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Transition metal complexes of triphosphorus macrocycles: A new class of homogeneous olefin polymerisation catalysts

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Some early transition metal (Ti, V, Cr) complexes of the triphosphorus macrocycle 1,5,9-triethyl-1,5,9-triphosphacyclododecane, [12]aneP_3Et_3, and related derivatives [12]aneP_3R_3 (R = Ph, C_3H_6OMe) have been examined for their reactivity towards ethene and propene. All complexes of the type [12]ane$P_3Et_3MCl_3$ display moderate catalytic activity in the homogeneous polymerisation of ethene when combined with an alkyl aluminium co-catalyst to give very high molecular weight polymers. Preliminary activation of chromium complexes with alkylating agents was also studied but these were inactive in the absence of a co-catalyst. Substitution of the P-borne alkyl group with a pendant ether function was found to switch the catalytic activity of chromium(III) complexes from polymerisation to oligomerisation. A nickel halide complex of [12]aneP_3Et_3 was also found to be active in alkene polymerisation.

Introduction

During the last two decades there have been tremendous advances in the field of catalyst design for alkene polymerisation.[1] Since Ziegler and Natta's discovery that titanium complexes polymerise ethene[2] and propene[3] in the presence of an alkyl aluminium initiator, and the subsequent expansion of this to the metallocene type catalysts,[1a] there has been a drive towards more controlled polymerisation. The result being that *ansa*-metallocenes[1b] and "constrained geometry" catalysts[1c] can now polymerise propene in a stereoregular fashion and display high enough activity to be commercially viable. In addition to the common metallocenes (mainly Group 4 and 5), there is a class of heterogeneous catalysts based on chromium; the Phillips[4] and Union Carbide[5] systems. These are notable in so far as they do not require a co-catalyst, and approximately one third of commercial poly(ethene) is made *via* the Phillips method. However, unlike the metallocenes, both the chromium-based catalysts are heterogeneous and therefore much less is known about the mechanism of these reactions and the nature of the active species is still uncertain. Theopold and co-workers[1d] have investigated model systems that are homogeneous and Gibson *et al.* have reported a highly active system based on a bis(imido)Cr(IV) alkyl cation.[6] There are still however, only a handful of well defined homogeneous catalysts based on chromium. The last few years have seen a dramatic increase in the logical design of catalyst systems that do not contain a cyclopentadienyl ligand,[1c] which also show some of the highest activities reported for metals other than titanium or zirconium. This strategy of catalyst design has recently been extended to iron[7] (which had previously shown no polymerisation potential) and aluminium.[8]

We have previously described the synthesis of the first symmetrical triphosphorus macrocyclic ligand in its uncomplexed state.[9] This can be compared to cyclopentadienyl ligands in that it is a six electron tridentate donor, albeit neutral. These properties should influence the properties of its complexes (*e.g.* low oxidation states should be accessible), and the ligand will be facially capping in an octahedral environment, forcing the remaining coordination sites to be mutually *cis*. In addition, the macrocyclic coordination effect should help limit phosphine dissociation, which is prevalent for related acyclic and tripodal phosphine complexes, especially of relatively electropositive metals. Of particular interest is the potential for stabilisation of relatively robust reaction intermediates, by exploiting the advantages arising from the macrocyclic ligand structure, which may support or enhance reactivity for which tertiary phosphine complexes are not commonly noted. With this in mind, we have investigated the coordination chemistry of the title ligand ([12]aneP_3R_3) with the early transition metals.[10] In this paper, we report the catalytic activity of these compounds with respect to the polymerisation of ethene and α-alkenes. To the best of our knowledge these are the first compounds of the early transition metals that contain only phosphine ligands and halides that polymerise (as opposed to oligomerise) ethene. The few complexes that have been reported contain π-bonded ligands in addition to the phosphine.[1d]

Results and discussion

Addition of a co-catalyst to a solution of [12]ane$P_3Et_3MCl_3$ (M = Ti, V, Cr) gives rise to low to moderately active polymerisation catalysts. The relevant polymerisation data is shown in Tables 1 and 2.

Titanium

The addition of MAO (methylaluminoxane) to a solution of [12]ane$P_3Et_3TiCl_3$ (**1**) in CH_2Cl_2 gives rise to a colour change from pale blue to light yellow. On addition of monomer, the system shows some catalytic activity. The reaction of [12]ane$P_3Et_3TiCl_3$ (**1**) with excess Et_3Al gives rise to yellow, diamagnetic solutions (δ $^{31}P\{^1H\} = -1.29$ ppm). The reaction of this material with 1-hexene (in $CDCl_3$) was followed by NMR spectroscopy (^{31}P, ^1H, ^{13}C). After 1 hour the NMR spectrum still shows the presence of monomer and there is a small broad peak at $\delta = -26.6$ ppm in the $^{31}P\{^1H\}$ NMR spectrum (presumably the metal complex with a growing alkyl chain). After approx. 2 hours the yellow solution turns deep red in colour, the peak at $\delta = -26.6$ ppm disappears from the ^{31}P NMR spectrum and no monomer is seen in the ^1H NMR spectrum. The GC-MS results of the 1-hexene reaction (run 12) show a large number of branched alkanes (C_9 and C_{12} predominate) which implies that more than one mechanism is

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Table 1 Polymerisation data for early transition metal complexes

Run	Catalyst[a](mmol)	Monomer	Solvent[b]	Pressure/bar	Initiator[c]	Yield/g	Activity/ gP mmol^{-1} h^{-1}	Activity[d]/ gP mmol^{-1} h^{-1} bar^{-1}
1	LTiCl$_3$ (**1**) (0.025)	Ethene	CH$_2$Cl$_2$	3	MAO (88 : 1)	0.707	32.57	10.85
2	LTiCl$_3$ (**1**) (0.076)	Ethene	CH$_2$Cl$_2$	6	Et$_3$Al (78 : 1)	0.423	5.56	1.85
3	LVCl$_3$ (**2**) (0.100)	Ethene	CH$_2$Cl$_2$	3	MAO (30 : 1)	5.421	53.90	17.97
4	LCrCl$_3$ (**3**) (0.086)	Ethene	CH$_2$Cl$_2$	3	MAO (92 : 1)	1.80	20.91	6.97
5	LCrCl$_3$ (**3**) (0.129)	Ethene	CH$_2$Cl$_2$	3	Et$_3$Al (12 : 1)	5.50	42.60	14.20
6	L^{1}CrCl$_3$ (**5**) (0.821)	Ethene	CH$_2$Cl$_2$	3	MAO (96 : 1)	1.081	13.17	4.39
7	LCrCl$_3$ (**3**) (0.034)	Ethene	PhMe	10	Et$_3$Al (116 : 1)	0.280	8.13	0.81
8	LCrR$_3$[e] (0.179)	Ethene	PhMe	3	MAO (20 : 1)	0.84	6.51	2.16
9	LTiCl$_3$ (**1**) (0.076)	Propene	CH$_2$Cl$_2$	3	MAO (40 : 1)	None	—	—
10	LVCl$_3$ (**2**) (0.251)	Propene	CH$_2$Cl$_2$	3	MAO (18 : 1)	None	—	—
11	LCrCl$_3$ (**3**) (0.086)	Propene	CH$_2$Cl$_2$	3	Et$_3$Al (19 : 1)	0.30	3.48	1.16
12	LTiCl$_3$ (**1**) (0.076)	1-Hexene	CH$_2$Cl$_2$	—	Et$_3$Al (61 : 1)	None	—	—
13	LCrCl$_3$ (**3**) (0.116)	1-Hexene	CH$_2$Cl$_2$	—	MAO (25 : 1)	0.845	7.27	—
14	LCrCl$_3$ (**3**) (0.099)	Norbornene	CH$_2$Cl$_2$	—	MAO (29 : 1)	0.271	2.74	—
15	L^{2}CrCl$_3$ (**4**) (0.038)	Ethene	CH$_2$Cl$_2$	3	Et$_3$Al (10 : 1)	0.021	—	–
16	L (0.015)	Ethene	CH$_2$Cl$_2$	3	Et$_3$Al (2 : 1)	None	—	—
17	[LNiBr]Br (**6**) (0.17)	Ethene	CH$_2$Cl$_2$	3	MAO (300 : 1)	0.765	8.85	2.95

[a] L = [12]aneP$_3$Et$_3$; L^1 = [12]aneP$_3$Ph$_3$; L^2 = [12]aneP$_3$C$_3$H$_6$OMe. [b] All reactions carried out in 50 cm^3 solvent at 25 °C except run 7 (temp. = 70 °C) [c] Expressed as the ratio Al : Cr. [d] For comparison with other reported systems see ref. 1*e*. [e] The formula designation refers to prior activation of **3** with alkylating agents rather than an established stoichiometry, R = CH$_2$SiMe$_3$.

Table 2 Properties of soluble polymers

Run	M_w	M_n	PDI (M_w/M_n)
3	1025000	32200	32
4	552000	2190	252
5	10400	1615	6.4
6	160500	520	310
8	187500	2730	68.7

involved, and therefore chain transfer to aluminium cannot be ruled out.[11] After work-up of the catalyst solution only a small amount (<0.1 g) of solid polymer is seen. The complex [12]aneP$_3$Et$_3$TiCl$_3$ also reacts with ethene (run 1). The polymer was isolated by removal of the solvent *in vacuo* but characterisation of the white, waxy solid was hampered by its insolubility (insoluble in tetrachlorobenzene at 200 °C), which implies that the polymer is cross-linked, highly branched or, in comparison to the other systems studied, of exceedingly high molecular weight.

In order to address possible macrocycle ligand transfer from Ti to Al, treatment of triethyl aluminium with one equivalent of macrocycle was found to yield an air sensitive oil that is soluble halocarbons and hydrocarbons. Comparison of NMR data suggest that this species (^{31}P{^{1}H} $\delta = -23.7$ ppm) is not formed in the Ti based catalysis. This aluminium macrocycle species was also inactive as a polymerisation catalyst under comparable conditions (run 16). Discrete Ti or Al complexes could not be isolated from these reaction mixtures and the nature of the diamagnetic species remains unclear.

Few titanium phosphine complexes in the +III (or lower) oxidation state have been reported which react with ethene catalytically and none that react with propene. Of the systems reported, (butadiene)$_2$Ti(dmpe)[12] and Cp$_2$Ti(PMe$_3$)$_2$[13] di- and tri-merise ethene; (butadiene)$_2$Ti(dppe)[5] is reported to have an activity of 0.040 gPE mmol^{-1} h^{-1} and there is a report of [(Me)$_2$Ti(dmpe)$_2$][14] polymerising ethene at 25°C and 4 atm, but no information on yields and activities was given (dmpe = 1,2-bis(dimethylphosphino)ethane; dppe = 1,2-bis(diphenylphosphino)ethane). The macrocycle complex **1** gives much higher activities than for any of these previously reported systems.

Vanadium

Addition of MAO to a solution of [12]aneP$_3$Et$_3$VCl$_3$ (**2**) in CH$_2$Cl$_2$ results in a colour change from dark green to red–brown. Addition of alkylating agents (RLi, R = CH$_2$SiMe$_3$, Me) to **2** also results in a similar colour change although vanadium alkyl complexes could not be isolated from these solutions; by comparison this red colour indicates the formation of V–C bonds in the reaction with MAO. This system is the most active of the complexes reported here, although less so than other non-Cp$^-$ containing catalysts reported recently.[15] It is interesting that the vanadium species is more active than titanium, whereas for the metallocenes the Group 4 metals display much higher activity. In a recent theoretical study of early transition metals bearing nitrogen ligands it was found that metal systems with a d^3 configuration showed the most catalytic potential; the alkene binding energy decreases with increasing d electron count. This indicates that, for nitrogen ligands, that chromium(III) should have higher activity than vanadium(III).[16] A recent investigation using (triazacyclohexane)CrCl$_3$ does show very high activities.[17]

The polymer produced from the vanadium catalyst is a high molecular weight polyethene (M_w *ca.* 1 million) but the molecular weight distribution appears to be bimodal. The high polydispersity indicates that there is more than one catalytic site or that there are also chain transfer reactions. The polymer includes material that corresponds to molecular weights of greater than 10 million, but this is probably cross-linked as opposed to linear polyethene. Since the polymer is not soluble in $C_6H_2Cl_4$ even at 120 °C, ^{13}C NMR spectroscopy could not be used to determine the degree of branching.

The reaction with propene gives no polymer on workup of the solutions. GC-MS analysis indicates that no oligomers are formed either.

Chromium

Addition of MAO or Et_3Al to a solution of [12]ane$P_3Et_3CrCl_3$ (**3**) in CH_2Cl_2 results in a colour change from deep blue to dark red. Attempts to isolate the product from the alkyl aluminium reaction yields a red, toluene soluble oil that slowly decomposes at −30 °C for R = Me, for R = Et a red oil that is thermally stable to 20 °C can be obtained. It has been reported that MAO is a much more effective alkylating agent and forms cationic species that may be more stable than when using trimethyl aluminium.[18] These relative thermal stabilities could however account for the fact that the initiation with Et_3Al gives a more active catalyst compared to the MAO initiation (runs 4 and 5, Table 1). The activity decreases in toluene at elevated temperature (run 7), presumably due to decomposition of the active species. On addition of ethene a further colour change is seen and from the resultant brown solution, white polyethene slowly precipitates (run 4). If this reaction mixture is left for a few hours, the rate of ethene uptake is reduced to zero and the solution returns to the original red colour. When more MAO is added, ethene uptake resumes and more polymer precipitates. This process may be repeated many times with no apparent loss of activity. Attempts to identify any complex from this red reaction mixture have been unsuccessful, the product decomposing on workup. It is reasonable to propose that this species contains a chromium centre with at least one alkyl chain. GC-MS analysis of an aliquot of the catalyst solution activated by MAO shows low concentrations of C_{2n+1} alkanes ($3 \leq n \geq 14$) and trace amounts of C_{2n} alkenes ($4 \leq n \geq 14$), as shown in Fig. 1. It is interesting to note that a similar product distribution is not observed for Et_3Al (Fig. 3).

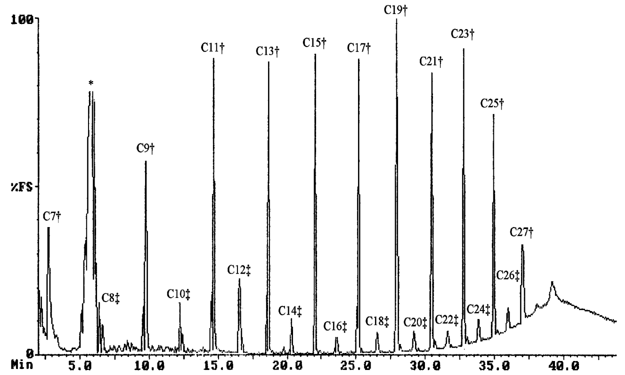

Fig. 1 GC-MS trace from [12]ane$P_3Et_3CrCl_3$ + MAO + C_2H_4 (* denotes toluene solvent; † = alkane; ‡ = alkene).

These hydrocarbons may arise from a mechanism involving chain transfer of the polymer chain to the aluminium centre, followed by hydrolysis to give saturated alkanes, as postulated by Deffieux *et al.* in the polymerisation of 1-hexene by various Group 4 metal catalysts,[11] and supported by the observations of Bazan *et al.* using a Cr(III) complex.[19] The appearance of roughly equal concentrations of the alkanes also implies that the rate of propagation is approximately equal to the rate of termination, and the larger molecular weight polymers are formed over a longer period of time. This could also explain the large polydispersity values seen for some of the polymers.

The ^{13}C NMR data for the soluble polyethenes generated from runs 4 and 5 show that the samples are completely linear, with little evidence of branching; this is in agreement with the presence of straight chain alkanes from the GC-MS data.

In contrast to the chromium complex reported here, the complex *mer*-PPPCrCl_3 (where PPP is the acyclic, linear triphosphine, $^nPrP(C_2H_4PEt_2)_2$) oligomerises ethene to 1-hexene with 96% selectivity.[20] The difference in polymerisation *vs.* oligomerisation behaviour between our facially capping phosphine compared to the meridonally coordinating phosphine may be due to the lack of axial steric protection from the linear phosphine which has been shown to be of importance in regulating the molecular weight of polymers produced from late transition metals.[21] The only other catalytically active chromium phosphine complexes are the pendant phosphine substituted cyclopentadienyl complexes (η^1:η^5-$R_2P(CH_2)_n$-$C_5H_4CrCl_2$, n = 2, 3 and indenyl analogues) studied by Jolly *et al.*[22] and the Cr(III) and Cr(II) complexes, [Cp*Cr(CH_3)(dmpe)][PF_6] and [Cp*Cr(CH_3)(dmpe)],[23] however these dmpe complexes are of low activity and it is believed propagation requires the dissociation of one of the chelating phosphines to form η^1-dmpe containing intermediates.

The polymers produced by the different initiators are markedly different in their physical properties (Fig. 2, Table 2).

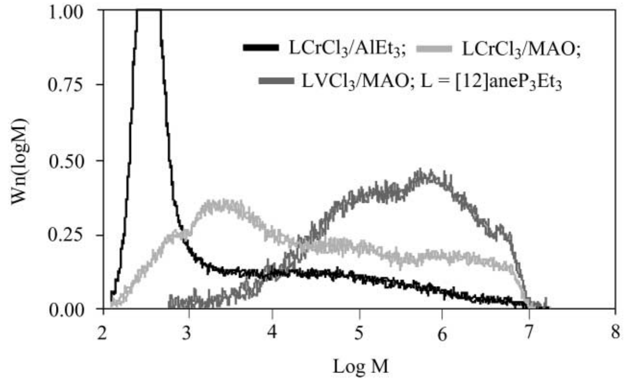

Fig. 2 Comparison of the molecular weight distributions of polymers produced from the Cr catalyst (**3**) with different alkyl aluminium activators and with the V analogue (**2**).

When MAO is used as an initiator (run 4) the resulting polymer appears to be of higher molecular weight (and of higher polydispersity) than the corresponding reaction with Et_3Al (run 5). This polymer (run 5) is formed as a mixture, the predominant component being of relatively low molecular weight (330). This is readily separated and the remaining polymer has a molecular weight of approx. 500 000.

Prior activation of **3** by reaction with three equivalents of $ClMgCH_2SiMe_3$ or $LiCH_2SiMe_3$ gives rise to red solutions (run 8) which do not polymerise alkenes in the absence of an initiator but do exhibit low activity in the presence of MAO. This depressed activity may be due to the more sterically encumbering trimethylsilylmethyl group inhibiting alkyl abstraction or alkene coordination. The molecular weights are also lower in this case but the polydispersity decreases dramatically. These results are in direct contrast to some of the Cr(III) alkyls reported by Theopold (*e.g.* Cp*Cr(CH_2SiMe_3)$_2$) which do not require any co-catalyst.[24] Gibson *et al.* have recently reported the synthesis of a chromium alkyl complex stabilised by salicylaldiminato ligands that is inactive for the polymerisation of ethene whereas the parent halide complex does show some activity.[25] Fryzuk *et al.* recently reported the complex (PNP)Cr(CH_2SiMe_3)$_2$, PNP = N($SiMe_2CH_2PPh_2$)$_2$, but this is not an active ethene polymerisation catalyst.[26] It has also been reported that alkylchromium complexes of the type $RCrCl_2(THF)_3$ (R = Me, Et, ^iBu) polymerise ethene at room temperature, but no details were given.[27]

We have also previously reported the synthesis of a series of pendant donor triphosphorus macrocycles.[28] We have tested the activity of the methoxypropyl pendant ether $[12]aneP_3(C_3H_6OMe)_3$ complex ($[12]aneP_3(C_3H_6OMe)_3CrCl_3$, **4**, Fig. 3) in ethene polymerisation in order to compare possible influences of hemi-labile donors. We have previously confirmed the mononuclear structure of **4** by X-ray crystallography[10] which also confirms the facial coordination of the three phosphorus donors and the absence of any metal–ether interaction. In the reaction of ethane with **4** activated by Et_3Al, no polymer was produced although GC-MS analysis (Fig. 4) showed the presence of even chain oligomers from C_8 to C_{24}, (run 15, Table 1). This dramatic difference in selectivity upon simple modification of the macrocycle substituents may be due to the ability of the pendant ether function to compete with alkene binding which might be expected to suppress propagation, but not necessarily termination.

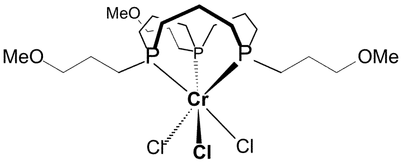

Fig. 3 $[12]aneP_3(C_3H_6OMe)_3CrCl_3$ (**4**).

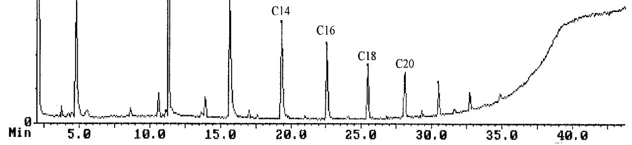

Fig. 4 GC-MS trace from $[12]aneP_3(C_3H_6OMe)_3CrCl_3$ + Et_3Al + C_2H_4 in CH_2Cl_2.

The chromium ethyl-macrocycle complex **3** also polymerises higher α-alkenes and norbornene (runs 11, 13 and 14 in Table 1). The activities are much lower than for the ethene reactions, presumably due to steric effects and the stronger M–C bond of the strained norbornene. No polymerisation or isomerisation of the double bond is observed with higher alkenes (*e.g.* 1-octadecene). Of the macrocycle adducts, the chromium complex is the only one found to polymerise propene, suggesting that the smaller titanium and vanadium may be too sterically encumbered to support a growing chain. The polypropene produced is highly crystalline with $T_g = 102$ °C and $T_m = 206.4$ °C ($\Delta H_f = 188$ J g^{-1}). This implies that the polymer is isotactic but due to the insolubility of the sample, ^{13}C NMR spectroscopy could not be used to probe the polymer microstructure. GPC analysis was also precluded although the insolubility of the polypropene implies a very high molecular weight.

It has been suggested that for metallocene catalysts, electronic effects predominate in the polymerisation of ethene, but for the polymerisation of propene the activities are more dependent on steric factors.[29] The tris(pyrazolyl)borate (Tp) ligand can be described as a six electron ligand similar to Cp, but zirconium Tp complexes are much less active than the corresponding zirconocene complexes under the same conditions (For example, the zirconium complex Cp_2ZrCl_2 has an activity for ethene polymerisation of 1490 kgPE $gcat^{-1}$ h^{-1} whilst the complex $TpZrCpCl_2$ shows a decrease to 76 kgPE $gcat^{-1}$ h^{-1}). The authors ascribe this decrease to the fact that the Tp ligand is larger and a better electron donor so that the metal is electronically “overloaded.”[30] The relative donating properties of Cp and Tp have been discussed recently and, for Group 6 metals, Tp was shown to be a better electron donor than Cp.[31] Comparison of tritertiaryalkyl phosphine macrocycles with the analogous triaryl phosphine, $[12]aneP_3Ph_3$ are of interest in this respect since, in principle, the latter should enable manipulation of the electronic influences of the ligand (as a better π-acceptor) although IR data for the complexes $[12]aneP_3R_3Mo(CO)_3$, (R = Ph, Et) indicate these ligands to have similar electronic properties ($\nu_{(CO)}$ = 1917, 1809 cm^{-1}; R = Ph and 1918, 1815 cm^{-1}; R = Et).[32] The chromium trichloro complex of the phenyl functionalised macrocycle ($[12]aneP_3Ph_3CrCl_3$) has not previously been reported. It is however, readily prepared by addition of the free macrocycle to suspensions of $CrCl_3(THF)_3$ in dichloromethane and is isolated as a blue microcrystalline solid which is readily soluble in chlorinated hydrocarbons, THF and toluene and slightly soluble in aliphatic hydrocarbons and diethyl ether. It is characterised by satisfactory analytical data, magnetic susceptibility and IR spectroscopy. The reaction of $[12]aneP_3Ph_3CrCl_3$ (**5**) with ethene activated by MAO (run 6, Table 1) is lower than that of the alkyl substituted macrocyclic complexes, a difference which may be due to steric factors arising from the bulkier P–Ph groups rather than any potential electronic effects. The molecular weight of the polymer also decreases markedly, again it might be expected that the rate of chain termination may be enhanced by more sterically demanding ligands. The low activities shown by all the macrocycle complexes described may be due to the macrocycle being generally more electron donating than Tp or Cp ligands.

Late transition metals

There is current interest in polymerisation and co-polymerisation reactions using late transition metals (*e.g.* Keim’s catalyst used for oligomerisation in the SHOP process[33]), especially based on diimine complexes of nickel and palladium.[34] Calculations suggest that steric protection in the axial position is essential for producing high molecular weight polymers as opposed to oligomers.[35] The synthesis and structure of cationic Ni(II) complexes of $[12]aneP_3Et_3$, $\{[12]aneP_3Et_3NiBr\}Br$ (**6**) and $[[12]aneP_3Et_3Ni(NCMe)_2][PF_6]_2$ (**7**) and the Ni(O) carbonyl, $[12]aneP_3Et_3Ni(CO)$ (**8**) have recently been reported.[36] The structure of **6** was shown to be heavily distorted from tetrahedral in a manner which could facilitate interaction with small substrate molecules.

The cationic nickel complex **6** polymerises ethene (run 17, Table 1) although the activities are lower than those reported in the literature for other systems;[1,37] the polymer produced is highly insoluble and thus presumably of very high molecular weight. Compound **6** is a very rare example of a Ni compound containing tertiary phosphine ligands that is active for ethene polymerisation;[38] the majority are based on diimmine ligands with bulky aryl substituents on the nitrogen or N–O, P–O chelating ligands. Indeed some catalysts, *e.g.* Keim’s P–O chelate ligand, are enhanced by the addition of phosphine scavenging ligands. The only other catalyst based on a macrocyclic ligand is $9[ane]S_3PtX_4$ which also shows relatively low activities (12 gP $mmol^{-1}$ h^{-1} bar^{-1}).[21] The co-polymerisation of ethene and CO has also been investigated with the Ni(II) and Ni(O) compounds **7** and **8**; under standard conditions reported in the literature (40 bar ethene, 5 bar CO and 50 °C) in dichloromethane or acetonitrile, **6** and **7** are inactive in ethane/CO co-polymerisation as well as alkene polymerisation. Insertions into $Ni–C_{(alkyl/aryl)}$ bonds, especially by CO, are quite common,[39] but insertion into Ni–CO bonds is less common and this presumably disfavours the initiation step. Additionally, since **7** is a compound of d^{10} Ni(O), it may be relatively resistant to coordinating additional ligands. In general, most ethene/CO co-polymerisation catalysts are cationic palladium complexes which contain bidentate phosphines and weakly coordinating anions;[40] there are relatively few nickel based co-polymerisation catalysts known,[41] in part due to the facile formation of $Ni(CO)_4$. Similar reactions were attempted with compound **3** although no activity was observed.

Conclusion

Electropositive transition metal complexes of macrocyclic triphosphines show activity in the polymerisation of alkenes when combined with an appropriate initiator. The pendant function on the macrocyclic ligand significantly influences the reactivity of the catalyst and the properties of the polymer product. The stability and activity of these systems is substantially greater than for related acyclic phosphine ligand complexes and is presumably due to the macrocyclic coordination effect. Polymerisation activity is also extended to nickel compounds which constitute a new class of homogeneous alkene polymerisation catalysts.

Experimental

All reactions were carried out under nitrogen (purified by passing over a CrO column) using standard Schlenk line techniques or in a vacuum atmospheres inert atmosphere box. The compounds $[12]aneP_3Et_3TiCl_3$, $[12]aneP_3Et_3VCl_3$, $[12]aneP_3R_3CrCl_3$, (R = Et, $(CH_2)_3OMe$),[10] $[12]aneP_3Ph_3$,[32] ($[12]aneP_3Et_3NiBr$)(Br), $[12]aneP_3Et_3Ni(CO)$, ($[12]aneP_3Et_3Ni(NCMe)_3$)(PF_6)[38] and $(C_6F_5Cu)_2$·dioxane[42] were prepared by literature procedures. Solvents were dried with standard drying agents and distilled immediately before use. Petroleum ether had bp 40–60 °C. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX400 spectrometer operating at 400.13 MHz and 100 MHz, respectively. ^{31}P NMR spectra were acquired using a JEOL FX90Q at 36.2 MHz and referenced to 85% H_3PO_4. MAO was used as a 10 wt% solution in toluene. 1-Hexene was dried over sodium–benzophenone, distilled and stored over molecular sieves. Ethene and propene polymerisation reactions were carried out in a 250 cm^3 stainless steel autoclave or in a glass pressure vessel (100 cm^3). GC-MS analyses were carried out on a HP 5890 GC and VGTRIO-1 mass spectrometer using a BPX-5 column.

Synthesis of $[12]aneP_3Ph_3CrCl_3$ (4)

To a suspension of $CrCl_3(THF)_3$ (0.04 g, 0.107 mmol) in dichloromethane (10 cm^3), was added a solution of $[12]aneP_3Ph_3$ (4.5 cm^3, 0.0244 M in hexanes, 0.109 mmol). The suspension was stirred (12 h) during which time the suspension dissolved and the solution became deep blue. The resulting solution was filtered, evaporated to dryness *in vacuo* and the solid residue was triturated with hexanes (3 × 10 cm^3) to give a pale blue powder. The blue solid was extracted into warm (30 °C) dichloromethane (30 cm^3) giving a green precipitate and a deep blue solution which was filtered. The blue solution was concentrated (10 cm^3) and cooled (−30 °C, 12 h) yielding a blue microcrystalline solid which was filtered, washed with hexane (10 cm^3) and dried *in vacuo*. Yield: 0.02 g, 0.033 mmol, 31% based upon $CrCl_3(THF)_3$. Analysis found (calc.): %C, 53.8 (53.25); %H, 5.8 (5.42). IR/cm^{-1} (Nujol): 2922, 1463, 1377, 1302, 1157, 1091, 1021, 966, 820, 722, 482, 309. $\mu_{eff} = 3.62\ \mu_B$ (Evans method).

Reactions with ethene and propene

In a typical reaction $[12]aneP_3Et_3CrCl_3$ (0.040 g, 0.086 mmol) was dissolved in CH_2Cl_2 (50 cm^3) and MAO (2 cm^3 of a 10 wt% solution in toluene, 92 : 1 Al : Cr) added. This was stirred for 15 minutes and transferred to an autoclave *via* cannula. The autoclave was evacuated, backfilled with ethene to a pressure of 3 bar and stirred for 1 hour. The reaction was deactivated by the addition of methanol (50 cm^3), the solid isolated by filtration and an aliquot of the solution was analysed by GC-MS spectroscopy. The white polymer was then washed with a 5% HCl solution in MeOH (200 cm^3), filtered and dried *in vacuo* (12 h at 0.1 mmHg). The reaction with the titanium catalyst gave no solid precipitate; removal of the solvent *in vacuo* and washing as above enabled recovery of the polymer. In the case of propene reactions, again the product polymer did not precipitate from the reaction mixtures which were worked up by evaporation *in vacuo* followed by washing as above.

Reactions with 1-hexene and norbornene

To a solution of the catalyst in an appropriate solvent was added the alkyl aluminium initiator and the solution stirred for 15 min. The monomer was then added in one portion and stirred for 1 h. The solvent was removed *in vacuo* to give a solid that was washed with a HCl/MeOH solution as above, filtered and dried *in vacuo* (12 h at 0.1 mmHg).

Preliminary activation of catalysts by alkylation

The following method is typical and was employed for the reactions of $[12]aneP_3Et_3MCl_3$ with lithium alkyls (RLi where for M = Ti, V, Cr; R = Bz, Ph, CH_2CMe_3, $CH_2C(Me)_2Ph$, CH_2SiMe_3, $CH(SiMe_3)_2$; M = Cr, R = ^nBu). To a cold (−78 °C) suspension of $[12]aneP_3Et_3CrCl_3$ (0.60 g, 1.29 mmol) in THF (10 cm^3) was added $LiCH_2SiMe_3$ (3.90 cm^3 of a 1.0 M solution in petrol, 3.9 mmol) and this was allowed to warm to room temperature over 2 h. After stirring at room temperature for 3 h the solvent was removed *in vacuo* and the red residue extracted with toluene (3 × 20 cm^3). The solvent was removed *in vacuo* to yield a red oil which was dissolved in petroleum ether (5 cm^3) and cooled to −35 °C. A red oil (0.48 g) was obtained after 3 h which was isolated by filtration at −40 °C and dried *in vacuo*. $\mu_{eff} = 3.58\ \mu_B$ (Evans method). A $AgNO_3$ halide test showed this material to be halide free, hydrolysis with D_2O gave only Me_3SiCH_2D and for R = ^nBu, there was no evidence of Cr–H bonds in the IR spectrum.

Reactions with ethene and CO

In a typical experiment $[12]aneP_3Et_3CrCl_3$ (0.053 g, 0.11 mmol) was dissolved in CH_2Cl_2 (50 cm^3) and MAO (2 cm^3 of a 10 wt% solution in toluene, 92 : 1; Al : Cr) added. After stirring for 15 minutes this was transferred to an autoclave, evacuated and backfilled first with CO (3 bar) and then C_2H_4 to a total pressure of 6 bar. This was sealed and stirred for 1 h. The excess gas was vented and MeOH (50 cm^3) added. A sample of the reaction mixture was analysed by GC-MS and the remaining solvent removed *in vacuo*.

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