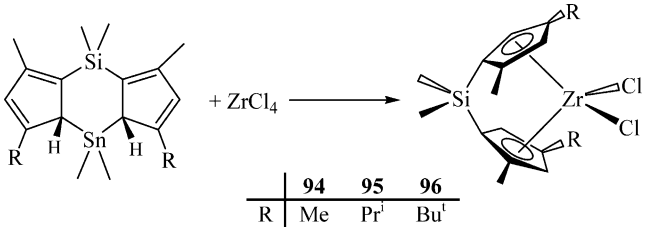
ence of a minor product, [Zr{$Me_2Si(\eta^5$-C_5H_2MePh-2,4)(η^5-C_5H_2PhMe-2,4)}Cl_2] (**100**), where the methyl and phenyl substituents adopt differing positions in the two C_5 rings (Fig. 11) [57]. **100** was obtained as a mixture of its *meso* and *rac* isomers and separation was achieved by fractional recrystallization [57]. The presence of Li_2{$Me_2Si(C_5H_2MePh$-2,4)(C_5H_2PhMe-2,4)$_2$} in the alkali-metal *ansa* precursor was responsible for the formation of **100**.

The titanium complex, [Ti{$Me_2Si(\eta^5$-$C_5H_2[SiMe_3]Bu^t$-2,4)$_2$}Cl_2] (**101**), was prepared from the titanium(III) chloride precursor and the dipotassium *ansa*-derivative [56b]. The final product was obtained on oxidation by air in the presence of HCl gas (Eq. (26)).



(26)

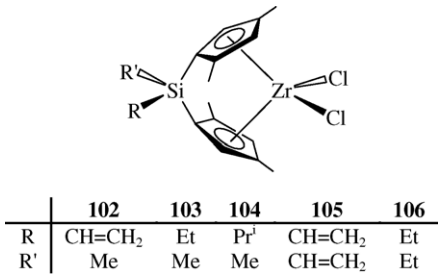
Transmetalation reactions of tin derivatives have been employed in the synthesis of **94**–**96** (Eq. (27)) [48]. The *meso* isomer is favoured for **94** and **96** (*meso*:*rac*, 9:1). However, **95** was obtained as a 1:1 mixture of its *rac* and *meso* isomers.



	94	95	96
R	Me	Pr^i	Bu^t

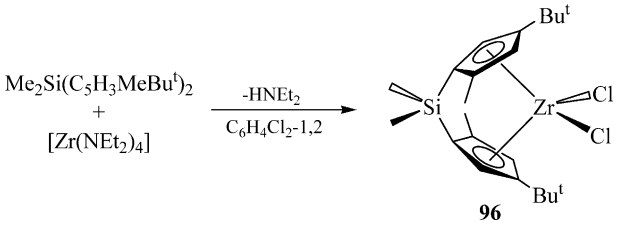
(27)

The preparation of **96** was also achieved, with a *rac*:*meso* ratio of 3:1, via amine elimination in the reaction between [$Zr(NEt_2)_4$] and the *ansa*-bis(cyclopentadiene) compound $Me_2Si(C_5H_3MeBu^t)_2$ in the chlorinated solvent $C_6H_4Cl_2$-1,2 (Eq. (28)) [53].



	102	103	104	105	106
R	$CH=CH_2$	Et	Pr^i	$CH=CH_2$	Et
R'	Me	Me	Me	$CH=CH_2$	Et

Fig. 12. Compounds **102**–**106**.

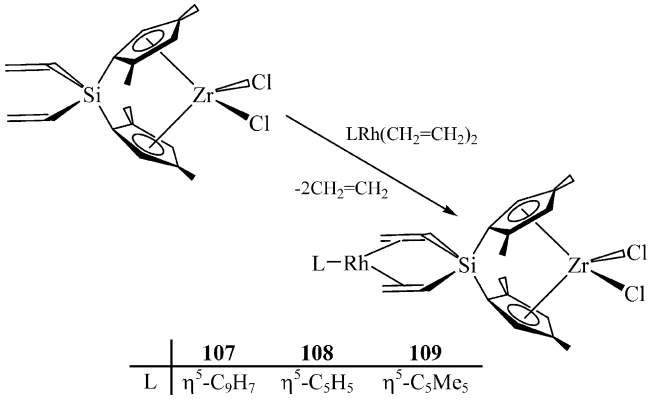


(28)

The irradiation of *meso*/*rac* mixtures of **96** and **97** in the presence of the dilithium salt of racemic binaphtholate yielded exclusively the *rac* isomer of the *ansa*-zirconocene binaphtholate complex [58]. However, the conversion to the dihalide complexes occurs with partial isomerization to the *meso* derivative.

By varying the substituents of the *ansa*-bridge atom, Suzuki and co-workers have prepared a family of *ansa*-metallocene complexes, **102**–**106** (Fig. 12) [59]. The reaction of the dilithium *ansa* derivative with zirconium tetrachloride gave the products as mixtures of their *rac* and *meso* isomers, although via fractional recrystallization the *rac* isomer was isolated in reasonable yields.

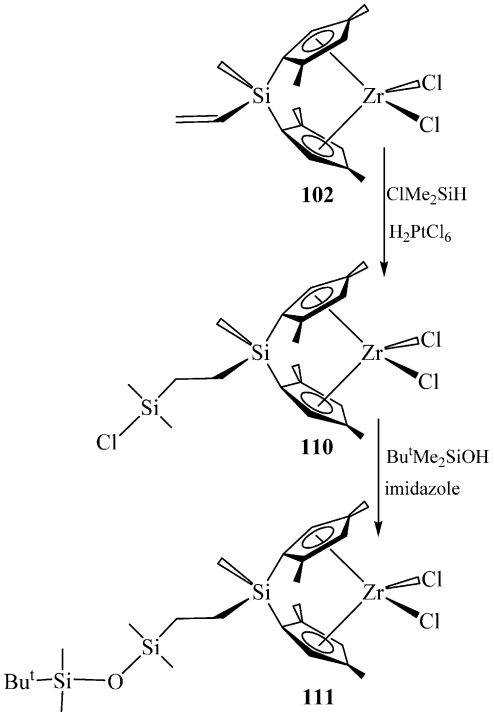
The reaction of *rac*-**105** with rhodium complexes gave the heterobimetallic derivatives, *rac*-[LRh(η^2-CH_2=CH)$_2$Si(η^5-$C_5H_2Me_2$-2,4)$_2ZrCl_2$] (L = η^5-C_9H_7 (**107**), η^5-C_5H_5 (**108**), η^5-C_5Me_5 (**109**)) (Eq. (29)), which showed higher catalytic activities in the polymerization of olefins than their parent complex [60]. The synthesis of the *meso* isomer of **107** has also been reported [61].



	107	108	109
L	η^5-C_9H_7	η^5-C_5H_5	η^5-C_5Me_5

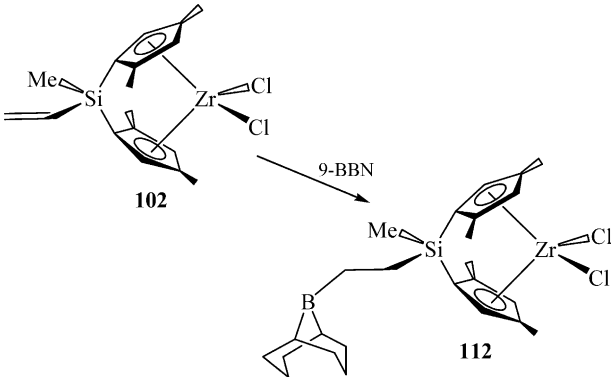
(29)

The hydrosilylation of *rac*-**102** by chlorodimethylsilane, in the presence of H_2PtCl_6, gave the *ansa*-zirconocene complex *rac*-[Zr{$ClMe_2SiCH_2CH_2(Me)Si(\eta^5$-$C_5H_2Me_2$-2,4)$_2$}$Cl_2$] (**110**) (Eq. (30)) [62]. **110** reacted with the silyl alcohol Bu^tMe_2SiOH, in the presence of imidazole to yield *rac*-[Zr{$Bu^tMe_2SiOSi(Me_2)CH_2CH_2(Me)Si(\eta^5$-$C_5H_2Me_2$-2,4)$_2$}$Cl_2$] (**111**), via the formation of Si–O–Si bonds (Eq. (30)) [62]. This strategy was employed successfully in the immobilization of **110** on silica by its reaction with surface Si–OH groups [62].



(30)

Hydroboration of *rac*-**102** by 9-BBN (9-borabicyclo[3,3,1]nonane) gave *rac*-[Zr{$Me((BC_8H_{14})CH_2CH_2)Si(\eta^5$-$C_5H_2Me_2$-2,4)$_2$}$Cl_2$] (**112**) (Eq. (31)) [62]. Using this same procedure, it was possible to immobilize the BH_3 derivative of *rac*-**102** by hydroboration on vinyl functionalized silica [62].



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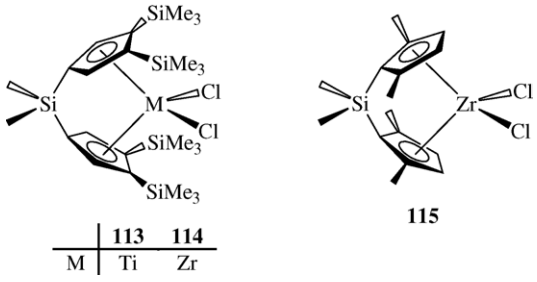


Fig. 13. Compounds **113**–**115**.

Only a handful of *ansa*-metallocene complexes have been reported where the di-substitution of the C_5 ring does not take place in the 2 and 4 positions. For example, the *ansa*-metallocene complexes, [M{$Me_2Si(\eta^5$-$C_5H_2(SiMe_3)_2$-3,4)$_2$}Cl_2] (M = Ti (**113**), Zr (**114**)), were prepared by the reaction of the dipotassium *ansa* precursor with the metal tetrachlorides (Fig. 13) [63]. In a similar manner, Lee and co-workers synthesized [Zr{$Me_2Si(\eta^5$-$C_5H_2Me_2$-2,5)$_2$}Cl_2] (**115**) (Fig. 13) [55b].

5. *ansa*-Metallocene complexes with symmetric ring tri-substitution

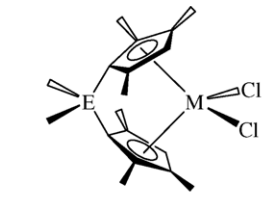
The complexes, [M{$Me_2E(\eta^5$-C_5HMe_3-2,3,5)$_2$}Cl_2] (M = Zr, E = Si (**116**), Ge (**117**); M = Hf, E = Si (**118**), Ge (**119**)), were prepared by the reaction of the dilithium *ansa* precursor with the metal tetrachlorides (Fig. 14) and obtained as mixtures of their *rac* and *meso* isomers which were separated by fractional recrystallization [45a,b,64]. Separation was also achieved by the hydrolysis, in the presence of amine, of a *meso*/*rac* mixture of **116**, **117** or **119**. The reaction was shown to take place only with the *meso* isomer to give the corresponding oxo derivative, and left the *rac* isomer remaining unaltered [65]. Employing the same synthetic protocol, Yamazaki et al. have reported the preparation of furyl and phenyl substituted *ansa*-zirconocene complexes, **120**–**125** (Fig. 14) [66].

6. *ansa*-Metallocene complexes with symmetric ring tetra-substitution

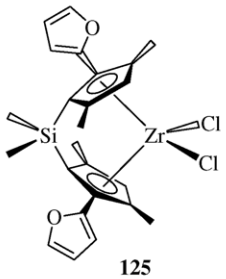
6.1. Silicon atom ansa-bridge

The permethylated silyl bridged *ansa* metallocene complexes, [M{$Me_2Si(\eta^5$-$C_5Me_4)_2$}Cl_2] (M = Ti (**126**), Zr (**127**), Hf (**128**)), were prepared by the reaction of Li_2{$Me_2Si(\eta^5$-$C_5Me_4)_2$} with the group 4 metal tetrachloride (Fig. 15) [12,67].

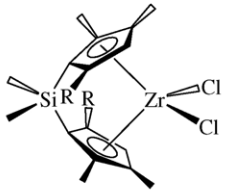
127 was also prepared unintentionally by Hey-Hawkins and co-workers as the decomposition product of a phosphine substituted metallocene intermediate (Eq. (32)) [24].



	116	117	118	119
M	Zr	Zr	Hf	Hf
E	Si	Ge	Si	Ge



125



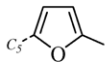
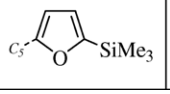
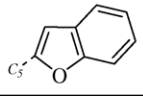
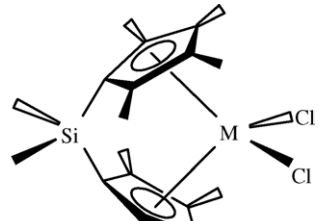
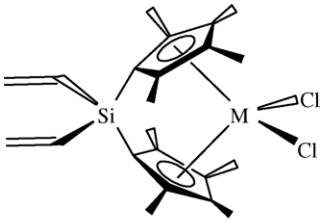
	120	121	122	123	124
R					

Fig. 14. Compounds **116**–**125**.



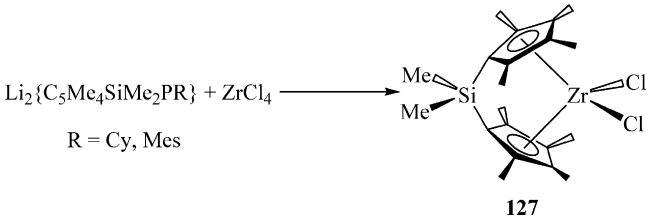
	126	127	128
M	Ti	Zr	Hf

Fig. 15. Compounds **126**–**128**.



	129	130
M	Zr	Hf

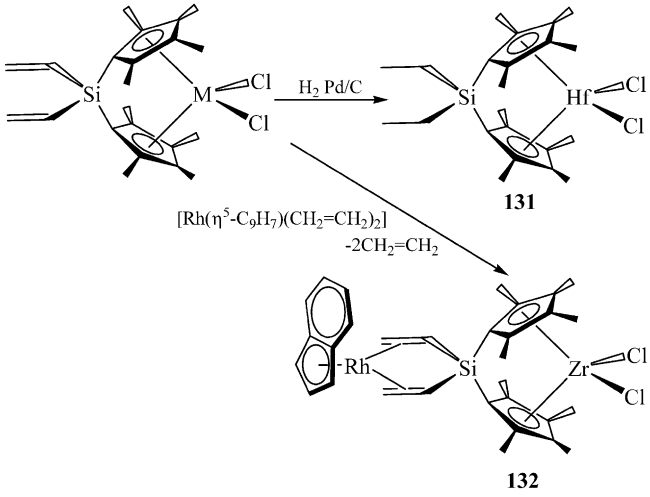
Fig. 16. Compounds **129** and **130**.



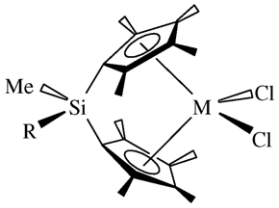
127

(32)

The divinylsilylene bridged *ansa*-complexes, [M{$(CH_2$=CH)$_2$Si(η^5-$C_5Me_4)_2$}Cl_2] (M = Zr (**129**), Hf (**130**)), were prepared from the lithium *ansa* precursor and the metal tetrachloride (Fig. 16) [61,67b]. The palladium catalyzed hydrogenation of **130** gave the diethylsilylene bridged complex [Hf{Et_2Si(η^5-$C_5Me_4)_2$}Cl_2] (**131**) (Eq. (33)) [67b]. The reaction of **129** with the rhodium complex [Rh(η^5-C_9H_7)(η^2-CH_2=CH_2)] yielded the heterobimetallic derivative, [(η^5-C_9H_7)Rh(η^2-CH_2=CH)$_2$Si(η^5-$C_5Me_4)_2ZrCl_2$] (**132**) (Eq. (33)) [61].



(33)



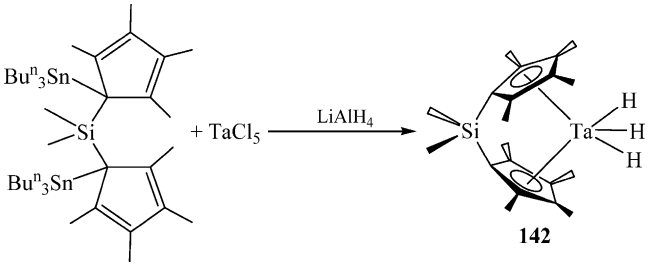
	133	134	135
M	Ti	Zr	Hf
R	H	H	H

	136	137	138	139	140	141
M	Ti	Ti	Zr	Zr	Hf	Hf
R	$CH{=}CH_2$	$CH_2CH{=}CH_2$	$CH{=}CH_2$	$CH_2CH{=}CH_2$	$CH{=}CH_2$	$CH_2CH{=}CH_2$

Fig. 17. Compounds **133**–**141**.

The MeSiH bridged *ansa*-metallocene complexes, $[M\{Me(H)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (M = Ti (**133**), Zr (**134**), Hf (**135**)), were prepared by the reaction of $Li_2\{Me(H)Si(\eta^5\text{-}C_5Me_4)_2\}$ with the corresponding group 4 metal tetrachloride (Fig. 17) [68]. In a similar manner, the complexes with vinyl or allyl substituents at the silicon bridge, $[M\{Me(R)Si(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (M = Ti, R = $CH{=}CH_2$ (**136**), $CH_2CH{=}CH_2$ (**137**); M = Zr, R = $CH{=}CH_2$ (**138**), $CH_2CH{=}CH_2$ (**139**); M = Hf, R = $CH{=}CH_2$ (**140**), $CH_2CH{=}CH_2$ (**141**)), were synthesized (Fig. 17) [39a].

The permethyl tantalocene trihydride compound, $[Ta\{Me_2Si(\eta^5\text{-}C_5Me_4)_2\}H_3]$ (**142**), was prepared via the reaction of $TaCl_5$ with the stannylated cyclopentadiene derivative (Eq. (34)) [69]. The reactivity of **142** in insertion processes was also described [69].

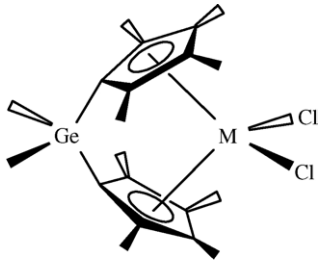


142

(34)

6.2. Germanium atom ansa-bridge

The germanium bridged *ansa*-metallocene complexes, $[M\{Me_2Ge(\eta^5\text{-}C_5Me_4)_2\}Cl_2]$ (M = Ti (**143**), Zr (**144**), Hf (**145**)), were prepared in a similar manner to their silicon bridge analogues (Fig. 18) [54,67b,70].



	143	144	145
M	Ti	Zr	Hf

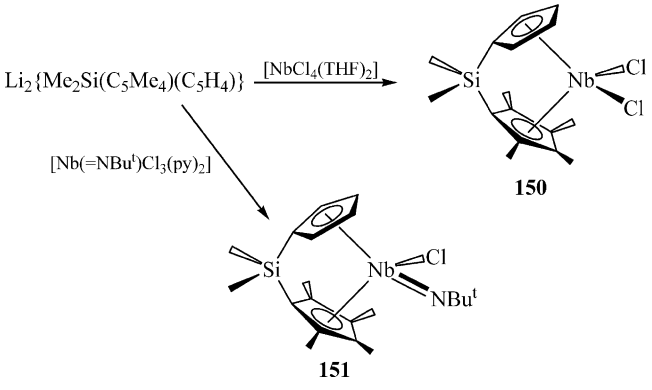
Fig. 18. Compounds **143**–**145**.

7. *ansa*-Metallocene mixed ring complexes with C_s symmetry

7.1. Silicon atom ansa-bridge

The mixed cyclopentadienyl *ansa*-metallocene complexes, $[M\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (M = Ti (**146**), Zr (**147**), Hf (**148**)) and $[Zr\{Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_2Bu^t_2\text{-}3,4)\}Cl_2]$ (**149**), were prepared via the conventional method of reaction between the dilithium *ansa*-derivative and the metal tetrachloride (Fig. 19) [46,71].

The *ansa*-niobocene dichloride, $[Nb\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**150**) [72], and imido, $[Nb(=NBu^t)\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl]$ (**151**) [71a], complexes were prepared via the reaction of the lithium *ansa*-derivative with the corresponding niobium precursor (Eq. (35)).

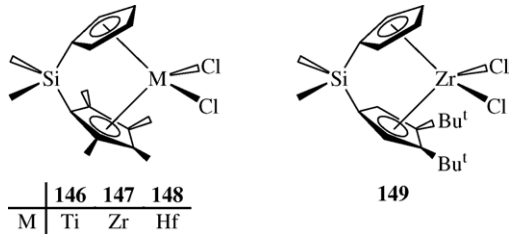


150 **151**

(35)

7.2. Germanium atom ansa-bridge

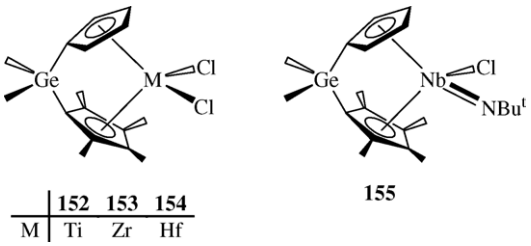
The group 4 metal germanium bridged *ansa*-metallocene complexes, $[M\{Me_2Ge(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (M = Ti



	146	147	148
M	Ti	Zr	Hf

149

Fig. 19. Compounds **146**–**149**.



	152	153	154
M	Ti	Zr	Hf

155

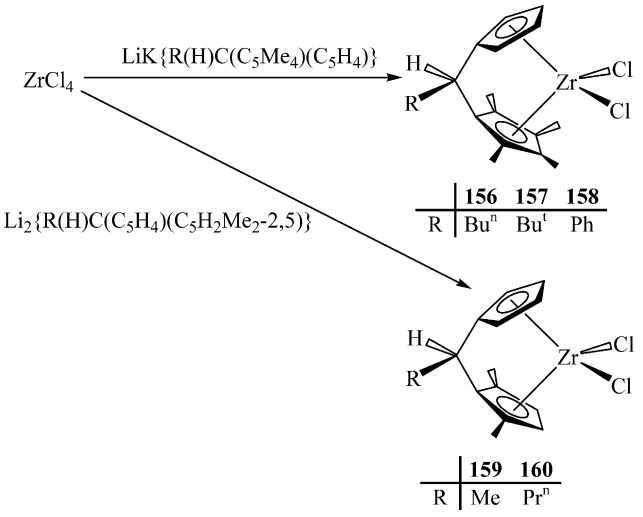
Fig. 20. Compounds **152**–**155**.

(**152**), Zr (**153**), Hf (**154**)), were prepared by the reaction of the lithium *ansa*-derivative and the group 4 metal tetrachloride (Fig. 20) [70,71b]. The synthesis of the *ansa*-niobocene imido complex, [Nb(=NBu^t){Me$_2$Ge(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl] (**155**), has also been reported (Fig. 20) [70].

8. *ansa*-Metallocene mixed ring complexes containing a chiral bridging atom

8.1. Carbon atom ansa-bridge

Using the corresponding lithium–potassium *ansa*-bis(cyclopentadienyl) compounds, the *ansa*-zirconocene complexes, [Zr{R(H)C(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (R = Bu^n (**156**), Bu^t (**157**), Ph (**158**)), were synthesized (Eq. (36)) [73]. The complexes, [Zr{R(H)C(η^5-C$_5$H$_4$)(η^5-C$_5$H$_2$Me$_2$-2,5)}Cl$_2$] (R = Me (**159**), Pr^n (**160**)), were prepared in a similar manner using the dilithium precursor (Eq. (36)) [55b].



	156	157	158
R	Bu^n	Bu^t	Ph

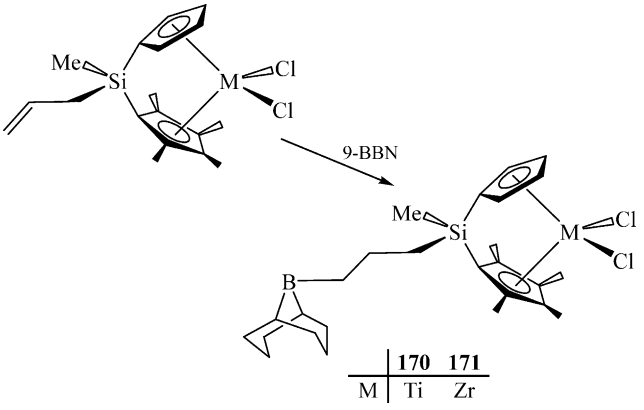
	159	160
R	Me	Pr^n

(36)

8.2. Silicon atom ansa-bridge

The synthesis of the asymmetrically alkyl substituted *ansa*-bridge complexes [Zr{Me(R)(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (R = Et (**161**), Ph (**162**)) was achieved in a similar manner to **147** (Fig. 21) [74].

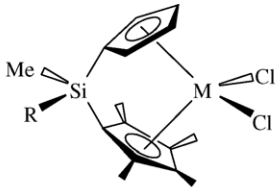
Complexes with vinyl or allyl groups as substituents of the *ansa*-bridge, [M{Me(R)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (M = Ti, R = CH=CH$_2$ (**163**), CH$_2$CH=CH$_2$ (**164**); M = Zr, R = CH=CH$_2$ (**165**), CH$_2$CH=CH$_2$ (**166**); M = Hf, R = CH=CH$_2$ (**167**), CH$_2$CH=CH$_2$ (**168**)), were synthesized from the reaction of the lithium *ansa*-derivative and the tetrachloride salts of the corresponding group 4 metal (Fig. 21) [39a]. **163** and **165** react with H$_2$ in the catalytic hydrogenation (Pd/C) of the vinylic double bond to give the "saturated" metallocene complexes, [M{Me(Et)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (M = Ti (**169**), Zr (**161**)) [39a]. The hydroboration of **164** and **166** by 9-BBN yielded [M{Me((BC$_8$H$_{14}$)CH$_2$CH$_2$CH$_2$)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (M = Ti (**170**), Zr (**171**)), resulting from the anti-Markonikoff addition at the double bond of the allyl group (Eq. (37)) [39a].



	170	171
M	Ti	Zr

(37)

The synthesis of the MeSiH bridged *ansa*-metallocene complexes, [M{Me(H)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (M = Ti (**172**), Zr (**173**), Hf (**174**)), was achieved by the reaction of the lithium *ansa*-derivative with the group 4 metal tetrachloride (Eq. (38)) [68]. The hydrosilylation of divinyldimethylsilane or tetravinyl silane by **172**–**174**, in the presence of the Karstedt catalyst (platinum(0) divinyltetramethylsiloxane), gave [M{CH$_2$=CH(Me)$_2$SiCH$_2$CH$_2$(Me)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (M = Ti (**175**), Zr (**176**), Hf (**177**)) and [M{(CH$_2$=CH)$_3$SiCH$_2$CH$_2$(Me)Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl$_2$] (M = Ti (**178**), Zr (**179**), Hf

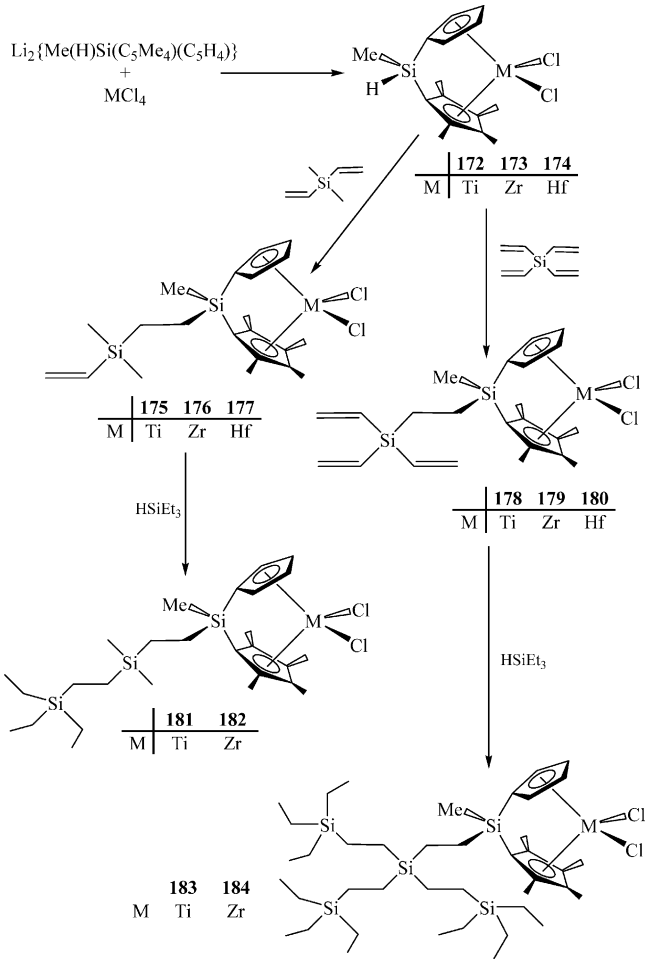


	161	162
M	Zr	Zr
R	Et	Ph

	163	164	165	166	167	168
M	Ti	Ti	Zr	Zr	Hf	Hf
R	$CH{=}CH_2$	$CH_2CH{=}CH_2$	$CH{=}CH_2$	$CH_2CH{=}CH_2$	$CH{=}CH_2$	$CH_2CH{=}CH_2$

Fig. 21. Compounds **161**–**168**.

(**180**)), formed by the reaction of only one of the double bonds of the silane substrate (Eq. (38)) [68]. Hydrosilylation by triethylsilane of the remaining vinyl groups in **175**, **176**, **178** and **179** produced the "dendrimer-like" complexes, $[M\{Et_3SiCH_2CH_2(Me)_2SiCH_2CH_2(Me)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (M = Ti (**181**), Zr (**182**)) and $[M\{(Et_3SiCH_2CH_2)_3SiCH_2CH_2(Me)Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (M = Ti (**183**), Zr (**184**)) (Eq. (38)) [68].



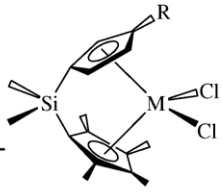
(38)

9. *ansa*-Metallocene mixed ring complexes with C_1 symmetry

9.1. Silicon atom ansa-bridge

The *ansa*-metallocene complexes, $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)\}Cl_2]$ (R = Me (**185**), Et (**186**), Pr^i (**187**), Bu^t (**188**), $SiMe_3$ (**189**)), were prepared by the reaction of $ZrCl_4$ with the corresponding lithium *ansa*-derivative (Fig. 22) [71a,75]. Using the same preparative method, the phosphine containing *ansa*-metallocene complexes were synthesized, $[M\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)\}Cl_2]$ (M = Ti, R = PPh_2 (**190**), $CH_2CH_2PPh_2$ (**191**); M = Zr, R = PPh_2 (**192**), $CH_2CH_2PPh_2$ (**193**); M = Hf, R = PPh_2 (**194**), $CH_2CH_2PPh_2$ (**195**)) (Fig. 22) [76]. Chiral substituents have also been incorporated in the *ansa*-metallocene system with the following compounds being reported: $[M\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)\}Cl_2]$ (M = Ti, R = menthyl (**196**), neomenthyl (**197**); M = Zr, R = menthyl (**198**), neomenthyl (**199**); M = Hf, R = menthyl (**200**)) (Fig. 22) [77]. **196** and **197** were prepared using $[TiCl_3(THF)_3]$ and the final products obtained on oxidation by HCl of the titanium(III) intermediates [77a,b].

Following the same synthetic protocol, the following *ansa*-metallocene complexes were prepared: $[Ti\{Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3SiMe_3)\}Cl_2]$ (**201**), $[Zr\{Me_2Si(\eta^5\text{-}C_5H_4)$

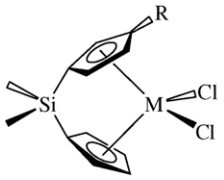


	185	186	187	188	189
M	Zr	Zr	Zr	Zr	Zr
R	Me	Et	Pr^i	Bu^t	$SiMe_3$

	190	191	192	193	194	195
M	Ti	Ti	Zr	Zr	Hf	Hf
R	PPh_2	$CH_2CH_2PPh_2$	PPh_2	$CH_2CH_2PPh_2$	PPh_2	$CH_2CH_2PPh_2$

	196	197	198	199	200
M	Ti	Ti	Zr	Zr	Hf
R	menthyl	neomenthyl	menthyl	neomenthyl	menthyl

Fig. 22. Compounds **185**–**200**.



	201	202	203	204	205	206
M	Ti	Zr	Zr	Zr	Zr	Zr
R	$SiMe_3$	Me	Pr^i	Bu^t	$SiMe_3$	cyclohexyl

	207	208	209	210
M	Zr	Hf	Hf	Zr
R	$CH_2CH{=}CH_2$	Me	$SiMe_3$	$CH_2CH_2NPr^i{}_2$

Fig. 23. Compounds **201**–**210**.

$(\eta^5\text{-}C_5H_3R)\}Cl_2]$ (R = Me (**202**), Pr^i (**203**), Bu^t (**204**), $SiMe_3$ (**205**), cyclohexyl (**206**), $CH_2CH{=}CH_2$ (**207**)) and $[Hf\{Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3R)\}Cl_2]$ (R = Me (**208**), $SiMe_3$ (**209**)) (Fig. 23) [45a,b,e,47,78]. The amino functionalized *ansa*-zirconocene complex, $[Zr\{Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3CH_2CH_2NPr^i_2)\}Cl_2]$ (**210**)), has been reported (Fig. 23) [79]. Mise and co-workers have prepared a series of C_1 symmetric *ansa*-zirconocene complexes, $[Zr\{Me_2Si(\eta^5\text{-}C_5H_2Me_2\text{-}2,4)(\eta^5\text{-}C_5H_3Me)\}Cl_2]$ (**211**), $[Zr\{Me_2Si(\eta^5\text{-}C_5H_2Me_2\text{-}3,4)(\eta^5\text{-}C_5H_3Me)\}Cl_2]$ (**212**), $[Zr\{Me_2Si(\eta^5\text{-}C_5H_3Bu^t)(\eta^5\text{-}C_5H_3Me)\}Cl_2]$ (**213**), $[Zr\{Me_2Si(\eta^5\text{-}C_5HMe_3\text{-}2,3,5)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**214**), $[Zr\{Me_2Si(\eta^5\text{-}C_5H_2Me_2\text{-}2,4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**215**) (**211** and **213** were obtained as a mixture of isomers) (Fig. 24) [45a,b].

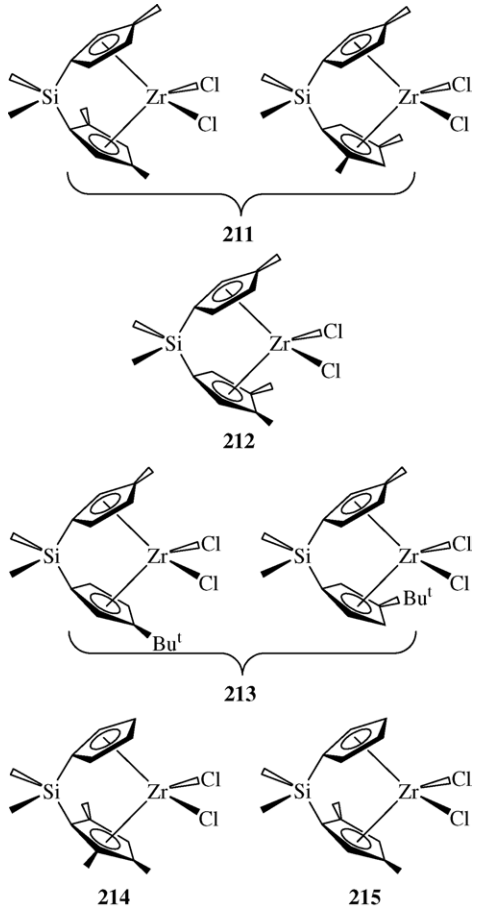
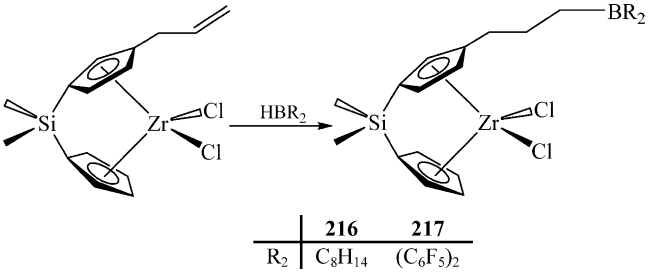


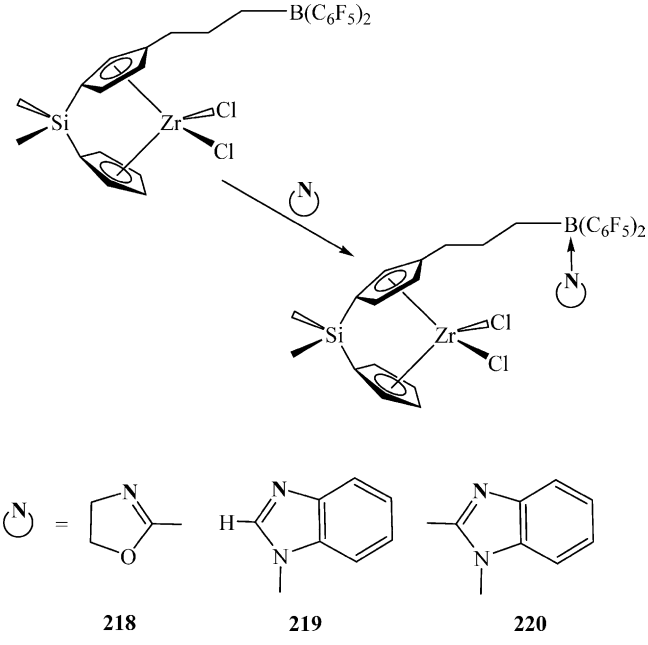
Fig. 24. Compounds **211**–**215**.

The reactivity of the pendant allyl group in **207** has been studied. Hydroboration of **207** by 9-BBN or $HB(C_6F_5)_2$ gave $[Zr\{Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3[CH_2CH_2CH_2BR_2])\}Cl_2]$ ($R_2 = C_8H_{14}$ (**216**), $(C_6F_5)_2$ (**217**)) (Eq. (39)) [80]. **217** reacts with the two electron donor ligands, 2-methyl-4,5-dihydrooxazole, *N*-methylbenzimidazole or 1,2-dimethylbenzimidazole to yield the corresponding adducts **218**–**220** (Eq. (40)) [80].



	216	217
R_2	C_8H_{14}	$(C_6F_5)_2$

(39)



(40)

The *ansa*-niobocene imido complexes, $[Nb(=NBu^t)\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)\}Cl]$ (R = Me (**221**), Pr^i (**222**), $SiMe_3$ (**223**), PPh_2 (**224**)), were prepared via the conventional route from the reaction of the lithium *ansa*-derivative with the niobium imido precursor $[Nb(=NBu^t)Cl_3(py_2)]$ (Fig. 25) [71a]. The presence of only one of the two possible isomers was observed and by X-ray

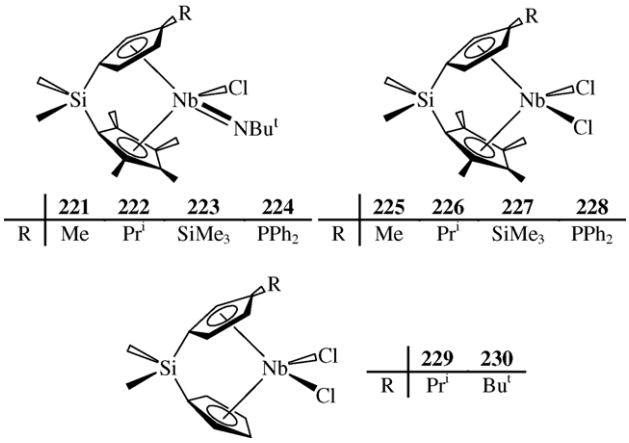
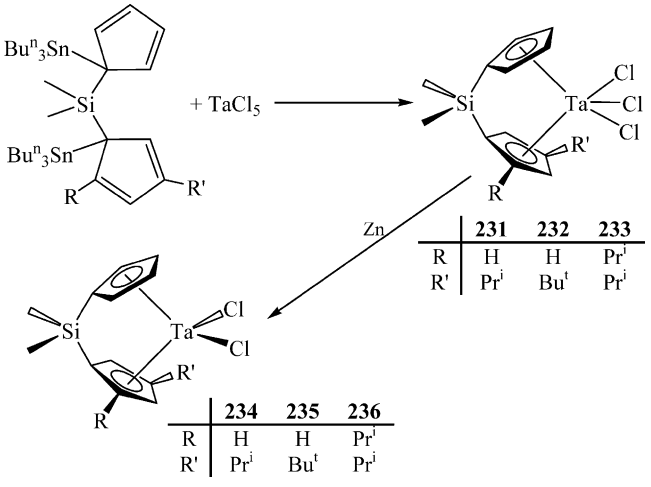


Fig. 25. Compounds **221**–**230**.

diffraction studies it was ascertained that the substituent R was orientated away from the imido group, thus minimizing steric congestion. In a similar manner, the niobocene dichloride complexes, [Nb{$Me_2Si(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3R)$}Cl_2] (R = Me (**225**), Pr^i (**226**), $SiMe_3$ (**227**), PPh_2 (**228**)) and [Nb{$Me_2Si(\eta^5$-$C_5H_4)(\eta^5$-$C_5H_3R)$}Cl_2] (R = Pr^i (**229**), Bu^t (**230**)), were prepared (Fig. 25) [72,16a]. The electrochemical behaviour of **225**–**248** has been described with respect to the R substituent present [72]. From **229** and **230**, olefin hydride complexes were prepared and studied as models of catalytically active metallocene species in polymerization [16a]. The tantalocene complexes, [Ta{$Me_2Si(\eta^5$-$C_5H_4)(\eta^5$-C_5H_2RR')}Cl_3] (R = H, R′ = Pr^i (**231**), Bu^t (**232**); R = R′ = Pr^i (**233**)), were prepared via the reaction of $TaCl_5$ with the corresponding stannylated cyclopentadiene (Eq. (41)) [16a]. The tantalocene(IV) dichloride derivatives, [Ta{$Me_2Si(\eta^5$-$C_5H_4)(\eta^5$-C_5H_2RR')}Cl_2] (R = H, R′ = Pr^i (**234**), Bu^t (**235**); R = R′ = Pr^i (**236**)), were obtained upon the reduction of **231**–**233** with zinc (Eq. (41)) [16a].



(41)

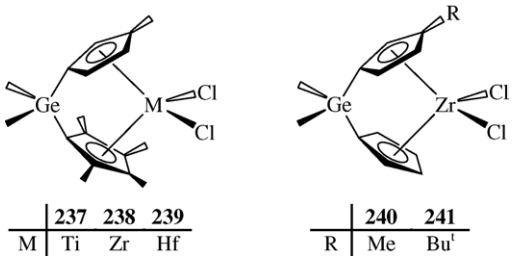


Fig. 26. Compounds **237**–**241**.

9.2. Germanium atom ansa-bridge

The germanium bridged *ansa*-complexes, [M{$Me_2Ge(\eta^5$-$C_5Me_4)(\eta^5$-$C_5H_3Me)$}Cl_2] (M = Ti (**237**), Zr (**238**), Hf (**239**)) and [Zr{$Me_2Si(\eta^5$-$C_5H_4)(\eta^5$-$C_5H_3R)$}Cl_2] (R = Me (**240**), Bu^t (**241**)), were prepared in a similar manner to their silicon analogues (Fig. 26) [54,70].

10. Structural influence of the catalyst in the stereoselective polymerization of α-olefins

Different geometric and electronic properties of the *ansa*-metallocene complex directly influence not only its catalytic activity in polymerization but also the physical make up of the polymer (molecular weight and distribution, microstructure, co-monomer incorporation).

It is generally recognized that zirconocene catalysts exhibit higher activities than titanocenes and hafnocenes in olefin polymerization [4] and this is reflected in the far higher number of *ansa*-zirconocene complexes reported compared with their group 4 counterparts.

The inclusion of substituents in the C_5 rings of the *ansa*-ligands has been exploited in the stereoselective polymerization of α-olefins. The symmetry of the complex was found to have a decisive effect in the process of stereoregulation [81]. For example, the C_2 symmetric *rac* isomer of the *ansa*-metallocene complexes produced highly isotactic polypropylene. This can be explained in a very simple way considering that the monomer and growing polymer chain are oriented towards the open spaces of the metallocene molecule (Fig. 27). Using this same concept, it can be seen that the *meso* isomer will be non-stereoselective in the polymerization of α-olefins.

C_s symmetric *ansa*-metallocene complexes containing a fluorenyl moiety have been shown to produce syndiotactic polypropylene and therefore, it appeared probable that the same should also be true for *ansa*-bis(cyclopentadienyl) catalysts. However, Morokuma and co-workers have predicted, via theoretical studies, that catalytic systems based on the C_s symmetric $H_2Si(C_5Me_4)(C_5H_4)$ ligand will be substantially non-enantioselective, due to repulsive interactions of either the methyl group of propylene or the growing polymer chain with the methyl groups of the C_5Me_4 moiety (Fig. 28) [82].

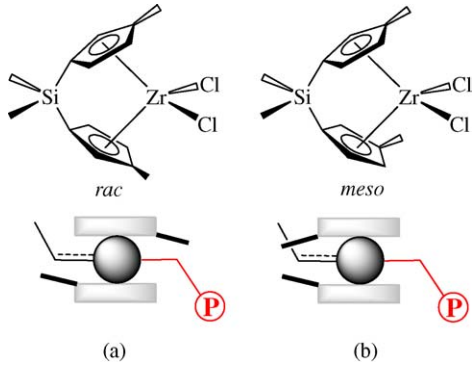


Fig. 27. (a) Steric control in C_2 symmetric *ansa*-metallocene complexes and (b) lack of steric control in the *meso* isomer.

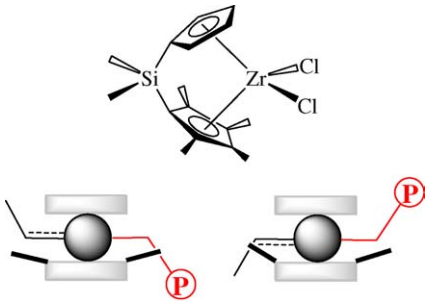


Fig. 28. Lack of steric control in C_s symmetric *ansa*-metallocene complexes.

Several experimental studies carried out are in agreement with Morokuma's proposal [46,68,70,75].

The C_1 symmetric *ansa*-metallocene compounds described in this survey have been shown to be isospecific, in the polymerization of α-olefins. If it is assumed that a chain migratory insertion mechanism takes place and that the two coordination positions are of a similar energy, then these catalysts should be isospecific if propylene coordination is enantioselective in favour of the same propylene enantiofaces (Fig. 29a). If propylene coordination is enantioselective in only one of the coordination positions, then the corresponding catalytic system should be *hemi*-isospecific (Fig. 29b).

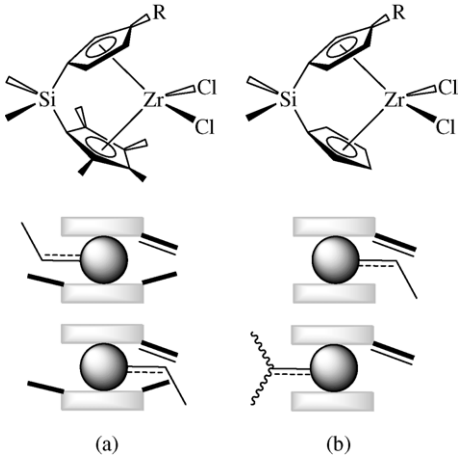


Fig. 29. Steric control in C_1 symmetric *ansa*-metallocene complexes: (a) isotactic and (b) hemi-isotactic.

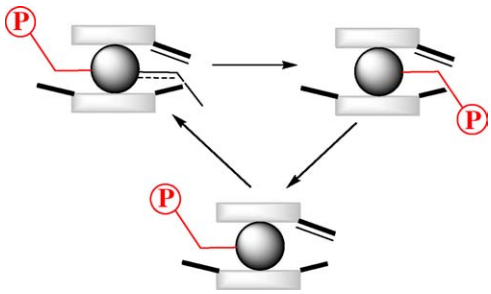


Fig. 30. Back skip mechanism.

If the two coordination positions are of distinct energies, a different scenario can be proposed. According to Morokuma and co-workers, the presence of a bulky alkyl β-substituent in the cyclopentadienyl moiety forbids the growing polymer chain to be located in the more crowded position [82]. The steric pressure of the ligand skeleton may force the growing chain to skip back to the less crowded position. Hence, insertion always occurs with the same relative disposition of the monomer and the growing polymer chain and thus leads to an isospecific polymer (Fig. 30). Examples of this back skip mechanism in the polymerization of propylene have been reported [75,83].

11. Conclusions

It is evident by the number of complexes included in this survey the importance of *ansa*-bis(cyclopentadienyl) systems. Catalytic activity and selectivity can be directly related to the *ansa*-metallocene catalyst and slight structural variations can be very influential. Therefore, emphasis has been placed in the design of *ansa*-metallocene complexes towards the goal of "made to measure" catalysts for the preparation of polyolefins with defined properties. The synthesis of *ansa*-metallocene complexes containing functional groups has also proved essential in the industry-imposed requirement of immobilized single-site catalysts. Whilst the interest in the production of polyolefins remains prominent, the chemistry of *ansa*-metallocene complexes will continue with its rapid evolution.

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