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Journal of Organometallic Chemistry 483 (1994) 159–166

Journal of Organometallic Chemistry

The influence of steric and electronic effects of substituents on the cyclopentadienyl ring on the behaviour of $(CpR)_2TiCl_2$ and $(CpR)CpTiCl_2/Et_3Al_2Cl_3$ catalysts in polymerization of ethene

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Received 16 February 1994

Abstract

A range of $(CpR)(CpR')TiCl_2$ complexes (R = R' = H, Me, Et, ^iPr, ^tBu, $SiMe_3$, CMe_2Ph, CO_2Me and R = H, R' = Me, ^tBu, $SiMe_3$, CMe_2Ph, CO_2Me) have been synthesized. Ethylene polymerization studies (50°C, 10 bar) in the presence of $Et_3Al_2Cl_3$ as co-catalyst revealed catalyst activity of > 20 g polyethylene $(mol\ Ti\ h)^{-1}$ when the combined Tolman cone angle for the two cyclopentadienyl rings was less than 260° and very low activity when the combined cone angle was larger. An analysis of available crystallographic data for $(CpR)_2TiCl_2$ complexes revealed that the Cl–Ti–Cl angle decreases as the size of R increases. It thus appears that the steric influence of R may affect polymerization activity both by restricting access of reactants to the metal as well as by modifying metal–reactant (or polymer) interactions.

Keywords: Titanium; Cyclopentadienyl; Catalysts; Olefin polymerization; Steric effects

1. Introduction

Since its discovery in the late 1950s, the Cp_2TiCl_2/aluminium alkyl catalyst system has been the subject of much study. However, very little information has been published on the effect of cyclopentadienyl ring substituents on ethylene polymerization behaviour. Indeed, to our knowledge, no comparative polymerization activity studies involving complexes containing monosubstituted cyclopentadienyl rings have appeared in the open literature. One pertinent study, that of $(CpR)(CpR')TiCl_2$ complexes (CpR = CpR' = CpH, $CpMe_4{}^iPr$; CpR = CpH, CpR' = $CpMe_4{}^iPr$) did show that increasing substitution of the cyclopentadienyl rings led to a decrease in ethylene polymerisation activity [1]. The only other related study, on R_2TiMe^+ cationic complexes, revealed an activity order for R of $CpSiMe_3$ > CpH [2], i.e. in this case monosubstitution of the cyclopentadienyl ring increased the catalytic activity. Finally, a report of catalytic studies in which the role of substituents on a cyclopentadienyl ring attached to a transition metal was examined is to be noted [3], as is a review on the importance of sterically demanding ring substituents in 'CpM' systems [4].

The $(CpR)(CpR')TiCl_2$/aluminium alkyl catalyst system is an excellent system for the study of substituent effects, particularly steric effects, on polymerization activity. Since in our earlier work [5], we had observed that the ethylene polymerization behaviour of $(CpR)_2ZrCl_2$ complexes was influenced to a small degree of steric effects associated with R, we had expected that steric effects would be more dominant in the related Ti complexes. Ti is much smaller than Zr or Hf; the atomic radius of Ti is 1.47 Å, compared with 1.60 Å for Zr and 1.59 Å for Hf. Also, the synthesis of a range of 'mixed ring' titanocenes, with one substituted and one unsubstituted cyclopentadienyl ring, has been reported [6]. Hence, a large range of compounds with different steric and electronic parameters was available for testing.

Here, the synthesis and characterization of a range of substituted titanocene compounds, $(CpR)_2TiCl_2$ and $(Cp)(CpR)TiCl_2$, are described. Ethylene polymeriza-

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0022-328X/94/$07.00
SSDI 0022-328X(94)24693-D

tion using these complexes have been studied, and the relationship between the structural and spectroscopic parameters and steric and electronic effects associated with these complexes examined. The recent Tolman steric parameters associated with cyclopentadienyl ring substituents have been used to evaluate steric effects [7].

2. Results and discussion

2.1. Synthesis of $(CpR)_2TiCl_2$ and $(CpR)CpTiCl_2$ complexes

The strategy governing the approach to the synthesis of monosubstituted cyclopentadienyl organometallic complexes, and also the reasons for the choice of particular substituents, have been outlined previously [7]. The same considerations apply here to the synthesis of symmetrical and 'mixed ring' (one substituted and one unsubstituted cyclopentadienyl ring) titanocene dichloride complexes.

Two main routes were used for the synthesis of symmetrically substituted metallocenes, viz. metallation of a substituted cyclopentadiene by ^nBuLi or the reduction or alkylation of a fulvene, both followed by reaction with $TiCl_4$. The preparation of the 'mixed ring' titanocene dichlorides was achieved by reaction of $CpTiCl_3$ with one equivalent of the substituted cyclopentadienyl salt. (Other related methods for making such 'mixed ring' compounds have been described [8–11] but were not used in the present work.)

Published procedures for most of these compounds were available and were followed, in some cases with minor modifications, as outlined in the Experimental section. The synthesis of the symmetrical $(CpR)_2TiCl_2$ compounds was straightforward. However, $(CpMe)_2TiCl_2$, even after recrystallization, was contaminated with 5.0 mol% of Cp_2TiCl_2, as a consequence of the presence of a considerable amount of cyclopentadiene in commercial methylcyclopentadiene. The other compounds were obtained in high purity (as indicated by NMR spectroscopy), except for $(CpCO_2\text{-}Me)_2TiCl_2$, which contained unidentified contaminants. An attempted synthesis of $(CpEt)_2TiCl_2$, carried out by analogy to a published procedure for $(CpMe)_2TiCl_2$, [6a] was unsuccessful.

The 'mixed ring' titanocene dichlorides were somewhat more difficult to obtain, since in some of the preparations, not only was the required mixed-ring compound observed, but also Cp_2TiCl_2, and often $(CpR)_2TiCl_2$. This type of complication has been noted previously [6a] and is due to ring exchange between $CpTiCl_3$ and Li[CpR], which occurs at, or even below, room temperature [6b]. In the case of $(CpMe)CpTiCl_2$, the product was contaminated with 10 mol% of Cp_2TiCl_2 and traces of $(CpMe)_2TiCl_2$. The attempted synthesis of $(CpEt)CpTiCl_2$ resulted in the formation of $(CpEt)_2TiCl_2$ containing 14 mol% of Cp_2TiCl_2. It was initially suspected that this ring exchange continued after the products had been redissolved in toluene and used in polymerization reactions at elevated temperature but the ^1H NMR spectra of the three contaminated titanocenes recorded (in C_6D_6) before and after heating at 50° for 1 h (conditions similar to those used in the polymerization studies) revealed that the concentrations of the contaminants were unaffected by this treatment. In all three cases the mixtures were used as polymerization catalysts and the activities obtained were corrected for the presence of Cp_2TiCl_2. The $(CpCO_2Me)CpTiCl_2$ product contained unidentified impurities as indicated by NMR spectroscopy.

2.2. Ethylene polymerization studies

Choice of reaction conditions

Cp_2TiCl_2 was found to polymerize ethylene with a high activity at room temperature and 1 bar ethylene pressure in the presence of $Et_2AlCl \cdot Cl_2AlEt$ as cocatalyst. However, initial experiments showed that the substituted complexes were much less active than titanocene dichloride. Thus, elevated temperatures (50°C) and pressures (10 bar) were required to obtain a comparable activity for the substituted complexes. Under these conditions, polymer characterization and comparisons of the various catalysts were possible.

As shown in Fig. 1, the polymerization activity increases with the Ti concentration above a certain minimum level ($\sim 1.5 \times 10^{-5}$ mol l^{-1} Ti). This minimum concentration is presumably required to remove trace impurities of water, air, etc. from the reactor, as has been observed for related zirconocene/alumoxane catalysts [12]. Thus, in all reactions, a Ti concentration of

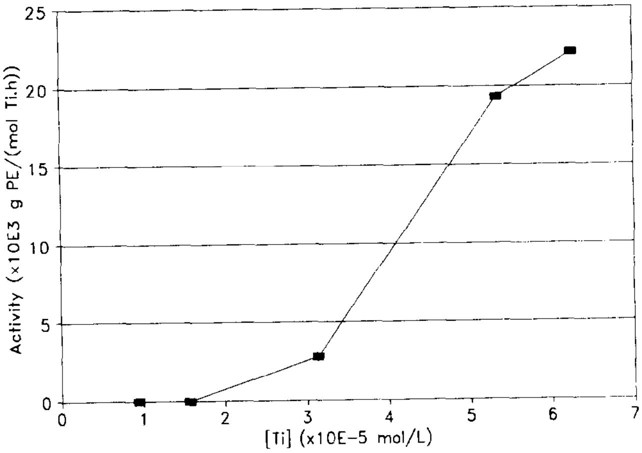


Fig. 1. The effect of Ti concentration on catalytic activity for ethylene polymerization with $(CpMe)_2TiCl_2/Et_3Al_2Cl_3$.

Table 1
Results of ethylene polymerization reactions carried out with $(CpR)_2TiCl_2$ and $(CpR)CpTiCl_2$ catalysts [a]

$(CpR')(CpR'')TiCl_2$		Activity $\times 10^3$ (g PE (mol Ti h)$^{-1}$)	T_m(°C)	DSC half band width (°C)
R′	R″			
H	H	190	136.8	8.3
Me	H	170	135.8	6.3
Me	Me	13.3	134.2	6.2
Et	Et	7.09	133.9	5.2
^iPr	^iPr	5.08	131.9	5.2
^tBu	H	112	131.7	5.3
^tBu	^tBu	0.28	129.3	4.6
$SiMe_3$	H	40.9	132.5	5.1
$SiMe_3$	$SiMe_3$	7.09	134.8	5.4
CMe_2Ph	H	3.41	132.9	4.8
CMe_2Ph	CMe_2Ph	0.20	132.6	4.1

[a] Experimental conditions: $T_{pol} = 50$°C, $P_E = 10$ bar, $t = 45$ min, [Ti] $= 6.25 \times 10^{-5}$ M, [Al] $= 1.21 \times 10^{-2}$ M.

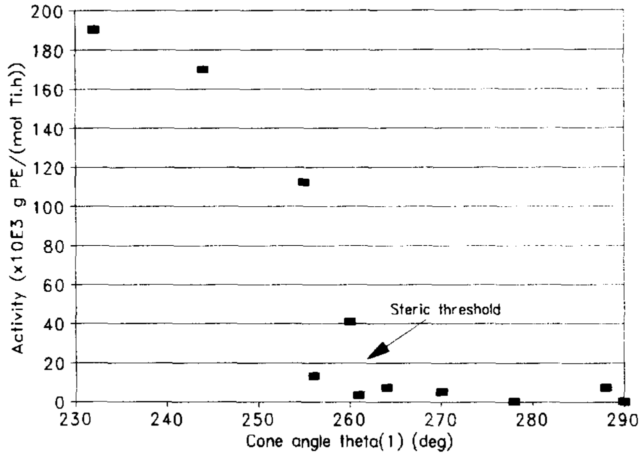


Fig. 3. The relationship between cone angle and ethylene polymerization activity for the titanocene catalysts.

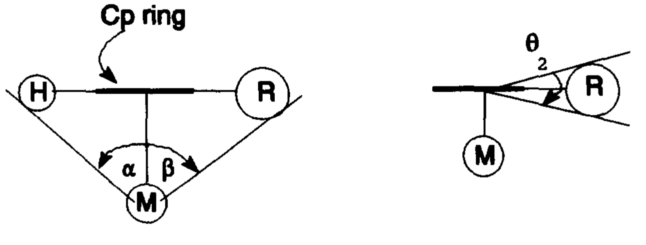
6.25×10^{-5} mol l^{-1} Ti was used to ensure effective polymerization.

Ethylene polymerization with the full set of titanocene complexes

The experimental conditions and the results of this series of experiments are given in Table 1. The activities shown for the catalysts which contained Cp_2TiCl_2 have been corrected by taking account of the contribution to the catalyst activity by the contaminant. Both CO_2Me-substituted catalysts were inactive in the polymerization, as might be expected for catalysts containing electron withdrawing substituents.

The activities of the series of catalysts span a far larger range than was found for a similar series of Zr complexes [5]. However, only the unsubstituted catalyst and the complexes with one small substituent show good polymerization activities, with Cp_2TiCl_2 showing the greatest activity.

A plot of the polymerization activities as a function of the cone angle parameter (see Fig. 2a)) is shown in Fig. 3. In order to differentiate between the complexes with one and those with two substituted rings, the cone angles were calculated as follows. Symmetrically substituted complexes were assigned a cone angle twice that of the normal cone angle (θ_1) for that substituent, and 'mixed ring' titanocenes were given a cone angle value equal to the sum of the cone angle of one substituted and one unsubstituted cyclopentadienyl ring. It is clear from the plot that there is a steric threshold (at $\theta_1 \approx 260°$) beyond which the catalysts exhibit very poor polymerization activity. The concept of a steric threshold has been discussed previously [13a–i], and appears to be a general phenomenon in organometallic chemistry. The only substituted catalysts which have polymerization activity, albeit lower than that of Cp_2TiCl_2, are the 'mixed ring' complexes with sterically less demanding substituents.



(a) (b)

Fig. 2. Measurement of the cyclopentadienyl ring cone angle (a) with metal as apex (θ_1), where $\theta_1 = 2(4/5)[\alpha + (1/5)\beta]$ and (b) with Cp ring centroid as apex (θ_2).

The catalysts exhibit a 'pure' steric effect in their polymerization behaviour. There is no correlation between activity and the Swain–Lupton field effect parameter, *F* [13j], and no multiple regression analysis of the relationship between activity data and steric and electronic parameters was found to be significant. These findings are in marked contrast to those reported for the Zr and Hf-based catalysts [5,14]. In the latter case, both steric and electronic effects played a role in determining catalytic activity, and electronic effects were more important than steric effects. Increase in the bulk of the catalyst served to increase catalytic activity slightly, whereas in the Ti study, the steric effect predominates and causes only catalyst deactivation. This set of results represents the first quantification of the effect of ligand size on soluble Ti Ziegler–Natta catalysts.

The polymer melting points cover a fairly large range (129–137°C). The values do not correlate with polymerization activity, nor with any steric or electronic parameters. No polymer molecular weights were determined.

2.3. The relationship between structural and spectroscopic parameters and steric and electronic effects associated with the titanocene complexes

The ^{1}H and ^{13}C NMR spectral data for the titanocene complexes are listed in Tables 2 and 3, respectively. Selected crystal structural data are given in Table 4.

Spectroscopic parameters

The ^{1}H ring resonances for most of the symmetrically substituted $(CpR)_2TiCl_2$ complexes are shifted upfield relative to that for unsubstituted Cp_2TiCl_2, but those of the $SiMe_3$- and CO_2Me-substituted complexes are shifted downfield. The ^{13}C ring resonances are also shifted relative to those for the unsubstituted titanocene. The C_1 resonances of all the rings with electron-donating groups attached to them are shifted to lower field since C_1 is deshielded by the substituent. The $C_{3,4}$ resonances, including those of $(CpSiMe_3)TiCl_2$, are more shielded than those of the unsubstituted complex. Both the C_1 and $C_{2,5}$ resonances of the $SiMe_3$-substituted complex are deshielded owing to the interaction of the Si d-orbitals with the cyclopentadienyl π-system [11]. All three ^{13}C ring resonances are shifted downfield in the case of $(CpCO_2\text{-}Me)_2TiCl_2$, as the electron-withdrawing group deshields all the cyclopentadienyl ring electrons.

The ‘mixed ring’ titanocenes exhibit similar trends in their NMR spectra, but, the upfield shifts in the ^{1}H NMR spectra are less marked, and the downfield shifts of the $SiMe_3$- and CO_2Me-substituted compounds are larger. Similarly, the upfield shifts for the C_1 resonances are less marked, whereas those of the $C_{3,4}$ resonances are very similar to those in the symmetrical compounds. The ^{13}C resonance of the unsubstituted ring in each case is very close to that for the unsubstituted titanocene. However, in the ^{1}H NMR spectra, the resonance for the unsubstituted ring there is an upfield shift for the CMe_2Ph-substituted complex, while the CO_2Me-group causes a downfield shift.

Structural parameters

No crystal structural data for ‘mixed ring’ titanocene complexes are available, and the data in Table 3 are thus based on information on the symmetrically substituted complexes. No correlation between the $Cp_{centroid}$–Ti–$Cp_{centroid}$ and Cl–Ti–Cl angles of these

Table 2
^{1}H NMR spectral data for $(CpR)_2TiCl_2$ and $(CpR)CpTiCl_2$ compounds [a]

R	η^5-C_5H_5	η^5-C_5H_4R	η^5-C_5H_4R
$(CpR)_2TiCl_2$			
H	6.60 (s, 10H)		
Me		6.40 (t, 2H, 2.6Hz)	2.33 (s, 3H, $-CH_3$)
		6.30 (t, 2H, 2.5Hz)	
Et		6.42 (t, 2H, 2.6Hz)	2.74 (q, 2H, 7.5Hz, $-CH_2CH_3$)
		6.33 (t, 2H, 2.6Hz)	1.18 (t, 3H, 7.5Hz, $-CH_2CH_3$)
^{i}Pr		6.42 (t, 2H, 2.6Hz)	3.22 (m, 1H, $-CH(CH_3)_2$)
		6.34 (t, 2H, 2.6Hz)	1.21 (d, 6H, $-CH(CH_3)_3$)
^{t}Bu		6.54 (t, 2H, 2.7Hz)	1.31 (s, 9H, $-C(CH_3)_3$)
		6.45 (t, 2H, 2.8Hz)	
$SiMe_3$		6.79 (t, 2H, 2.4Hz)	0.28 (s, 9H, $Si(CH_3)_3$)
		6.57 (t, 2H, 2.4Hz)	
CMe_2Ph		6.48 (m, 2H)	7.24 (m, 5H, $-C_6H_5$)
		6.09 (m, 2H)	1.77 (s, 6H, $-CH_3$)
CO_2Me		7.18 (t, 2H, 2.8Hz)	3.90 (s, 3H, $-CH_3$)
		6.56 (t, 2H, 2.8 Hz)	
$(CpR)CpTiCl_2$			
H	6.60 (s, 10H)		
Me	6.60 (s, 5H)	6.45 (t, 2H, 2.6Hz)	2.33 (s, 3H, $-CH_3$)
		6.33 (t, 2H, 2.6Hz)	
^{i}Pr[b]	6.55 (s, 5H)	6.46 (m, 4H)	3.23 (m, 1H, $-CH(CH_3)_2$)
			1.21 (d, 6H, $-CH(CH_3)_2$)
^{t}Bu	6.56 (s, 5H)	6.63 (t, 2H, 2.6Hz)	1.30 (s, 9H, $-C(CH_3)_3$)
		6.49 (t, 2H, 2.6Hz)	
$SiMe_3$	6.56 (s, 5H)	6.88 (t, 2H, 2.4Hz)	0.29 (s, 9H, $-Si(CH_3)_30$
		6.63 (t, 2h, 2.5Hz)	
CMe_2Ph	6.32 (s, 5H)	6.65 (t, 2H, 2.71Hz)	7.29 (m, 5H, $-C_6H_5$)
		6.49 (t, 2H, 2.7Hz)	1.76 (s, 6H, $-CH_3$)
CO_2Me[c]	6.65 (s, 5H)	7.14 (t, 2H)	3.91 (s, 3H, $-CH_3$)
		6.65 (t, 2H)	

[a] Solvent: $CDCl_3$; δ(ppm) relative to Me_4Si. [b] Ref. [20]. [c] Ref. [21].

Table 3
^{13}C NMR spectral data for $(CpR)_2TiCl_2$ and $(CpR)CpTiCl_2$ compounds [a]

R	η^5-C_5H_5	η^5-C_5H_4R			η^5-C_5H_4R
		C_1	$C_{1,5}$	$C_{3,4}$	
$(CpR)_2TiCl_2$					
H	120.2				
Me		133.8	123.2	115.4	16.4 (–CH_3)
Et		140.4	121.1	115.7	23.9 (–CH_2CH_3) 14.0 (–CH_2CH_3)
^iPr		146.1	119.3	115.7	29.3 (–$CH(CH_3)_3$) 22.7 (–$CH(CH_3)_3$)
^tBu		149.2	119.6	117.2	34.4 (–$C(CH_3)_3$) 31.0 (–$CH(CH_3)_3$)
$SiMe_3$ [b]		132.7	129.7	119.6	0.00 (–$Si(CH_3)_3$)
CMe_2Ph		149.2	121.2	118.1	1146.6, 128.2, 126.3, 126.2(–C_6H_5) 41.1 (–$C(CH_3)_2Ph$) 29.0 (–$C(CH_3)_2Ph$)
CO_2Me		139.8	124.4	121.6	162.7 (CO_2Me) 52.6 (–CH_3)
$(CpR)CpTiCl_2$					
H	120.2				
Me	119.6	134.6	123.8	115.7	16.4 (–CH_3)
^tBu	120.1	149.5	119.0	118.6	34.3 (–$C(CH_3)_3$) 31.0 (–$CH(CH_3)_3$)
$SiMe_3$	120.1	132.4	129.0	121.1	0.00 (–$Si(CH_3)_3$)
CMe_2Ph	120.4	148.6	120.0	119.7	146.2, 128.2 and 126.4 (–C_6H_5) 40.9 (–$C(CH_3)_2Ph$) 29.2 (–$(CH_3)_2Ph$)

[a] Solvent; $CDCl_3$, δ (ppm) relative to Me_4Si. [b] Ref. [15].

complexes was observed. The complexes with smaller substituents (R = Me, Et, ^iPr) have their substituents arranged in the *syn*-conformation, whereas for R = ^tBu, $SiMe_3$ the substituents adopt the *anti*-conformation (Fig. 4). Similar results have been noted for the Zr complexes [14]. The torsion angle for the C_1–$Cp_{centroid}$–$Cp^*_{centroid}$–C^*_1 system for each complex (Fig. 5) was calculated from the crystal structure data. For the compounds with substituents in the *syn*-conformation, the torsion angle decreases as the size of the substituent increases, i.e. the vertical separation of the

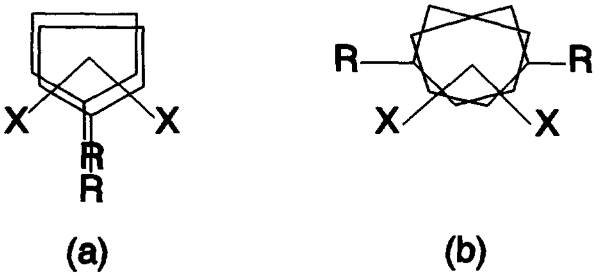


Fig. 4. Arrangement of cyclopentadienyl ring substituents in $(CpR)_2TiCl_2$ complexes: (a) *syn*- and (b) *anti*-conformations.

Table 4
Selected crystal structural data for $(CpR)_2TiCl_2$ complexes

R	Cp_c–M–Cp_c [a]	Cl–M–Cl	M–Cp_c (Å)	M–Cl (Å)	Ring conformation [b]
H	131.6	95.1	2.058	2.364	Staggered
Me	130.2	93.2(8)	2.067	2.361	*syn*
Et	132.0	93.3	2.067	–	*syn*
^iPr	132.9(3)	92.5(1)	2.068(4)	2.372(1)	*syn*
1^tBu	131.5	92.5(5)	2.093	2.370(2)	*anti*
$SiMe_3$	131.02	91.63	–	–	*anti*

[a] Cp_c is the centroid (the centre of gravity of each C_5-ring ligand). [b] See text for definitions.

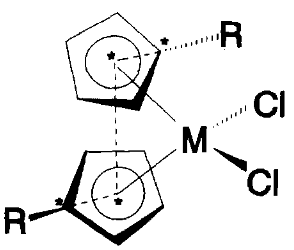


Fig. 5. The C_1–$Cp_{centroid}$–$Cp^*_{centroid}$–C_1^* torsion angle for $(CpR)_2MCl_2$ complexes.

substituents is increased. Presumably when the steric strain becomes too large the torsion angle widens to almost 180°, and the substituents thus adopt an *anti*-conformation. It should be noted that in solution there is free rotation about the $Cp_{centroid}$–Ti axis, and so these different conformations may not affect the polymerization results.

There is a clear correlation between the Cl–Ti–Cl angle and the cone angle (θ_1) of the substituted cyclopentadienyl system (Fig. 6). We have observed a similar related trend for known $(CpR)_2ZrCl_2$ complexes [14]. There is however no linear correlation between either of these angles and ^1H or ^{13}C NMR resonance data. The C_1 resonance of the cyclopentadienyl ring varies more with the crystal structural parameters than the other cyclopentadienyl carbon resonances, but no trend is apparent. This suggests that the steric effect of ring substituents may not only influence the space available to the reactants and the polymer chain but also affect the orbital interaction between the metal and these species. The ^1H ring resonances for the substituted complexes do not change appreciably with increasing cone angle (θ_1), except in the case of the $SiMe_3$-substituted compound; this applies to both the symmetrically substituted complexes and the 'mixed ring' titanocenes.

Attempts were made to quantify the relationships between the NMR data and steric and electronic effects associated with the ring substituent. In the investigation, the CO_2Me-substituted complexes were excluded because the electron withdrawing nature of the substituent(s) causes large changes in the spectroscopic data which are not reflected in structural changes. Multiple linear regression analysis of all combinations of the ^{13}C C_1 resonance and the average of the two ^1H ring resonances versus a steric parameter (θ_1 or θ_2) (Fig. 2) and an electronic parameter (Hammett substituent constants) was performed, but no statistically significant correlations were found.

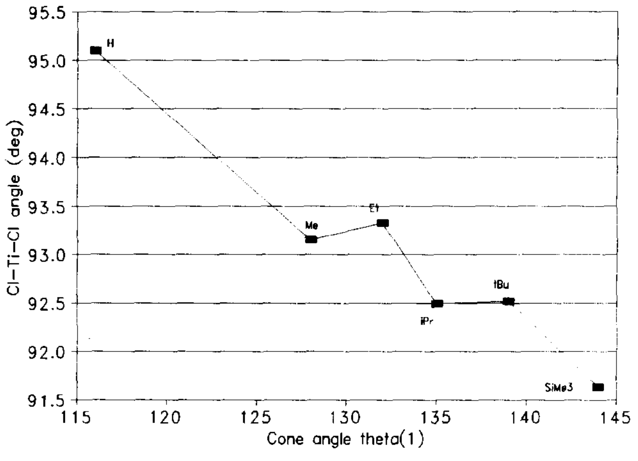


Fig. 6. Cl–Ti–Cl angle versus cone angle, θ_1, for $(CpR)_2MCl_2$ complexes.

3. Conclusion

Ethylene polymerization studies were carried out with a range of titanocene complexes which were synthesized. The steric effect dominated the order of activities; only the unsubstituted catalyst and those with one small substituent exhibited high activity. Comparison of polymerization activity with cone angle demonstrated the presence of a steric threshold, beyond which catalytic activity was very low. This marked difference in polymerization behaviour between these catalysts and their Zr analogues is ascribed to the smaller size of Ti, which results in an increases in the steric crowding of the ligands around the Ti active centre, thus limiting access of monomer to the active site and influencing the interaction of the metal with reactant and polymer.

The attempts to correlate ground state structural phenomena associated with the substituents, R, on the cyclopentadienyl ring with the electronic and steric properties of R have revealed only minimal relationships. The finding that the Cl–Ti–Cl angle decreased as the cone angle (θ_1) increased is, however, significant, and the values of the angles correlate with the polymerization activities observed for the various complexes. Indeed, the correlation suggests that the size of the ring substituent influences both the space available for reaction to occur on the Ti atom as well as the potential overlap of the Ti orbitals with those of the reactants and products.

4. Experimental details

4.1. Synthesis of $(CpR)_2TiCl_2$ and $(CpR)CpTiCl_2$ complexes

Cyclopentadiene dimer (1 : 1 mixture with decalin) was cracked to provide crude CpH which was then distilled through a 40 cm Vigreux column (b.p. 42°C) and collected in a flask kept at 0°C. Methylcyclopentadiene dimer was cracked under N_2 to provide crude MeCpH, which was then distilled through a 20 cm

Vigreux column (b.p. 74–75°C) and collected in a flask kept at −78°C. Other substituted cyclopentadienes, RCpH (R = Et, ^{t}Bu, $SiMe_3$) were prepared by published procedures [15–17], as were 6,6-dimethylfulvene [18] and sodium carbomethoxycyclopentadienide, Na[$CpCO_2Me$] [19].

Cp_2TiCl_2 and $CpTiCl_3$ were purchased from Merck and Strem Chemicals, respectively, and used without purification. $(CpMe)_2TiCl_2$ was made by a published procedure [4] and found, after recrystallization, to contain 5.0 mol% of Cp_2TiCl_2. $(CpMe)CpTiCl_2$ was also made by a published procedure and found, after recrystallization, to be contaminated with 10.0 mol% of Cp_2TiCl_2 and a small amount of $(CpMe)_2TiCl_2$. $(CpR)_2TiCl_2$ and $(CpR)CpTiCl_2$ (R = ^{t}Bu, $SiMe_3$) were made by the type of procedure used for similar compounds [4] (see method for R = ^{t}Bu below). $(CpCMe_2Ph)_2TiCl_2$ and $(CpCMe_2Ph)CpTiCl_2$ were made by published procedures [20], but were recrystallized from toluene. $(CpCO_2Me)_2TiCl_2$ and $(CpCO_2Me)CpTiCl_2$ were also made by published methods [21], but both products were found to be impure by NMR spectroscopy. Other complexes were made by modifications of literature procedures as detailed below. The ^1H and ^{13}C NMR spectral data are collected in Tables 2 and 3, respectively.

4.2. Attempted synthesis of $(CpEt)CpTiCl_2$

A solution of ^{n}BuLi in hexane (6.3 ml, 10.0 mmol) was added dropwise to one of freshly cracked EtCpH (0.85 g, 9.09 mmol) in hexane (20 ml) at room temperature. The solution became viscous and a white precipitate of Li[CpEt] separated. The suspension was stirred at room temperature for 1 h to ensure completion of the reaction, the solvent was then removed in vacuo, and the white residue was suspended in diethyl ether (20 ml). The suspension was added via a cannula to a solution of $CpTiCl_3$ (1.80 g, 8.26 mmol) in diethyl ether (30 ml). The red solution was stirred at room temperature for 18 h. The solvent volume was reduced by half in vacuo, and 6 M aqueous HCl (20 ml) was added. The precipitate was filtered off and washed with 6 M aqueous HCl until the washings were colourless. The solids were then washed with cold diethyl ether (2 × 5 ml) and dried in vacuo. Recrystallization of the red solid from hot toluene yielded dark red, needle-like crystals (0.103 g), which were shown by NMR spectroscopy to the $(CpEt)_2TiCl_2$ contaminated with 14 mol% of Cp_2TiCl_2 and a small amount of $(CpEt)CpTiCl_2$.

4.3. Synthesis of $(Cp^tBu)_2TiCl_2$

A solution of ^{n}BuLi in hexane (14.4 ml, 24.1 mmol) was added dropwise to a solution of freshly cracked ^{t}BuCpH (2.66 g, 21.9 mmol) in hexane (25 ml) at room temperature. The solution became viscous and a white precipitate of Li[Cp^tBu] separated. The mixture was stirred at room temperature for 30 min to ensure completion of the reaction, the solvent was then removed in vacuo, and the white residue was suspended in diethyl ether (20 ml). The suspension was cooled to 0°C and added via a cannula to a solution of $TiCl_4$ (2.00 g, 10.5 mmol) in diethyl ether (30 ml) at 0°C. The red mixture was stirred at room temperature for 18 h and the solvent then removed in vacuo to leave a red solid, which was collected on a frit and washed with 1 M aqueous HCl (40 ml) containing NaCl (1.56 g) and then 6 M aqueous HCl until the washings were colourless. The red solid was then washed with dry ethanol (2 × 5 ml) and diethyl ether (2 × 5 ml) and dried in vacuo. It was then recrystallized from CH_2Cl_2/hexane at −20°C to give crystals of the desired compound in 16% yield.

4.4. Synthesis of $(Cp^tBu)CpTiCl_2$

A solution of ^{n}BuLi in hexane (5.7 ml, 9.13 mmol) was added dropwise to a solution of freshly cracked ^{t}BuCpH (0.99 g, 8.23 mmol) in hexane (20 ml) at room temperature. The solution became viscous and a white precipitate of Li[Cp^tBu] separated. The mixture was stirred at room temperature for 1 h to ensure completion of the reaction, the solvent then removed in vacuo and the white residue suspended in diethyl ether (20 ml). The suspension was cooled to 0°C and added via a cannula to a solution of $CpTiCl_3$ (1.80 g, 8.23 mmol) in diethyl ether (30 ml) at 0°C. The red mixture was stirred at room temperature for 18 h and the solvent volume then reduced by half in vacuo, and 9 M aqueous HCl (20 ml) was added. The solids were filtered off and washed with 9 M aqueous HCl until the washings were colourless. The red solid was then washed with cold diethyl ether (3 × 5 ml) and dried in vacuo. Recrystallization from hot toluene gave red crystals of the desired product in 24% yield.

4.5. Ethylene polymerization reactions

The procedure outlined in [3] was used, with the following modifications Ethyl aluminium sesquichloride ($Et_2AlCl \cdot EtAlCl_2$) was used as co-catalyst in place of aluminoxane and was injected into the autoclave immediately after the introduction of catalyst solution into the reactor. Typical reaction conditions were: $T_{pol} = 50°C$, $p_E = 10$ bar, $[Ti] = 6.25 \times 10^{-5}$ M, $[Al] = 1.21 \times 10^{-2}$ M, Al/Ti = 194, $t_{pol} = 45$ min.

Acknowledgements

We thank AECI, the FRD and the University for financial support, and Mr A. Cameron (AECI) for helpful discussions.

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