Linked cyclopentadienyl–amido complexes of zirconium; ligand dependence of cation–anion interactions and ethene polymerisation activity

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Abstract

A range of zirconium dichloride complexes $[C_5H_4(CH_2)_nNR]ZrCl_2$ ($n = 2$, R = iPr, tBu; $n = 3$, R = Me, Et, iPr) with linked cyclopentadienyl–amide ancillary ligands were prepared by amine elimination routes. Their dibenzyl derivatives $[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)_2$ react with $B(C_6F_5)_3$ to give the ionic species $\{[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)\}$ $[PhCH_2B(C_6F_5)_3]$. In bromobenzene solvent, the position of the equilibrium between the solvent-separated ion pair and the species in which the anion is η^6-coordinated to the metal centre through the B-benzyl phenyl group is strongly dependent on ligand bridge length and substitution. This gives an indication of the overall steric requirement of the ligand system. The activity of the $[C_5H_4(CH_2)_nNR]ZrCl_2$/methylaluminoxane catalysts in the homopolymerisation of ethene was probed. The $[C_5H_4(CH_2)_nNiPr]Zr$-system found to be several times more efficient for $n = 3$ than for $n = 2$, with the $[C_5H_4(CH_2)_3NMe]Zr$-system being the most active of the compounds studied. © 1998 Elsevier Science B.V.

1. Introduction

Linked cyclopentadienyl–amido ligands of the type Cp-(bridge)-amido have been highly successful in combination with group 4 transition metals to give catalyst systems for the copolymerisation of ethene with α-olefins, when used in conjunction with MAO (methylaluminoxane) or perfluoroarylborate-derived activators for the generation of the catalytically active cationic alkyl species [1,2]. Especially the use of the $C_5Me_4SiMe_2NtBu$-ligand [3,4] allows a ready and random incorporation of comonomer over a wide compositional range. It is suggested that the small Cp(CT)–M–N angle enforced by the ligand system is responsible for this property ('constrained geometry catalyst'), thus reducing the steric hindrance on a specific side of the metal centre [5].

One feature of the linked Cp-amido ligand system is that it is relatively straightforward to vary independently various ligand features, such as bridge length and amide or cyclopentadienyl substitution pattern, thus making studies of ligand structure–catalyst property relationships possible. Earlier our group developed a rela-

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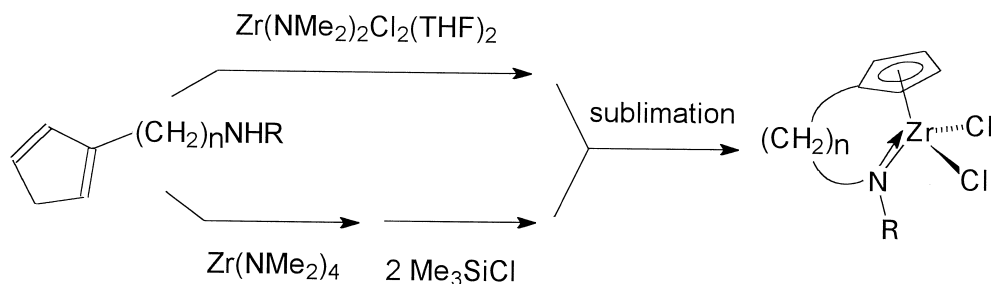
Scheme 1.

tively simple route for the synthesis of the $-(CH_2)_3-$ bridged cyclopentadienyl–methyl-amide ligand and for the attachment of this ligand to zirconium by an amine elimination reaction [6]. We have now prepared a range of Cp–amide zirconium complexes $[C_5H_4 (CH_2)_n NR] ZrCl_2$ ($n = 2$; R = iPr, tBu; $n = 3$, R = Me, Et, iPr) which allows a systematic study of their properties.

A useful spectroscopic 'probe' for the total of steric restrictions imposed by the ligand that is relatively independent of electronic factors can be provided by the strength of the cation–anion interaction in well-defined cationic species derived from these complexes. The interaction of the $[PhCH_2B(C_6F_5)_3]$-anion with the cationic metal centre generated by the reaction of $B(C_6F_5)_3$ with transition-metal benzyl complexes is sensitive to the steric hindrance around the metal centre. For example, in the reaction products of $(C_5R_5)Zr(CH_2Ph)_3$ with $B(C_6F_5)_3$ the phenyl group of the anion is η^6-bound to the metal centre for R = H [7], whereas for R = Me the product exists in solution as a solvent-separated ion pair [8].

We prepared the dibenzyl zirconium complexes $[C_5H_4(CH_2)_n NR]Zr(CH_2Ph)_2$ ($n = 2$; R = iPr, tBu; $n = 3$, R = Me, Et, iPr) and studied their reactions with $B(C_6F_5)_3$. Cation–anion interactions were studied by NMR spectroscopy and showed a clear dependence on ligand bridge length and substitution pattern. This relation is discussed, together with the catalytic properties of representative $[C_5H_4(CH_2)_n NR]ZrCl_2/MAO$

combinations in the catalytic homopolymerisation of ethene.

2. Synthesis of the complexes

The ligands $C_5H_5(CH_2)_n NHR$ ($n = 2$; R = iPr, tBu; $n = 3$, R = Me, Et, iPr) were obtained conveniently by reaction of $Br(CH_2)_n NHR \cdot HBr$ with an excess of CpNa, as described before for the $n = 3$, R = Me derivative [6]. The corresponding zirconium dichloride complexes $[C_5H_4(CH_2)_n NR]ZrCl_2$ were prepared according to two amine elimination routes (Scheme 1). Reaction of the ligand with $Zr(NMe_2)_2 Cl_2 (THF)_2$ [9] in toluene at 75°C followed by sublimation of the crude product afforded pure $[C_5H_4(CH_2)_n NR]ZrCl_2$ for $n = 2$, R = iPr, tBu and $n = 3$, R = iPr. For $n = 3$, R = Me,

Table 1
^{1}H-NMR data for $[C_5H_4(CH_2)_n NR]ZrCl_2$ (300 MHz, CDCl$_3$, δ in ppm)

n, R	Cp	NCH$_2$	–CH$_2$–	Cp–CH$_2$	R, α	R, β
2, iPr	6.3	4.12		3.02	4.43	1.13
	6.3	(6.6)		(6.6)	(6.3)	(6.3)
2, tBu	6.38	4.09		2.92		1.25
	6.32	(6.6)		(6.6)		
3, Me	6.46	2.95	2.17	2.80	3.27	
	6.05					
3, Et	6.52	2.92	2.15	2.81	3.81	1.21
	6.02				(6.5)	(6.5)
3, iPr	6.52	2.85	2.09	2.79	4.86	1.23
	5.98				(5.9)	(5.9)

Multiplicities according to assignment, coupling constants (Hz) in parentheses.

Table 2
^{13}C-NMR data for $[C_5H_4(CH_2)_nNR]ZrCl_2$ (75.4 MHz, $CDCl_3$, δ in ppm)

n, R	Cp ipso	Cp CH		N–CH$_2$	–CH$_2$–	Cp–CH$_2$	R, α	R, β
2, iPr	141.75	115.53	111.70	63.34		28.76	49.13	19.05
		(173.4)	(174.6)	136.7)		(129.4)	(124.5)	(127.0)
2, tBu	141.46	115.53	113.46	64.98		29.42	57.66	27.24
		(173.4)	(174.6)	(135.5)		(130.6)		(125.7)
3, Me	127.64	114.17	112.31	55.85	26.01	28.95	37.24	
		(176.6)	(172.1)	(134.9)	(128.2)	(127.0)	(135.5)	
3, Et	128.03	114.48	112.20	51.27	26.31	29.83	42.93	12.69
		(174.6)	(171.0)	(134.9)	(128.2)	(127.0)	(130.6)	(127.4)
3, iPr	127.98	114.67	112.01	44.28	26.54	30.47	46.27	19.65
		(173.4)	(172.1)	(134.3)	(128.8)	(127.6)	(116.0)	(127.4)

Multiplicities according to assignment, coupling constants (Hz) in parentheses.

Table 3
^{1}H-NMR data for $[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)_2$ (300 MHz, C_6D_6, δ in ppm)

n, R	Cp	NCH$_2$	–CH$_2$–	Cp–CH$_2$	R, α	R, β	ZrCH$_2$	Ph o-H	Ph m-H	Ph p-H
2, iPr	5.72	3.48		2.44	3.57	0.94	1.67	6.58	7.12	6.94
	5.27	(6.6)		(6.6)	(6.1)	(6.1)	1.05	(7.4)	(7.4)	(7.3)
							(9.2)			
2, tBu	5.57	3.35		2.24		1.13	1.94	6.70	7.11	6.93
	5.47	(6.6)		(6.6)			1.43	(7.2)	(7.3)	(7.3)
							(10.3)			
3, Et	5.60	2.45	1.53	2.21	3.05	1.00	1.62	6.61	7.11	6.94
	5.39				(6.5)	(6.5)	1.22	(7.3)	(7.3)	(7.3)
							(9.5)			
3, iPr	5.59	2.50	1.58	2.23	4.00	1.12	1.86	6.70	7.14	6.95
	5.30				(5.8)	(5.8)	1.01	(7.4)	(7.4)	(7.3)
							(9.5)			

Multiplicities according to assignment, coupling constants (Hz) in parentheses.

Table 4
^{13}C-NMR data for $[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)_2$ (75.4 MHz, C_6D_6, δ in ppm)

n, R	Cp ipso	Cp CH		N–CH$_2$	–CH$_2$–	Cp–CH$_2$	ZrCH$_2$
2, iPr	135.83	113.06	108.64	59.98		29.39	50.34
		(170.9)	(170.9)	(130.0)		(127.6)	(128.2)
2, tBu	134.80	113.60	110.98	61.49		29.90	52.86
		(170.9)	(172.1)	(134.3)		(127.6)	(124.5)
3, Et	122.69	110.64	110.31	39.66	26.77	30.11	49.61
		(170.9)	(170.9)	(127.6)	(125.7)	(126.4)	(127.6)
3, iPr	122.63	111.43	110.75	43.49	27.06	30.84	50.98
		(170.9)	(169.7)	(132.5)	(127.0)	(126.4)	(125.1)

n, R	R, α	R, β	Ph ipso C	Ph o-CH	Ph m-CH	Ph p-CH
2, iPr	44.95	21.23	146.53	130.32	125.59	121.85
	(120.9)	(125.7)		(157.5)	(153.8)	(162.4)
2, tBu	56.84	28.02	146.24	129.28	126.96	121.79
		(124.5)		(156.3)	(155.0)	(162.4)
3, Et	50.72	14.89	145.66	129.51	126.30	121.82
	(132.5)	(126.6)		(157.5)	(153.8)	(162.0)
3, iPr	42.07	21.59	146.51	129.39	126.53	121.77
	(114.8)	(126.1)		(157.5)	(153.8)	(162.4)

Multiplicities according to assignment, coupling constants (Hz) in parentheses.

Et the dimethylamido derivatives $[C_5H_4(CH_2)_nNR]Zr(NMe_2)_2$ were formed through reaction of the ligand with $Zr(NMe_2)_4$, and were converted in situ to the corresponding dichlorides through subsequent reaction with 2 equiv of Me_3SiCl [10–12]. The dichlorides were obtained free from coordinated dimethylamine after sublimation.
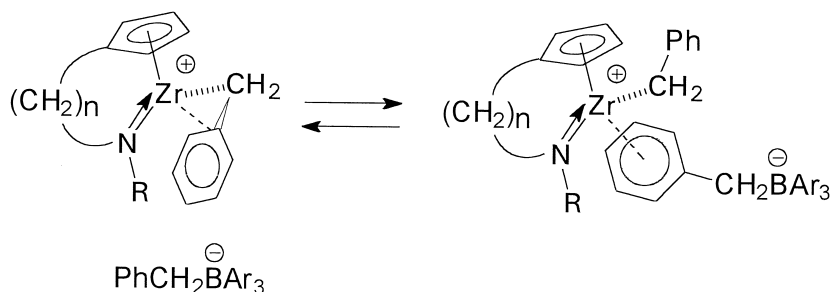
The dibenzyl complexes $[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)_2$ were prepared either by reaction of the free ligand with $Zr(CH_2Ph)_4$ ($n = 2$, R = iPr) or by reaction of the dichloride complex with two equiv of $PhCH_2MgX$ (X = Cl, Br) in ether followed by extraction with pentane. For comparison, the dibenzyl compound $(C_5Me_4SiMe_2NtBu)Zr(CH_2Ph)_2$ was prepared in similar fashion from the corresponding dichloride [1,12].

The dichloride and dibenzyl complexes were all characterised by ^{1}H- and ^{13}C-NMR spectroscopy (Tables 1–4) and for several examples by elemental analysis. For $n = 3$, R = Me the dibenzyl complex was reported in the literature [6]. In contrast to the Me_2Si-bridged complex $[(C_5H_4SiMe_2NtBu)ZrCl(\mu\text{-}Cl)]_2$, which was found to be dimeric in the solid state [1] and in solution [12], the $-CH_2CH_2-$ bridged complex $[C_5H_4(CH_2)_2NtBu]ZrCl_2$ was found to be monomeric in solution (cryoscopy in benzene). For the $n = 2$, R = iPr complex the observed molecular weight (351 g mol^{-1}) was significantly larger than the calculated value (311 g mol^{-1}), but for this compound the monomeric species still is the predominant one in solution. The dibenzyl complexes all show characteristic

AB-patterns for the diastereotopic benzyl methylene protons in the ^{1}H-NMR spectrum, with $^2J_{HH}$ couplings between 9 and 11 Hz. In their ^{13}C-NMR spectra the $Zr–CH_2$ moiety is found in the range δ 60–50 ppm with typical $^1J_{CH}$ couplings between 120 and 130 Hz. These features are similar to those of other relatively electron-deficient neutral group 4 metal benzyl complexes (for some recent examples see [13–15] and references cited therein).

3. Reaction with $B(C_6F_5)_3$

In C_6D_5Br solvent, all Cp–amide zirconium dibenzyls were found to react cleanly with the Lewis acidic borane $B(C_6F_5)_3$ by abstraction of one benzyl group to give cationic zirconium benzyl species with $PhCH_2B(C_6F_5)_3$-anions. In these products, $\{[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)\}[PhCH_2B(C_6F_5)_3]$, the interaction between the cationic and anionic moieties were found to be highly dependent on the nature of the $[C_5H_4(CH_2)_nNR]$-ligand. It is known from an increasing number of literature examples that in sterically unhindered cationic transition-metal complexes the phenyl group of the $PhCH_2B(C_6F_5)_3$-anion can coordinate in η^6-fashion to the electron-deficient transition-metal centre [7,15–17]. Typical structurally characterised examples are found in $[CpZr(CH_2Ph)_2][\eta^6\text{-}PhCH_2B(C_6F_5)_3]$ [7] and $[Zr(CH_2Ph)_3][\eta^6\text{-}PhCH_2B(C_6F_5)_3]$ [16]. The NMR spectroscopic features of the anion respond to η^6-coor-

Scheme 2.

Table 5

Relative amounts (%) of η^6-bound and free anion at $-35°C$ as determined for the complexes $\{[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)\}[PhCH_2B(C_6F_5)_3]$ by ^{19}F-NMR spectroscopy

n, R	Bound	Free
2, *i*Pr	92	8
2, *t*Bu	13	87
3, Me	85	15
3, Et	31	69
3, *i*Pr	5	95
Me$_4$C$_5$SiMe$_2$NtBu	2	98

dination in various ways, one of the most indicative is a small but distinct change in ^{19}F-NMR $\Delta\delta[(m\text{-F})-(p\text{-F})]$, which for the η^6-coordinated anion is about 4 ppm, compared to 3 ppm for the free anion [15].

By ^{19}F-NMR at low temperature ($-35°C$) it is seen that for the complexes $\{[C_5H_4(CH_2)_nNR]\ Zr(CH_2Ph)\}\ [PhCH_2B(C_6F_5)_3]$ there is an equilibrium in bromobenzene solvent between the contact (η^6-coordinated) ion pair and the solvent-separated ion pair (Scheme 2). The resonances of the two species are well-separated, and at a specific concentration (0.2 M) the ratio of these two species was determined for the various Cp–amide ligands (Table 5). It is seen that for a bridge length $n = 2$ changing the substituent R from *i*Pr to *t*Bu shifts the equilibrium from a predominantly bound to a predominantly free anion. Similarly, for R = *i*Pr it is seen that a lengthening of the bridge from $n = 2$ to $n = 3$ effects a comparable change. In the corresponding titanium dichloride complexes $[C_5H_4(CH_2)_nN\textit{i}Pr]TiCl_2$ it was seen by single crystal X-ray diffraction [18] that an increase in bridge length from $n = 2$ to $n = 3$ does not significantly alter the M–C/N/Cl distances. Instead the Cp(centroid)–Ti–N and Ti–N–C(bridge) angles increase and the Ti–N–C(*i*Pr) angle decreases, pushing the *i*Pr-substituent forward, thus restricting the remaining coordination space around the metal centre. For the cationic Zr complex with $n = 3$, R = Et an intermediate situation is found, for which both

the contact ion pair and the solvent-separated ion pair species can be readily observed by ^1H- and ^{13}C-NMR spectroscopy as well. It thus seems that this equilibrium can give a reasonable indication of the relative steric restrictions imposed by the ligand system.

The complexes $[C_5H_4(CH_2)_nNR]Zr(\eta^1\text{-}CH_2Ph)[\eta^6\text{-}PhCH_2B(C_6F_5)_3]$ are characterised in their ^1H- and ^{13}C-NMR spectra by various features, including diastereotopic B-CH$_2$ protons and an η^1-benzyl group bound to Zr that is freely rotating around the CH$_2$–Ph bond. The η^1-benzyl group is evidenced by the downfield shift of the ipso carbon (around $\delta 150$ ppm), and on the methylene group by the relatively small $^1J_{CH}$ of 120 Hz and the relatively large $^2J_{HH}$ of around 10–11 Hz. For the aromatic protons of the anion five separate resonances are found, significantly upfield shifted from the positions in the free anion [7,17]. A full listing of ^1H- and ^{13}C-NMR data of a representative example ($n = 3$, R = Me) can be found in the experimental section.

The solvent-separated species $\{[C_5H_4(CH_2)_nNR]\ Zr(\eta^2\text{-}CH_2Ph)\}\ [PhCH_2B(C_6F_5)_3]$ are characterised in their ^1H- and ^{13}C-NMR spectra by features that show an asymmetric structure (at $-35°C$) and indicate an additional interaction of the Zr-bound benzyl group with the metal centre. These include a significant upfield shift of the ipso carbon (δ around 122 ppm) and for the methylene group a $^1J_{CH}$ larger than 140 Hz together with a small $^2J_{HH}$ of around 7–8 Hz [13,19–22]. A full listing of ^1H- and ^{13}C-NMR data of a representative example ($n = 3$, R = *i*Pr) can be found in the experimental section.

The cations $\{[C_5H_4(CH_2)_nNR]Zr(\eta\text{-}CH_2Ph)\}^+$ are thermally quite robust in solution. Variable temperature ^1H-NMR spectroscopy from $-35°C$ to $65°C$ of this species for $n = 2$, R = *t*Bu shows fluxional behaviour by which at high temperatures a spectrum of a symmetrically averaged structure is observed. Estimated free energies of activation from the coalescence of the benzyl *o*-H and ZrCH$_2$ pro-

tons respectively are 12.4 kcal mol^{-1} ($T_c = 260$ K) and 13.4 kcal mol^{-1} ($T_c = 290$ K).

4. Ethene homopolymerisation

The catalytic activities of the $[C_5H_4(CH_2)_nNR]ZrCl_2$/MAO catalysts in the homopolymerisation of ethene were probed in toluene under various conditions. The results are listed in Table 6. Note that the activities listed in the last column are only based on the observed productivity over the 30 min run time extrapolated to 1 h. They do not take into account possible differences in activity profile for the various catalysts over the run time, and should be used as relative measures of catalyst efficiency within the series rather than as absolute activities.

At 80°C and 20 bar ethene pressure the difference in activity between the $n = 2$, R = iPr and $n = 2$, R = tBu catalysts was found to be minimal. However, for R = iPr the catalyst with bridge length $n = 3$ was found to be about four times more efficient than with bridge length $n = 2$. This is remarkable in that for the $[C_5Me_4(SiMe_2)_nNtBu]$Ti-system the efficiency of the catalyst dropped considerably upon increasing the bridge length from $n = 1$ to $n = 2$ [1,5].

At a catalyst concentration of 2×10^{-4} mol l^{-1} the catalyst with $n = 3$, R = Me and $[C_5Me_4(SiMe_2)NtBu]ZrCl_2$ both showed relatively high activities resulting in a significant exotherm of about 15°C, the latter catalyst being somewhat more productive. At a lower catalyst concentration (3.3×10^{-5} mol l^{-1}) this exotherm was eliminated and the $n = 3$, R = Me catalyst proved to be the more productive. The relative trends in activity for the other catalysts were found to be still valid at this lower concentration.

In the $(C_5R_4SiMe_2NtBu)MCl_2$/MAO system (M = Ti, Zr) it was observed that the presence of the methyl substituents on the Cp-moiety greatly improved catalyst efficiency [1,5]. It appears that the $[C_5H_4(CH_2)_nNR]ZrCl_2$/MAO system can exceed the efficiency of the above Zr system for the longer bridge length ($n = 3$) in the ethene homopolymerisation under the applied conditions, provided the substituent on the amido functionality is small. It is possible that the $(C_5Me_4SiMe_2NtBu)ZrCl_2$/MAO system has a steeper activity versus temperature slope than the other catalysts described here, as the system responds more strongly to the exotherm observed in the polymerisation at relatively high catalyst concentration. This is also suggested by the observation that under milder polymerisation conditions (50°C, 5 bar ethene)

Table 6
Ethene homopolymerisation with $[C_5H_4(CH_2)_nNR]ZrCl_2$/MAO catalysts (toluene solvent, Al/Zr = 520, 30 min run time)

Catalyst	[Zr] $\times 10^5$ (mol l^{-1})	T (°C)	$p(C_2H_4)$ (bar)	PE yield (g)	Act. (g mmol^{-1} h^{-1})
2, iPr	20	50	5	1.2	60
3, iPr	20	50	5	1.3	65
cat[a]	20	50	5	0.2	10
2, iPr	20	80	20	3.4	170
2, tBu	22	80	20	3.4	155
3, iPr	21	80	20	17.4	829
3, Me	21	80[b]	20	49.7	2367
cat[a]	20	80[b]	20	55.0	2750
2, iPr	3.3	80	20	0.4	81
3, iPr	3.3	80	20	3.0	606
3, Me	3.3	80	20	8.0	1617
cat[a]	3.3	80	20	3.3	667

[a]$(C_5Me_4SiMe_2NtBu)ZrCl_2$.
[b]Significant exotherm.

the activity of this catalyst is even less than that of the $n = 2, 3$, R = iPr catalysts.

5. Conclusions

A range of zirconium dichloride complexes with linked Cp–amido ancillary ligands, $[C_5H_4(CH_2)_nNR]ZrCl_2$ ($n = 2$, R = iPr, tBu; $n = 3$, R = Me, Et, iPr) can be prepared readily using amine elimination reactions employing $Zr(NMe_2)_4$ (followed by reaction with Me_3SiCl) or $Zr(NMe_2)_2Cl_2(THF)_2$. The position of the equilibrium between the contact ion pair and the solvent-separated ion pair in the complexes $\{[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)\}[PhCH_2B(C_6F_5)_3]$ can give a reasonable indication of the change in steric requirements of the ligand upon variation in bridge length and/or substituent on the amido functionality. The $[C_5H_4 (CH_2)_nNR]ZrCl_2$/MAO combinations are catalysts for the homopolymerisation of ethene, which are more efficient for the longer ligand bridge length $n = 3$ than for $n = 2$. The observed ligand dependence of the polymerisation efficiency does not clearly correlate with overall ligand steric hindrance as deduced from the bound/free anion equilibrium for the cationic benzyl complexes. Within the series of complexes with unsubstituted Cp ligands the match between metal centre and bridge length appears to be of prime importance. It is presently uncertain if the observed effects are specific for the (Cp–amide)ZrCl$_2$/MAO combination or if they are valid also when other activators/counterions are used. This would require separate studies on the MAO-free systems, where great care has to be taken to eliminate effects of impurities in the solvent and feed.

Despite the obvious limitations of the present study, it seems that comparative reactivity studies of the series of Cp-bridge–amido complexes obtained can yield interesting information on the structure–activity relationships in homogeneous Ziegler-type catalysts.

6. Experimental

6.1. General considerations

All organometallic compounds mentioned in this paper are air and moisture sensitive and manipulations were performed under nitrogen atmosphere using standard Schlenk and glove box (Braun MB-200) techniques. Solvents (toluene, THF, ether and pentane) were purified by distillation from K or Na/K alloy. $ZrCl_4$ (Aldrich, 99.5 + %) was used without further purification. Deuterated solvents were distilled from Na/K alloy (C_6D_6) or degassed and dried over 4 Å mol. sieves (CDCl$_3$, C_6D_5Br). $Zr(NMe_2)_4$ [23] and $B(C_6F_5)_3$ [24] were synthesized according to published procedures. $Zr(NMe_2)_2Cl_2(THF)_2$ was prepared from $Zr(NMe_2)_4$ and $ZrCl_4$ in THF according to a modification of the literature procedure [9]. A 1.5 M solution of MAO in toluene (AKZO Nobel) was used as received. Ethene (AGA, polymer grade) was passed over a supported copper scavenger (BASF R 3-11) and mol. sieves (3 Å) before being passed to the reactor. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded using Varian Gemini-200, VXR-300 or Unity-500 spectrometers. The chemical shifts are reported in ppm and referenced internally using the residual solvent resonances relative to TMS (δ 0 ppm). Elemental analyses were performed by the Microanalytical Department of the Chemical Laboratories of the University of Groningen; data given are the average of at least two independent determinations. Molecular weights were determined by cryoscopy in benzene.

6.2. Synthesis of $(C_5H_5)(CH_2)_nNHR$

The various ligands of this type were prepared by the reaction of $Br(CH_2)_nNHR \cdot HBr$ with a threefold excess of CpNa in THF in analogous fashion to that reported for $n = 3$, R = Me [6]. Yields after vacuum distillation or vacuum transfer 60–80%. The ligands are obtained as mixtures of the 1,2- and 1,3-isomers.

6.3. Synthesis of $[C_5H_4(CH_2)_nNR]ZrCl_2$ from $Zr(NMe_2)_4$

6.3.1. n = 3, R = Me

To a solution of 6.76 g (25.27 mmol) of $Zr(NMe_2)_4$ in 30 ml of toluene (0°C) was added 3.4 g (24.8 mmol) of $C_5H_5(CH_2)_3N(H)Me$. The mixture was warmed to 50°C and stirred for 0.5 h. The resulting light green–yellow solution was cooled to 0°C and 6.4 ml (50.4 mmol) of Me_3SiCl was added. A light yellow precipitate formed which dissolved upon heating to reflux. After refluxing for 4 h a clear brownish yellow solution was formed. The solvent was removed in vacuo and the residue rinsed twice with 30 ml of pentane. After drying in vacuo, the residue was extracted with 60 ml of hot toluene. Concentrating at 80–90°C to 15 ml and slowly cooling to −20°C produced cream coloured crystals of the $NHMe_2$ adduct of the title compound. Yield: 6.48 g (18.92 mmol, 75% based on $[C_5H_4(CH_2)_3NMe]ZrCl_2 \cdot HNMe_2$). ^1H NMR (200 MHz, $CDCl_3$): δ 6.20 (m, J_{HH} = 2.68 Hz, 2H, C_5H_4); 6.07 (m, J_{HH} = 2.68 Hz, 2H, C_5H_4); 2.99 (s, 3H, NMe); 2.93 (m, 2H, NCH_2); 2.75 (m, 2H, $C_5H_4CH_2$); 2.62 (d, $^3J_{HH}$ = 5.86 Hz, 6H, $HNMe_2$); 2.12 (m, 2H, NCH_2CH_2). Sublimation of 0.95 g (2.77 mmol) of $[C_5H_4(CH_2)_3NMe]ZrCl_2 \cdot HNMe_2$ at 150–160°C and 10^{-3} Torr yielded 0.75 g of $[C_5H_4(CH_2)_3NMe]ZrCl_2$ (2.52 mmol, 91%), pure by NMR spectroscopy.

6.3.2. n = 3, R = Et

This compound was obtained in similar fashion, using the appropriate ligand, in 66% overall yield. ^1H- and ^{13}C-NMR data of the compounds mentioned are found in Tables 1 and 2.

6.4. Synthesis of $[C_5H_4(CH_2)_nNR]ZrCl_2$ from $Zr(NMe_2)_2Cl_2(THF)_2$

6.4.1. n = 2, R = iPr

To a clear yellow solution of 2.1 g (5.3 mmol) of $Zr(NMe_2)_2Cl_2 \cdot (THF)_2$ in 50 ml of toluene, 0.8 ml (5.3 mmol) of $C_5H_5(CH_2)_2N(H)–i$-Pr was added. Subsequently the reaction mixture was stirred for 18 h at 75°C. The resultant yellow solution was filtered and the volatiles were removed in vacuo giving a yellow solid. This was stripped of remaining toluene by stirring with 10 ml of pentane that was then pumped off. The residual light yellow solid was rinsed 3 times with 25 ml of pentane and dried in vacuo. After sublimation (0.05 mm Hg, 60°C) the title compound was isolated free from residual dimethylamine as an off white solid. Yield: 1.2 g (3.9 mmol; 74%). Analysis for $C_{10}H_{15}NCl_2Zr$: calculated: C, 38.58; H, 4.86; Zr, 29.30; found: C, 38.58; H, 4.81; Zr, 29.20. Molecular weight for $C_{10}H_{15}NCl_2Zr$: calculated: 311 g/mol; found (cryoscopy): 351 g/mol.

Other derivatives made by this route (using the appropriate ligand):

– $n = 2$, R = tBu: yield 69%. Analysis for $C_{11}H_{17}NCl_2Zr$: calculated: C, 40.60; H, 5.27; Zr, 28.03; found: C, 40.55; H, 5.27; Zr, 28.13. Molecular weight for $C_{11}H_{17}NCl_2Zr$: calculated: 325 g/mol; found (cryoscopy): 332 g/mol.

– $n = 3$, R = iPr: yield 71%. Analysis for $C_{11}H_{17}NCl_2Zr$: calculated: C, 40.60; H, 5.27; Zr, 28.03; found: C, 40.66; H, 5.27; Zr, 28.05.

^1H- and ^{13}C-NMR data of the compounds mentioned are found in Tables 1 and 2.

6.5. Synthesis of $[C_5H_4(CH_2)_2N–i$-$Pr]Zr(CH_2Ph)_2$

To a cooled (0°C) solution of 1.33 g (2.92 mmol) of $Zr(CH_2Ph)_4$ in 10 ml of toluene, 446 μl (2.99 mmol) of $C_5H_5(CH_2)_2N(H)–i$-Pr was added. The mixture was stirred overnight at ambient temperature. After removal of the solvent the sticky residue was stripped of remaining solvent by stirring with 10 ml of pentane which was subsequently pumped off. The brown powder was then extracted with ether. Upon concentrating the solution and standing overnight at −20°C, 0.55 g crystalline material

was obtained. Further concentation and cooling of the mother liquor yielded a second crop of 0.25 g of product. Total yield: 0.80 g (1.89 mmol, 65%) of $[C_5H_4(CH_2)_2N-i-Pr]Zr(CH_2Ph)_2$. Anal. calc. for $C_{24}H_{29}NZr$: C, 68.19; H, 6.92; Zr, 21.58; found: C, 68.44; H, 7.15; Zr, 21.47. ^{1}H- and ^{13}C-NMR data are found in Tables 3 and 4.

6.6. Synthesis of $[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)_2$ from the corresponding dichlorides

6.6.1. n = 3, R = iPr

To a cooled suspension ($-20°C$) of 2.13 g (6.55 mmol) $[C_5H_4(CH_2)_3N-i-Pr]ZrCl_2$ in 30 ml of ether 15 ml of a 0.93 M (13.9 mmol) $PhCH_2MgCl$ solution in ether was added dropwise. After warming to room temperature the mixture was stirred for 4 h during which the colourless mixture turned light yellow. Removal of the solvent yielded a light yellow residue which was stripped of residual ether by stirring with with 30 ml of pentane which was subsequently pumped off. The solids were extracted with 50 m of pentane and the resulting light yellow solution was concentrated to 15 ml. Light yellow crystals were obtained on standing overnight at $-20°C$. This yielded 1.92 g of product. A second crop (0.51 g) was obtained by further concentration and cooling of the mother liquor. Total yield: 2.43 g (5.56 mmol. 85%) of $[C_5H_4(CH_2)_3N-i-Pr)Zr(CH_2Ph)_2$, pure by NMR spectroscopy.

Other derivatives made by this route:

– $n = 2$, R = tBu: yield 65%. Analysis for $C_{25}H_{31}NZr$: calculated: C, 68.75; H, 7.15; Zr, 20.89; found: C, 68.39; H, 7.10; Zr, 20.80. The somewhat low carbon value found may reflect some zirconium carbide formation during combustion.

– $n = 3$, R = Et: yield 65%.

– $(C_5Me_4SiMe_2NtBu)Zr(CH_2Ph)_2$: yield 75% (for full details, see below).

^{1}H- and ^{13}C-NMR data of the compounds mentioned are found in Tables 3 and 4.

6.7. Synthesis of $[C_5Me_4SiMe_2N-t-Bu]$ $Zr(CH_2Ph)_2$

To a cooled (0°C) solution of 1.71 g (4.15 mmol) of $[C_5Me_4SiMe_2N-t-Bu]ZrCl_2$ in 20 ml of ether 9.6 ml of a 0.93 M (8.9 mmol) solution of $PhCH_2MgCl$ in ether was added dropwise. After stirring for 1.5 h at room temperature the solvent was removed in vacuo leaving a light yellow residue. The residue was stripped of remaining ether by stirring with 20 ml of pentane which was subsequently pumped off. Extracting the residue with 50 ml of pentane gave a clear light yellow solution. The solution was concentrated at reflux to 10 ml and cooling overnight to $-20°C$ resulted in 1.23 g of light yellow crystals. A second crop (0.40 g) was obtained by further concentration and cooling of the mother liquor. Total yield 1.63 g (3.12 mmol, 75%) of $[C_5Me_4$ $SiMe_2NtBu]Zr(CH_2Ph)_2$. ^{1}H NMR (300 MHz, C_6D_6): δ 7.12 (t, $^3J_{HH} = 7.51$ Hz, 4H, m-Ph), 6.90 (t, $^3J_{HH} = 7.33$ Hz, 2H, p-Ph), 6.78 (d, $^3J_{HH} = 7.33$ Hz, 4H, o-Ph), 1.91 (s, 6H, C_5Me_4), 1.87 (d, $^2J_{HH} = 10.99$ Hz, 2H, CH_2Ph), 1.78 (s, 6H, C_5Me_4), 1.61 (d, $^2J_{HH} = 10.99$ Hz, 2H, CH_2Ph), 1.14 (s, 9H, CMe$_3$), 0.42 (s, 6H, SiMe$_2$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 147.10 (s, $ipso$- Ph), 130.01 (s, C_5Me_4), 129.08 (d, $^1J_{CH} = 156.3$ Hz, o-Ph), 127.26 (d, $^1J_{CH} = 153.8$ Hz, m-Ph), 126.22 (s, C_5Me_4), 122.08 (d, $^1J_{CH} = 161.1$ Hz, p-Ph), 97.87 (s, $ipso$-C_5Me_4), 61.02 (t, $^1J_{CH} = 122.1$ Hz, CH_2Ph), 56.63 (s, CMe_3), 33.80 (q, $^1J_{CH} = 124.5$ Hz, CMe_3), 14.44 (q, $^1J_{CH} = 127.0$ Hz, C_5Me_4), 11.46 (q, $^1J_{CH} = 126.6$ Hz, C_5Me_4), 6.69 (q, $^1J_{CH} = 119.2$ Hz, SiMe$_2$).

6.8. Reaction of $[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)_2$ with $B(C_6F_5)_3$ in C_6D_5Br

In these experiments 0.08 mmol of a Zr dibenzyl complex and an equimolar amount of $B(C_6F_5)_3$ were dissolved in 0.4 ml of C_6D_5Br, giving 0.2 M solutions of the various ionic

complexes without noticeable byproducts (as seen by NMR). Low temperature ($-35°C$) ^{1}H- and ^{13}C-NMR data of two representative species (one contact ion pair, $n = 3$, R = Me, and one solvent-separated ion pair, $n = 3$, R = iPr) are given below. ^{1}H-NMR assignments were aided by recording ^{1}H,^{1}H-COSY spectra.

$[C_5H_4(CH_2)_3NMe]Zr(\eta^1\text{-}CH_2Ph)[\eta^6\text{-}PhCH_2B(C_6F_5)_3]$: ^{1}H-NMR (500 MHz, C_6D_5Br, $-35°C$): δ 1.17, 1.63 (m, $-CH_2-$), 1.63, 1.68 (d, 10.8 Hz, ZrCH$_2$), 2.22, 2.35 (m, CpCH$_2$), 2.42–2.40 (2H, N–CH$_2$), 3.12, 3.26 (br, BCH$_2$), 4.58, 5.20, 5.34, 5.48 (Cp H), 6.52 (d, 7.3 Hz, 2H, ZrBz o-H), 6.57, 6.60, 6.80, 6.92, 7.10 (BBz ArH), 6.95 (ZrBz p-H), 7.20 (2H, ZrBz m-H). ^{13}C-NMR (125.7 MHz, C_6D_5Br, $-35°C$): δ 26.65 (t, 128.7 Hz, $-CH_2-$), 32.40 (t, 128.7 Hz, CpCH_2), 34.6 (br, BCH$_2$), 43.98 (q, 132.4 Hz, NMe), 54.41 (t, 120.3 Hz, ZrCH$_2$), 105.56 (d, 166.0 Hz, Cp CH), 109.21 (d, 169.7 Hz, Cp CH), 116.37 (d, 173.5 Hz, Cp CH), 117.07 (d, 180.9 Hz, Cp CH), 122.40 (d, 159.4 Hz, ZrBr p-CH), 123.11 (d, 167.5, BBz p-CH), 124 (v.br., BC), 125.13 (d, 153.0 Hz, ZrBz m-CH), 127.11 (d, part overlap, BBz CH), 128.16 (d, 162.4 Hz, BBz CH), 128.42 (d, 156.6 Hz, ZrBz o-CH), 128.79 (d, part overlap, BBz CH), 129 (overlap, BBz CH), 133.35 (Cp C$ipso$), 136.7 (d, $J_{CF} = 247$ Hz, m-CF), 138.2 (d, $J_{CF} = 247$ Hz, p-CF), 148.1 (d, $J_{CF} = 242$ Hz, o-CF), 149.05 (ZrBz C$ipso$), 155.95 (BBz C$ipso$). ^{19}F-NMR (282 MHz, C_6D_5Br, $-35°C$): $\delta -132.9$ (o-F), -162.0 (p-F), -166.0 (m-F), $\Delta\delta(p-m) = 4.0$.

$\{[C_5H_4(CH_2)_3NiPr]Zr(\eta^2\text{-}CH_2Ph)\}[PhCH_2B(C_6F_5)_3]$: ^{1}H-NMR (500 MHz, C_6D_5Br, $-35°C$): δ 0.92 (d, 5.4 Hz, iPr Me), 1.03 (d, 4.9 Hz, iPr Me), 1.47, 1.62 (m, $-CH_2-$), 1.64, 2.75 (d, 7.8 Hz, ZrCH$_2$), 2.15, 2.20 (m, CpCH$_2$), 2.4 (m, 2H, NCH$_2$), 3.22 (m, iPr CH), 3.45 (br, 2H, BCH$_2$), 4.50, 5.25, 5.62, 5.97 (Cp CH), 6.26 (d, 6.4 Hz, ZrBz o-H), 6.77 (d, 7.3 Hz, ZrBz o-H), 6.91 (t, 7.1 Hz, BBz p-H), 7.07 (m, BBz m-H), 7.24, 7.31 (ZrBz m-H), 7.26 (BBz o-H), 7.28 (ZrBz p-H). ^{13}C-

NMR (125.7 MHz, C_6D_5Br, $-35°C$): δ 20.77, 22.05 (q, 127.7 Hz, iPr Me), 25.44 (t, 129.5 Hz, $-CH_2-$), 28.38 (t, 129.7 Hz, CpCH_2), 31.8 (v.br. BCH$_2$), 39.81 (d, 108.1 Hz, iPr CH), 44.48 (t, 135.5 Hz, NCH$_2$), 53.43 (t, 144.5 Hz, ZrCH$_2$), 108.57 (d, 171.6 Hz, Cp CH), 109.30, 109.41 (d, about 174 Hz, Cp CH), 115.16 (d, 172.0 Hz, Cp CH), 121.82 (ZrBz C$ipso$), 122.93 (d, 160.4 Hz, BBz p-CH), 124.04 (d, 160.4 Hz, ZrBz CH), 127.18 (d, 156.7 Hz, BBz m-CH), 128.11 (d, 164.1 Hz, ZrBz CH), 128.82 (d, part. overlap, BBz m-CH), 131.82 (d, 160.4 Hz, ZrBz CH), 132.25 (Cp C$ipso$), 132.74 (d, 164.1 Hz, ZrBz CH), 133.29 (d, 164.1 Hz, ZrBz CH), 148.60 (BBz C$ipso$). ^{19}F-NMR (282 MHz, C_6D_5Br, $-35°C$): $\delta -132.5$ (o-F), -164.8 (p-F), -167.8 (m-F), $\Delta\delta(p-m) = 3.0$.

6.9. Ethene polymerisation experiments

Ethene slurry polymerisation reactions were carried out in a thermostated (electrical heating, water cooling) Medimex 11 stainless steel autoclave. For each run a total of 200 ml of toluene (300 ml for the last five entries in Table 6) was used as solvent. The appropriate Cp–amide zirconium dichlorides were stirred for 15 min in 10 ml of toluene with 175 equiv of MAO (33% of the total amount of MAO used, Al/Zr = 520) before use. The remaining MAO was brought directly into the reactor with the solvent. At the desired reaction temperature the catalyst solution was injected into the reactor and ethene pressure was admitted, after which the ethene pressure was kept constant. After 30 min the runs were terminated by venting the reactor and quenching with methanol. The polymers were slurried in acidified methanol for several hours, repeatedly rinsed with ethanol and petroleum ether and dried in vacuo at 70°C. The data in Table 6 represent single runs, performed as a series using the same batch of MAO/toluene activator and solvent for internal consistency. Duplo runs performed for several experiments showed a variance in catalyst activity of about 15–20%.

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