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Carbon-bridged diphosphine ligands for chromium-catalysed ethylene tetramerisation and trimerisation reactions

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Abstract

The use of carbon-bridged diphosphine ligands in chromium-catalysed ethylene tri- and tetramerisation reactions has been investigated. Two- and three-carbon spacer ligands all showed activity for selective oligomerisation, with a structure–selectivity correlation between P–Cr–P bite angle and 1-octene:1-hexene ratio evident. Activated chromium complexes of single carbon spacer diphosphines were also shown to be effective tetramerisation catalysts, provided that the ligand is innocent under the conditions of catalyst activation. A catalyst with the bis(diphenylphosphino)benzene ligand was found to be exceptionally active, although the combined 1-hexene and 1-octene selectivity was lower than with the best diphosphinoamine (PNP) ligands. The yield losses to by-products can to an extent be minimised by the use of high reaction temperatures and pressures. Unlike with the PNP-based systems, attempts to activate the Cr/bis(diphenylphosphino)benzene catalyst in situ from a chromium salt and free ligand resulted in low activity and high polymer formation. The effect of different phosphine substitution on catalyst selectivity was explored. Steric constraints around the catalytic centre (*ortho*-alkylphenyl phosphines) resulted in a shift towards 1-hexene formation, as with PNP catalysts. Additionally, the basicity of the phosphines appears to influence catalyst selectivity, with alkyl phosphines favouring trimerisation. An interplay between phosphine basicity and bridge structure is in evidence, however, as a catalyst containing a ligand with both basic phosphine atoms and a small bite angle was shown to be selective towards 1-octene.

Keywords: Chromium; Phosphine ligands; Ethylene trimerisation; Ethylene tetramerisation; Homogeneous catalysis

1. Introduction

Traditional linear alpha olefin (LAO) production processes typically produce a broad and relatively inflexible distribution of LAO homologues [1]. Selective processes for the production of 1-hexene and 1-octene will enable industry to meet incremental demand growth for these valuable homologues without co-producing other low-value olefinic products. To this end, numerous catalysts for ethylene trimerisation to 1-hexene have been reported, and a process is now practiced commercially [2]. Recently, the first catalysts for the selective tetramerisation of ethylene to 1-octene were reported [3]. The active catalyst is typically generated by a combination of a chromium salt and a diphosphinoamine ligand ($Ar_2PN(R)PAr_2$) in the presence of an aluminoxane activator. Mechanistic studies [4] on these catalyst systems indicate that the 1-octene is liberated from a metallacyclononane catalytic intermediate, formed by an extension of the metallacyclic mechanism previously proven for ethylene trimerisation reactions [5]. The exact nature of the active catalyst species is still not clear, although there is evidence for a Cr(I)–Cr(III) redox couple [6].

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The uniqueness of the PNP–Cr system in its ability to selectively produce 1-octene (unlike numerous other catalysts for 1-hexene) has led to considerable interest in the features of the ligand which confer the unusual selectivity. Several studies have examined the influence of the ligand's aryl (Ar) substituents on catalyst selectivity; in particular on the selectivity split between 1-hexene and 1-octene [7]. In general, substitution at the *ortho*-position by coordinating groups (e.g.–OMe) or sterically demanding groups (e.g. –Et) causes a switch in selectivity from 1-octene to 1-hexene. Variations of the PNP N-substituent have also been explored: increasing the steric bulk of alkyl or aryl groups enhances the overall selectivity to total alpha olefins (1-hexene plus 1-octene), while lowering the 1-octene:1-hexene ratio [8]. It has also been reported that potentially coordinating ether groups on the PNP nitrogen substituent may increase overall productivity by enhancing catalyst stability [9].

The relationship between structure and selectivity is thus well studied for diphosphinoamine (PNP) ligands. Relatively little, by contrast, has been reported on the application of diphosphine ligands with different spacers in tetramerisation reactions, although it is known that hydrazyl-bridged diphosphines (PNNP) and even a classical carbon-bridged ligand such as bis(diphenylphosphino)ethane can be used to obtain an active tetramerisation catalyst [3]. With the aim of further elucidating the role of ligand structure in these novel catalytic reactions, we now report a detailed study on the use of carbon-bridged diphosphine ligands in ethylene trimerisation and tetramerisation reactions.

2. Experimental

2.1. General

All solvents were purified by percolation under N_2 through activated alumina. MMAO-3A (modified methylaluminoxane) was purchased from Akzo-Nobel.

2.2. Catalyst testing procedure

A 300 ml autoclave was charged with methylcyclohexane (95 ml) and MMAO-3A (volume calculated for correct Al:Cr) and heated to just below the desired reaction temperature. The procatalyst (suspension or solution in methylcyclohexane, 5 ml) was added to the autoclave, which was pressurised with ethylene (50 bar) and stirred with a gas-entraining stirrer at 1000 rpm. Ethylene was fed on demand to maintain the reactor pressure, and the uptake was monitored with a flow meter. The temperature was maintained at reaction temperature with an internal cooling coil and external cooling. The reaction was stopped by addition of ethanol (2 ml) after either 30 min or 110 g ethylene uptake. The reactor was cooled to 0 °C and slowly depressurised. A weighed aliquot of nonane was added as an internal standard, and the liquid products were analysed using GC-FID. The polymeric products were recovered by filtration and overnight drying in an oven at 100 °C.

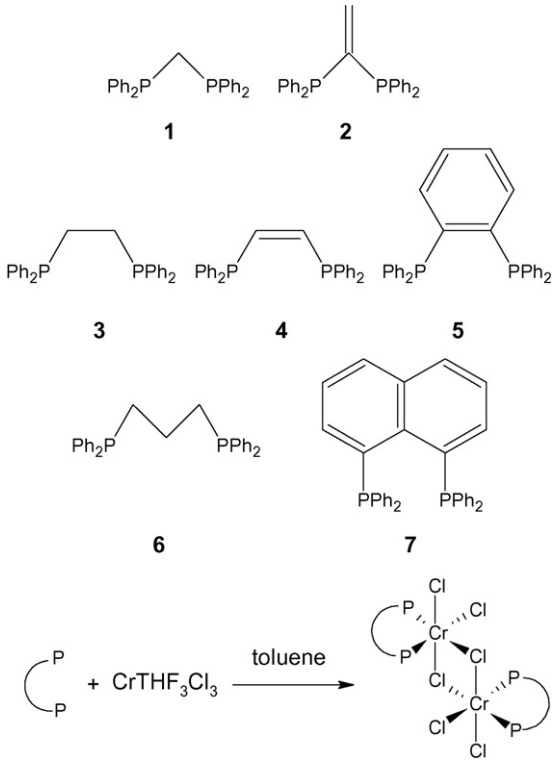

Fig. 1. Carbon-bridged diphosphine ligands, complexed with Cr and evaluated in selective ethylene oligomerisation reactions.

2.3. Ligand synthesis

Ligands **1**–**6** and **12** (see Figs. 1 and 3) were obtained from commercial sources. Ligands **7** [10], **8** [11] and **11** [12] were prepared by literature methods.

*1,2-Bis(di[2-ethylphenyl]phosphino)benzene (**9**).* 1-Bromoethylbenzene (5.0 g, 27 mmol) was added dropwise to a flask containing excess magnesium turnings in THF (40 ml) at 0 °C. A vigorous reaction ensued. After 3 h, the solution was added dropwise to bis(dichlorophosphino)benzene (1.7 g, 6.1 mmol) in THF (30 ml) at 0 °C. The mixture was warmed to room temperature and stirred overnight. After filtration through celite, the solvent was removed *in vacuo* and the crude product was recrystallised from dichloromethane/ethanol. (2.2 g, 65%); δ_H ($CDCl_3$, 400 MHz): 0.99 (12H, t, $J = 7.2$ Hz, $-ArCH_2CH_3$), 2.50–2.70 (8H, m, $-ArCH_2CH_3$), 6.77–6.80 (4H, m, Ar), 6.99–7.00 (2H, m, Ar), 7.18–7.20 (4H, m, Ar), 7.21–7.24 (10H, m, Ar). $\delta_{C\{H\}}$ ($CDCl_3$, 100 MHz): 14.9 ($-ArCH_2CH_3$), 27.4 ($-ArCH_2CH_3$), 125.7 (Ar), 128.0 (Ar), 128.5 (Ar), 128.9 (Ar), 134.1 (Ar), 134.3 (Ar), 135.7 (Ar), 143.8 (Ar), 148.6 (Ar). $\delta_{P\{H\}}$ ($CDCl_3$, 162 MHz) −30.3 ppm (s).

*1,2-Bis(diisopropylphosphino)benzene (**10**).* 2-Bromopropane (3.0 g, 24 mmol) was added dropwise to a flask containing excess magnesium turnings in THF (40 ml) at 0 °C. A vigorous reaction ensued. After 3 h, the solution was added dropwise to bis(dichlorophosphino)benzene (1.5 g, 5.4 mmol) in THF (30 ml) at 0 °C. The mixture was warmed to room temperature and stirred overnight. After filtration through celite, the solvent was removed *in vacuo* and the crude product was recrystallised from dichloromethane/ethanol. (1.2 g, 72%);

δ_H ($CDCl_3$, 400 MHz): 0.88–0.93 (12H, m, $-CH_2CH_3CH_3$), 1.12–1.18 (12H, m, $-CH_2CH_3CH_3$), 2.09–2.14 (4H, m, $-CH_2CH_3CH_3$), 7.27–7.32 (2H, m, Ar), 7.50–7.52 (2H, m, Ar). $\delta_{C\{H\}}$ ($CDCl_3$, 100 MHz): 19.57 ($-CH_2CH_3CH_3$), 20.3 ($-CH_2CH_3CH_3$), 25.0 ($-CH_2CH_3CH_3$), 127.8 (Ar), 132.5 (Ar), 144.3 (Ar). $\delta_{P\{H\}}$ ($CDCl_3$, 162 MHz) −31.0 ppm (br s).

2.4. Preparation of complexes

$[L_2CrCl_2(\mu\text{-}Cl)]_2$ (L_2 = **1**–**7**) was prepared in quantitative yields according to literature procedure [3]. The complexes were characterised by elemental analysis, or used directly without characterisation. [(**1**)$CrCl_2(\mu\text{-}Cl)]_2$: Found (calculated for $C_{50}H_{44}Cl_6P_4Cr_2$). C, 55.48 (55.32); H, 3.91 (4.00). [(**3**)$CrCl_2(\mu\text{-}Cl)]_2$: Found (calculated for $C_{52}H_{48}Cl_6P_4Cr_2$). C, 56.05 (56.09); H, 4.27 (4.34). [(**4**)$CrCl_2(\mu\text{-}Cl)]_2$: Found (calculated for $C_{52}H_{44}Cl_6P_4Cr_2$). C, 56.15 (56.29); H, 3.85 (4.00). [(**5**)$CrCl_2(\mu\text{-}Cl)]_2$: Found (calculated for $C_{60}H_{48}Cl_6P_4Cr_2$). C, 59.67 (59.58); H, 3.91 (4.00).

$L_2CrCl_3(THF)$ (L_2 = **5**, **8**, **11**, **12**). A mixture of $CrTHF_3Cl_3$ (1.0 g, 2.7 mmol) and ligand (1.1 equiv.) was stirred in THF (30 ml) at room temperature. After stirring overnight, the complex was precipitated by addition of pentane. The filtered blue powders were washed with pentane and dried *in vacuo*. (**5**)$CrCl_3$(THF): Found (calculated for $C_{34}H_{32}Cl_3OP_2Cr$). C, 60.20 (60.33); H, 4.59 (4.76); (**8**)$CrCl_3$(THF): Found (calculated for $C_{17}H_{38}Cl_3OP_2Cr$). C, 42.65 (42.49); H, 8.00 (7.94). (**11**)$CrCl_3$(THF): Found (calculated for $C_{18}H_{40}Cl_3OP_2Cr$). C, 43.52 (43.87); H, 8.45 (8.18). (**12**)$CrCl_3$(THF): Found (calculated for $C_{10}H_{24}Cl_3OP_2Cr$). C, 31.29 (31.56); H, 6.30 (6.36).

Crystals of (**5**)$CrCl_3$(THF) suitable for X-ray structure solution were grown from evaporating THF. Crystal data and structure refinements for (**5**)$CrCl_3$(THF): $C_{34}H_{32}Cl_3CrOP_2$, M_r 676.89, crystal size 0.1 mm × 0.01 mm × 0.01 mm, blue plate, triclinic, space group *P*-1, T = 93(2) K, a = 9.768(3) Å, b = 10.257(3) Å, c = 17.699(4) Å, α = 101.123(6)°, β = 95.817(2)°, γ = 115.983(5)°, V = 1528.9(7) Å^3, Z = 2, D_c = 1.470 Mg/m^3, μ = 0.769 mm^{-1}, reflections measured = 9764, independent reflections (R_{int}) = 5280(0.0162), final $R1$ = 0.0297, $wR2$ [$I > 2\sigma(I)$] = 0.0708. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 212528. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

3. Results and discussion

A range of carbon-bridged bis-diphenylphosphine ligands (Fig. 1) were obtained from commercial sources (**1**–**6**) or prepared via literature methods (**7** [10]) and complexes of the form $[L_2CrCl_2(\mu\text{-}Cl)]_2$ were prepared by reaction of the ligand with $CrTHF_3Cl_3$ [3].

These complexes were activated with MMAO-3A and screened for ethylene oligomerisation using typical tri- or tetramerisation conditions. The results, with a comparison against two diphosphinoamine (PNP) ligands, are shown in Table 1.

All of the complexes with 2- or 3-carbon spacer ligands (**3**–**7**) were successfully activated for selective oligomerisation reactions. Although various parameters are at play here (as exemplified by the unselective catalysis with ligands **1** and **2**), there appears to be some general correlation between P–Cr–P bite angle and the 1-octene:1-hexene ratio. The PNP ligands, which have very small bite angles (ca. 67° [3]) have the highest 1-octene:1-hexene ratios, although clearly this ratio is also strongly influenced by the N-substitution. The 2-carbon spacer ligands (**3**–**5**), which typically coordinate to transition metals with P–M–P bite angles of around 81–83° [13], produce slightly more 1-hexene at the expense of 1-octene, while the 3-carbon spacer ligands with still larger bite angles – typically ca. 91° for complexes of **6** [13] – gave the lowest 1-octene:1-hexene ratios. Ligand **7**, with a large (ca. 90°) bite angle, unusual out-of-plane binding mode and an inflexible backbone [14], produces more 1-hexene than 1-octene. The poor activities obtained using

Table 1
Screening of complexes $[L_2CrCl_2(\mu\text{-}Cl)]_2$ (L_2 = carbon-bridged diphosphine ligands) in chromium-catalysed ethylene oligomerisation reactions

Ligand (L_2)	Activity ($\times 10^3$ g/g Cr/h)	1-Hexene (mass%)[a]	C_6 cyclics (mass%)[a]	1-Octene (mass%)[a]	C_{10}–C_{14} (mass%)[a]	Polymer (mass%)[b]	1-Octene:1-hexene ratio
PNP[c]	1072	6.7	9.5	61.4	8.5	1.7	9.1
PNP[d]	1868	14.1	4.4	69.3	7.7	0.8	4.9
1	21	Schulz–Flory distribution of LAO's (α = 0.55)					
2	<10	Unselective distribution of oligomers					
3	144	15.7	8.7	59.3	6.5	4.9	3.8
4	303	7.3	17.3	46.7	10.8	5.2	6.4
5	2240	13.0	13.5	56.8	7.6	0.9	4.4
6	13	8.6	8.1	30.3	16.2	24.3	3.5
7	70	61.9	2.6	31.4	2.9	4.0	0.51

Conditions: 5–30 μmol Cr (for each reaction, amount of Cr chosen to ensure significant ethylene uptake but controllable exotherm), MMAO-3A activator (Al:Cr = 500:1), 60 °C, 50 bar C_2H_4, methylcyclohexane (100 ml).

[a] Mass% of liquid products (oligomers).

[b] Mass% of total product (oligomers + polymer).

[c] $Ph_2PN(Et)PPh_2$.

[d] $Ph_2PN(^iPr)PPh_2$.

Table 2
Evaluation of [(**5**)$CrCl_2$(μ-Cl)]$_2$/MMAO-3A for selective oligomerisation under different reaction conditions

C_2H_4 pressure (bar)	Temperature (°C)	Activity ($\times10^3$ g/g Cr/h)	1-Hexene (mass%)[a]	C_6 cyclics (mass%)[a]	1-Octene (mass%)[a]	C_{10}–C_{14} (mass%)[a]	Polymer (mass%)[b]	1-Octene:1-hexene ratio
50	60	2240	13.0	13.5	56.8	7.6	0.9	4.4
50	80	5930	27.4	10.7	53.6	5.9	0.3	1.9
70	60	3410	10.2	13.0	57.5	7.8	1.5	5.6
70	80	7200	24.7	10.6	54.8	5.2	0.8	2.2
70	100	4570	38.9	8.0	45.5	4.7	3.2	1.2

Conditions: 1.5 μmol Cr, MMAO-3A activator (Al:Cr = 500:1), methylcyclohexane (100 ml).
[a] Mass% of liquid products (oligomers).
[b] Mass% of total product (oligomers + polymer).

diphosphines with saturated linkers (**3**, **6**) suggest that ligand rigidity and/or electronic effects play an important role in catalyst performance as well.

Very high catalyst activity – among the highest obtained under comparable conditions – was obtained when the chromium complex of bis(diphenylphosphino)benzene (**5**) was evaluated. However, under the catalytic conditions employed, the selectivity is inferior compared to the best PNP ligands in two respects: increased formation of C_6 cyclic products (methylcyclopentane and methylenecyclopentane) and lower 1-octene to 1-hexene ratio. In an effort to improve selectivity through choice of reaction conditions while retaining the benefit of high activity, this system was then selected for further study. The results are shown in Table 2.

The selectivity trends for this catalyst systems are in line with those reported for Cr/PNP catalyst systems [15]. The 1-octene/1-hexene split is strongly influenced by temperature, while the formation of C_6 cyclics is suppressed at higher temperatures. However, even at 100 °C, a substantial amount (8%) of these undesirable cyclic products is still found. Reactions at higher pressures and temperatures resulted in catalyst activity increases. The observed rates under these conditions are amongst the highest ever reported, with a nominal hourly activity of more than 7 million g ethylene/g Cr at 80 °C, 70 bar ethylene. Even at 100 °C, where catalyst deactivation and polymer formation are problematic for many tri- and tetramerisation catalysts, very high rates and relatively low polymer formation were nevertheless obtained.

Cr/PNP tri-/tetramerisation catalyst systems are often prepared in situ by combining a Cr(III) salt such as $Cr(acac)_3$, the free ligand and aluminoxane at the beginning of the catalytic reaction. This approach avoids the process complexity and cost of preparing a procatalyst Cr–ligand complex while still obtaining an active and selective catalyst. Attempts to apply similar in situ complexation with the carbon-bridged diphosphine ligands were however less successful. A typical comparative example of this behaviour is shown in Table 3. While the product selectivities within the liquid products were effectively identical to those obtained with the activated complex, the catalyst activities were dramatically attenuated and the amount of solids (polymers and waxes) greatly increased. These are indications of poor catalyst activation, where part of the incompletely activated chromium acts as a linear chain growth catalyst. The reasons for the poor in situ activation compared with PNP ligands are unknown.

Dimeric complexes of the form [L_2CrCl_2(μ-Cl)]$_2$ are typically highly insoluble in hydrocarbon solvents before activation. A more soluble monomeric procatalyst complex which retains excellent catalytic performance is thus desirable. Reaction of **5** with $CrTHF_3Cl_3$ in THF at room temperature gave the soluble monomer complex (**5**)$CrCl_3$(THF) in high yield. The complex may be dissolved in the catalytic solvent at room temperature without immediate dimerisation, and this procatalyst was then evaluated under catalytic conditions (Table 3). Although the amount of polymer obtained was slightly higher than when the dimer procatalyst was used, the rates and selectivities are comparable.

The molecular structure of (**5**)$CrCl_3$(THF) is shown in Fig. 2. The expected distorted octahedral structure is observed. The P–Cr–P bite angle is 77.8°, substantially larger than the 66.7° bite angle of a Cr–PNP procatalyst complex [3], but smaller than the average for transition metal complexes of this ligand [13]. The Cr–P bond distances are similar to those in the Cr–PNP complex [3].

Table 3
Catalyst performance with different Cr/**5** procatalyst sources

Procatalyst	Efficiency ($\times10^3$ g/g Cr/h)	1-Hexene (mass%)[a]	C_6 cyclics (mass%)[a]	1-Octene (mass%)[a]	C_{10}–C_{14} (mass%)[a]	Polymer (mass%)[b]	1-Octene:1-hexene ratio
[(**5**)$CrCl_2$(μ-Cl)]$_2$	2240	13.0	13.5	56.8	7.6	0.9	4.4
$Cr(acac)_3$/**5**[c]	48	13.4	13.9	57.1	6.4	21.3	4.3
(**5**)$CrCl_3$(THF)	1543	11.3	12.8	53.9	8.7	3.5	4.8

Conditions: MMAO-3A activator (Al:Cr = 500:1), 60 °C, 50 bar C_2H_4, methylcyclohexane (100 ml).
[a] Mass% of liquid products (oligomers).
[b] Mass% of total product (oligomers + polymer).
[c] Non-reacting mixture.

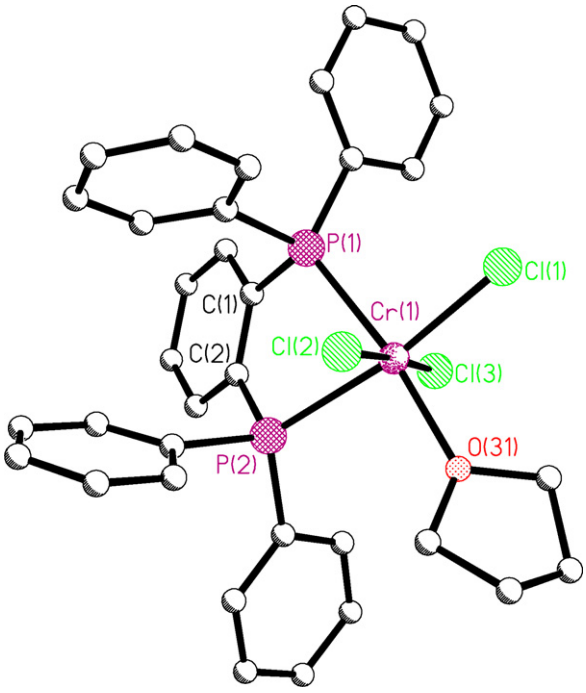

Fig. 2. Molecular structure of (**5**)$CrCl_3$(THF). Selected bond distances and angles: Cr(1)–P(1) 2.4619(7) Å; Cr(1)–P(2) 2.5558(9) Å; P(1)–Cr(1)–P(2) 77.82(2)°.

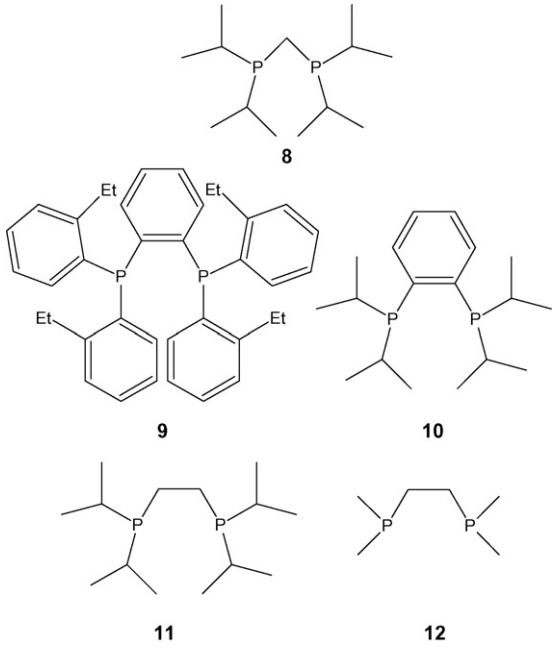

Fig. 3. Carbon-bridged diphosphine ligands with varying phosphine substitution.

The failure to obtain selective oligomerisation catalysts with the 1-carbon spacer ligands **1** and **2** (Table 1) – direct analogues of PNP ligands – was ascribed to non-innocence of the ligands under the reaction conditions. Bis(diphenylphosphino)methane (dppm, **1**) is known to be susceptible to deprotonation at the bridging methylene by metal alkyl Lewis bases [16]. In the hope that decreasing the acidity of the methylene hydrogens would prevent ligand deprotonation, the more basic diphosphine ligand bis(diisopropylphosphino)methane (**8**, Fig. 3) was prepared [11], complexed to chromium and evaluated under catalytic conditions. The successful tetramerisation activity obtained (Table 4) strongly supports our hypothesis of non-innocence of dppm, and demonstrates that single-spacer diphosphines, other than PNP ligands, may indeed be successfully applied in selective oligomerisation reactions. Selectivity comparisons of **8** with the other carbon-bridged ligands have limited value due to the very different steric and electronic environment caused by the isopropyl substituents; however it is noteworthy that the relatively high 1-octene:1-hexene ratio is consistent with the narrow bite angle expected for a single-atom spacer diphosphine ligand (cf. typical bite angles of 72° for dppm) [13].

As with Cr–PNP catalysts [7], modification of the phosphine substituents on carbon-bridged diphosphines can affect the C_6/C_8 selectivity of the catalysts. Making use of the 1,2-phenylene bridge successfully identified in the screening experiments, diphosphines 1,2-bis(R_2P)C_6H_4 (R = 2-ethylphenyl, **9**; R = isopropyl, **10**; Fig. 3) were prepared. Attempts to prepare chromium(III) complexes of **9** were unsuccessful, so the ligands were tested in situ. The results, with comparison against **5**, are shown in Table 4. While the in situ activation method again resulted in poor activities and high polymer formation, it is clear that the change in phosphine substitution causes a swing from tetramerisation (**5**, phenyl substituents) to trimerisation (**9**, 2-ethylphenyl or **10**, isopropyl substituents). The effect of *ortho*-alkylphenyl substitution has already been noted with Cr/PNP catalysts [7b], but the dramatic selectivity

Table 4
The effect of variations in phosphine substitution on catalyst selectivity

Procatalyst	Activity ($\times 10^3$ g/g Cr/h)	1-Hexene (mass%)[a]	C_6 cyclics (mass%)[a]	1-Octene (mass%)[a]	C_{10}–C_{14} (mass%)[a]	Polymer (mass%)[b]	1-Octene:1-hexene ratio
(**8**)$CrCl_3$(THF)	174	14.5	12.0	62.3	7.5	4.7	4.3
Cr(acac)$_3$/**5**	48	13.4	13.9	57.1	6.4	21.3	4.3
Cr(acac)$_3$/**9**	31	59.2	2.5	10.7	13.1	65.6	0.18
Cr(acac)$_3$/**10**	39	82.8	1.8	10.5	12.7	24.0	0.13
[(**3**)$CrCl_2$(μ-Cl)]$_2$	144	15.7	8.7	59.3	6.5	4.9	3.8
(**11**)$CrCl_3$(THF)	11	90.0	0.8	5.8	4.5	2.1	0.06
(**12**)$CrCl_3$(THF)	7	86.2	0.9	9.0	4.3	20.4	0.10

Conditions: 20 μmol Cr, MMAO-3A activator (Al:Cr = 500:1), 60 °C, 50 bar C_2H_4, methylcyclohexane (100 ml).
[a] Mass% of liquid products (oligomers).
[b] Mass% of total product (oligomers + polymer).

change effected by the isopropyl substituents was unexpected. This observation suggests that, apart from steric considerations, electronic factors also play a prominent role in determining the reaction selectivity.

To investigate the interplay between steric and electronic factors for carbon-bridged ligands further, alkyl substituted diphosphines $R_2PCH_2CH_2PR_2$ (R = ^{i}Pr, **11**, R = Me, **12**; Fig. 3) were obtained (**12**) or prepared (**11**) [12]. Cr complexes of these ligands were prepared and tested under catalytic conditions. The results, with comparison against the phenyl-substituted analogue **3**, are shown in Table 4. Given the propensity of even the unhindered methyl-substituted diphosphine **12** for trimerisation, it appears that the basicity of the phosphine plays a distinct role in determining selectivity, with more basic phosphines favouring hexene formation. A complex interplay between bridge structure (bite angle) and phosphine bacisity is evident, however; witness the tetramerisation selectivity with methylene bridged ligand **8** *versus* the trimerisation selectivity with ethyl-bridged **11**.

4. Conclusions

It is clear that a wide array of different structural parameters of diphosphine ligands affect the catalyst activity, selectivity and activation. In addition to steric and coordinative mediation of catalyst selectivity by the phosphine aryl substituents [7], the ligand backbone also influences the selectivity. None of these parameters should be viewed in isolation; however, bite angle, rigidity, phosphine basicity and bridge unsaturation all appear to play a role in the catalyst selectivity.

An extremely active ethylene tetramerisation catalyst using bis(diphenylphosphino)benzene as ligand was identified. While this system displays unprecedented activity, even at high temperatures, the selectivity is inferior to that obtained with the best PNP ligands. The selectivity to valuable products (1-hexene and 1-octene) can be improved to some extent by the use of high temperatures ($\geq$80 °C) and pressures (70 bar). Efforts to develop new, more selective ligands based on the 1,2-bis(phosphino)aryl template are underway.

Variation of phosphine substitution can cause a switch from 1-octene formation toward 1-hexene. Steric mediation of the selectivity by *ortho*-alkylphenyl substituents was expected based on PNP analogies; however the switch to trimerisation caused by increasing phosphine basicity has not previously been observed. Apart from other effects, a complex relationship between bridge structure and phosphine basicity appears to determine the catalyst selectivity.

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