This article is published as part of the *Dalton Transactions* themed issue entitled:

New Talent

Showcasing the strength of research being carried out by tomorrow's leaders in the field of inorganic chemistry

Guest Editor Polly Arnold
University of Edinburgh, UK

Published in issue 2, 2010 of *Dalton Transactions*

Image reproduced with permission of Mark Muldoon

Articles in the issue include:

Visit the *Dalton Transactions* website for more cutting-edge inorganic and organometallic research
www.rsc.org/dalton

Ligand effects in chromium diphosphine catalysed olefin co-trimerisation and diene trimerisation†

Lucy E. Bowen, Manutsavin Charernsuk, Thomas W. Hey, Claire L. McMullin, A. Guy Orpen and Duncan F. Wass*

Received 3rd July 2009, Accepted 21st September 2009
First published as an Advance Article on the web 16th October 2009
DOI: 10.1039/b913302j

A series of symmetric and unsymmetric *N*,*N*-bis(diarylphosphino)amine ('PNP') ligands ($Ar_2PN(R)PNAr'_2$: R = Me, Ar_2 = *o*-anisyl, Ar'_2 = Ph, **1**, R = Me, Ar_2 = *o*-tolyl, Ar'_2 = Ph, **2**, R = Me, Ar_2 = Ph(*o*-ethyl), Ar'_2 = Ph, **3**, R = Me, Ar_2 = Ar'_2 = *o*-anisyl, **4**, R = ^{i}Pr, Ar_2 = Ar'_2 = Ph, **5**) and symmetric *N*,*N*′-bis(diarylphosphino)dimethylhydrazine ('PNNP') ligands ($Ar_2PN(Me)N(Me)PAr_2$: Ar_2 = *o*-tolyl, **6**, Ar_2 = *o*-anisyl, **7**) have been synthesised. Catalytic screening for ethene/styrene co-trimerisation and isoprene trimerisation was performed *via* the *in situ* complexation to $[CrCl_3(THF)_3]$ followed by activation with methylaluminoxane (MAO). PNNP catalytic systems showed a significant increase in activity and selectivity over previously reported PNP systems in isoprene trimerisation. Comparing the symmetric and unsymmetric variants in ethene and styrene co-trimerisation resulted in a switch in selectivity, an unsymmetric catalytic $(o\text{-anisyl})_2PN(Me)PPh_2$ (**1**) ligand system affording unique incorporation of two styrenic monomers into the co-trimer product distribution differing from the familiar two ethene and one styrene ω-substituted alkenes. Complexes of the type $[(diphosphine)Cr(CO)_4]$ **8–11** were also synthesised, the single-crystal X-ray diffraction of which are reported. We propose the mechanisms of these catalytic transformations and an insight into the effect of the ligand series on the chromacyclic catalytic intermediates.

Introduction

In recent years, catalysts have emerged capable of the selective trimerisation of ethene to commercially valuable 1-hexene *via* a distinctive metallocyclic mechanism.[1] In 2002, we reported catalysts based on chromium complexes with ligands of the type $Ar_2PN(Me)PAr_2$ (Ar = *ortho*-methoxy-substituted aryl group) with productivity figures over an order of magnitude better than previous systems.[2] This unprecedented performance led to interest both from a mechanistic viewpoint and in ligand structural modification, the most significant subsequent development being the report from Bollmann and co-workers that relatively minor changes to the ligand structure and reaction conditions can lead to ethene tetramerisation rather than trimerisation.[3] Only limited studies have been conducted into the selective oligomerisation of other olefinic substrates until we recently reported the trimerisation of isoprene and the co-trimerisation of ethene and styrene to primarily linear trimers.[4,5] These two novel chromium PNP systems showed far superior results to previous catalysts in both activity and selectivity, the latter being accounted for by the Briggs' type metallacyclic mechanism by which our catalysts operate.[6] These systems are of potential interest allowing the selective syntheses of isoprenoid products and ω-substituted alkenes from simple substrates. The former species, in particular, are a vast and diverse class of natural products, such as 3,7,11-trimethyl-1,3,6,10-dodecatetraene (α-Farnesene), found in apple coatings, and 7,11-dimethyl-3-methylene-1,6,10-dodecatriene (*trans*-β-Farnesene), an essential oil. Hydrogenated sesquiisoprenoid motifs are also extremely important in nature, the side chain of vitamin E being an excellent example.

We report here a more detailed study of the systems from our preliminary communications, in which a wider range of ligands and reaction conditions have been explored. We also report structural studies of model chromium complexes for these catalysts.

Results and discussion

Ligand synthesis

A library of symmetric and unsymmetric PNP and symmetric PNNP ligands were synthesised (Fig. 1). Ligands **1–3** are novel and ligands **4–7** have been previously reported.[2,3,7,8]

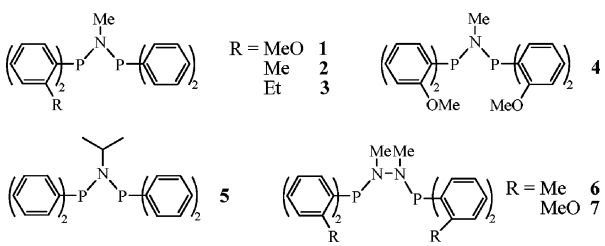


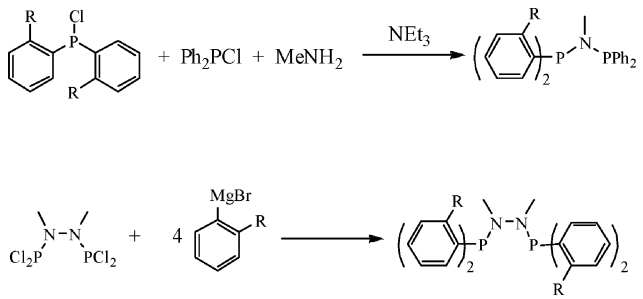
Fig. 1 Diphosphine ligands.

Ligand **4** is a benchmark for ethene trimerisation to 1-hexene and ligand **5** for tetramerisation to 1-octene.[9]

School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK BS8 1TS. E-mail: duncan.wass@bristol.ac.uk

† CCDC reference numbers 739221–739224. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b913302j

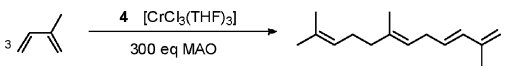
The ligands were synthesised by one of two common methods (Scheme 1). PNNP species were obtained by the reaction of a Grignard reagent with the commercially available $Cl_2PN(Me)N(Me)PCl_2$. Unsymmetric PNP ligands were synthesised *via* the controlled addition of one equivalent of substituted chlorophosphine to methylamine followed *in situ* by the addition of a further equivalent of diphenylchlorophosphine. Intermediate species of the type $Ar_2PN(Me)H$ can be isolated and purified although this is not critical. These unsymmetric ligands gave a characteristic set of doublets in their $^{31}P\{^1H\}$ NMR spectra, typically occurring in the range from 40–70 ppm. PNP ligands (**1**–**3**) were obtained in low to moderate yields (22–36%), in general high yields being sacrificed for high purity. The yields of the PNNP ligands varied in a similar range from 19–52%.



Scheme 1 PNP and PNNP ligand synthesis.

Isoprene trimerisation

We recently reported the selective trimerisation of isoprene to form terpenes (eqn (1)). This was far more productive [826 g (g_{Cr} h)$^{-1}$] than previous nickel based catalysts [6 g (g_{Cr} h)$^{-1}$].[10,11]



(1)

Unfortunately, although excellent selectivity of isoprene trimers could be achieved, the specific products obtained were a mixture of cyclic species (minor product) and linear 2,6,11-trimethyl-substituted-dodecatetraenes; this differs from the natural 2,6,11-trimethyl-substituted-dodecatetraene products in the position of one methyl group. We postulated that the relative stability of tentative allyl catalytic intermediates would favour the head-to-tail, tail-to-tail trimerisation which give rise to the unnatural products, as shown in Fig. 2. With this in mind, we hypothesised that an unsymmetrical ligand may destabilise the more bulky allyl species on one side of the metallacycle, leading to the desired product. We were also keen to explore a wider range of reaction parameters to better understand the optimum conditions for trimerisation.

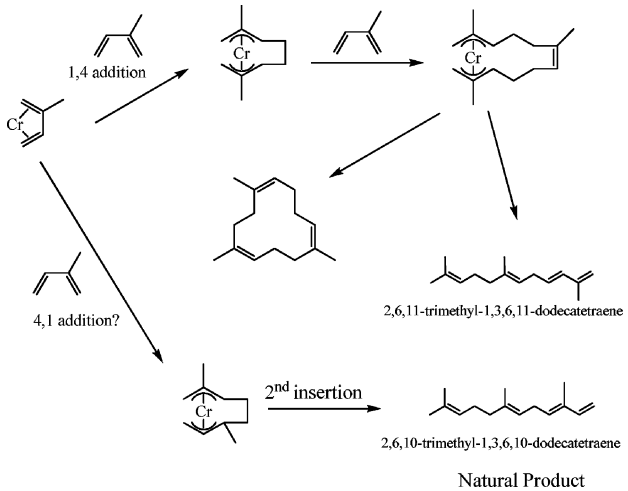


Fig. 2 Postulated trimerisation mechanism.

Optimisation reactions using ligand 4

Ligand **4** was used as a benchmark, the variables of temperature and isoprene concentration being investigated (Table 1).

Generally, as the concentration of isoprene is increased (runs 1–4), the productivity increases and the total percentage of trimer is approximately constant, albeit with a slight increase in

Table 1 Trimerisation of isoprene using ligand **4**

				Product distribution/wt%			
				Trimers			
				Wt% within trimer fraction			
Run	Isoprene/mol dm^{-3}	Temper-ature/°C	Prod.[a]	Total trimer	Linear[b]	Cyclic[b]	Other[e]
1	0.5	70	73	82	32	68	18
2	2.3	70	510	87	61	39	13
3	4.5	70	530	69	77	23	31
4	6.8	70	826	79	70	30	21
5	6.8	57	400	75	75	25	25
6	6.8	45	349	68	88	12	32
7	6.8	25	19	100	73	27	0
8[c]	6.8	70	0	0	—	—	—
9[d]	6.8	70	0	0	—	—	—

Note: we have presented selectivities as wt% within the trimer fraction to facilitate comparison; this is a different format to our preliminary communications (ref. 4 and 5). Conditions unless stated otherwise: 20 μmol ligand, 20 μmol [$CrCl_3(THF)_3$], 300 equivalents of MAO, toluene diluent, 44 mL total volume; temperature controlled by external bath; 1 h run time.[a] Productivity/g (g_{Cr} h)$^{-1}$. [b] Overall selectivity. [c] No [$CrCl_3(THF)_3$] added. [d] No MAO added. [e] Largely (>80%) tetramers.

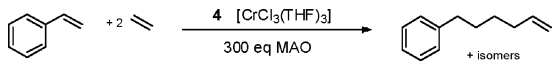
higher oligomers. The ratio of linear to cyclic trimers increases with isoprene concentration. This ratio depends on the rate of reductive elimination of the intermediate illustrated in Fig. 2 to give the cyclic *vs.* linear isomers, suggesting that the incoming substrate may facilitate this elimination in the latter case. It is noteworthy (runs 4–7) that higher temperatures in general are required for good rates in isoprene trimerisation compared to ethene trimerisation; at 25 °C only low activity is observed here whereas ligand **4** is extremely active with ethene even at this temperature. The total trimer fraction decreases at higher temperature at the expense of higher oligomers as does the ratio of linear to cyclic trimers.

Using these optimised conditions (run 4), ligands **1–7**, 1,2-bis(diphenylphosphino)ethane and bis(diphenylphosphino)-methane were tested (Table 2). PNP ligand derivatives demonstrate similar productivity with more bulky ligands in general giving slightly better results (runs 10–14); ligand **4** remains the most active. A more marked increase in productivity is seen when comparing PNP to PNNP ligand systems (runs 15 and 16). The increased bite angle of these ligands (*vide infra*) is an obvious point of difference and is a possible cause for this enhanced performance. Surprisingly, dppe and dppm were inactive for isoprene trimerisation under these conditions (runs 17 and 18). As in ethene tri/tetramerisation, it seems that ligands with nitrogen backbone motifs have a distinctive performance, something we have attributed to the delocalisation of the potential nitrogen lone pair over the entire ligand chelate. Unsymmetric PNP ligands (runs 10–12) showed very high selectivities towards linear trimers compared to the symmetric PNP analogues (runs 13 and 14). However, the best performance we have observed to date is for ligand **7**, a PNNP structure with pendant MeO groups; this combines excellent productivity with outstanding selectivity to trimeric products under these conditions.

Analysis of the trimer products by a combination of NMR spectroscopy and GC compared to standards reveals that in every case the 2,6,11-trimethyl dodecene/ane products are obtained; clearly the propensity for head-to-tail, tail-to-tail trimerisation is not easily overcome by the ligands explored here.

Ethene and styrene co-trimerisation

In 2006, we reported the co-trimerisation of styrene and ethene using chromium PNP catalysts, co-trimers formed from one styrene and two ethene units being formed exclusively (eqn (2)).[5] The isomers obtained were a function of ligand structure, with the linear isomer being favoured by **4** and branched isomers in all other cases. Based on product analysis, a mechanistic scheme was proposed in which 2,1-regiochemistry of styrene insertion is favoured.



(2)

Using the optimised conditions from our initial communication, we explored a broader range of ligands described here (Table 3).

The most active ligand was the previously reported symmetric *o*-methoxy PNP ligand **4** which was also the only ligand to show a major selectivity towards linear trimers (run 22). In other cases, even when two MeO groups are present (ligand **1**, run 19) the branched trimer 3-phenylhexene resulted as observed before; this isomer is consistent with 2,1-insertion of styrene. Somewhat surprisingly, the PNNP systems showed no co-trimerisation activity under these conditions. Of particular interest is the result for the unsymmetrical ligand **1** (run 19); this is the only system we have yet found which allows the incorporation of *two* styrene and *one* ethene units, albeit in low yield. The reason for this change in selectivity is not yet understood, but it is noteworthy that a simple argument for reduced ligand sterics allowing more incorporation of the bulkier styrene substrate cannot hold; the less bulky ligand **5**, and indeed the sterically equivalent **3**, do not show this selectivity.

Synthesis and structural study of model [Cr(CO)$_4$(diphosphine)] complexes

In order to probe the structure of these ligands in greater depth, we synthesised and structurally characterised a selection of complexes of the type [Cr(CO)$_4$(diphosphine)]. We have previously reported that such model systems are useful, in that a combination of structural study and IR spectroscopy can benchmark these ligands against the growing portfolio of related complexes for

Table 2 Isoprene trimerisation with various ligands

			Product distribution (wt%)			
			Trimers			
			Wt% within trimer fraction			
Run	Ligand	Prod./g (g_{Cr} h)$^{-1}$	Total trimer	Linear	Cyclic	Other
10	**1**	585	98	99	1	2
11	**2**	669	86	87	13	14
12	**3**	346	94	86	14	6
13	**4**	826	79	70	30	21
14	**5**	298	95	74	26	5
15	**6**	1483	65	87	13	35
16	**7**	1103	100	87	13	0
17	dppe	0	0	0	0	0
18	dppm	0	0	0	0	0

Conditions unless stated otherwise: 20 μmol ligand, 20 μmol [$CrCl_3(THF)_3$], 300 equivalents of MAO, 6.8 mol dm^{-3} substrate concentration, toluene diluent, 44 mL total volume; 70 °C controlled by external bath; 1 h run time.

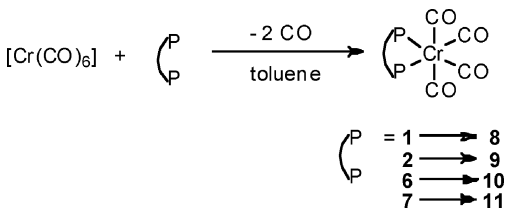
Table 3 Ethene and styrene co-trimerisation

Run	Ligand	Prod./g (g_{Cr} h)$^{-1}$	Product distribution (wt%)		
			2 Ethene + styrene		
			Linear	Branched	Ethene +2 styrene
19	**1**	2617	4	90	6
20	**2**	127	1	99	0
21	**3**	184	1	99	0
22	**4**	7926	85	15	0
23	**5**	3791	5	95	0
24	**6**	0	0	0	0
25	**7**	0	0	0	0
26	dppe	0	0	0	0
27	dppm	0	0	0	0

Conditions unless stated otherwise: 20 μmol ligand, 20 μmol [$CrCl_3(THF)_3$], 300 equivalents of MAO, 1 bar ethene, 6.8 M substrate concentration, toluene diluent, 44 mL total volume; 25 °C controlled by external bath; 1 h run time.

trimerisation-active ligands. A bonus is that such complexes may also be used as catalyst precursors.[12]

The complexes were synthesised in reasonable yields (27–52%) by treatment of the ligand with [$Cr(CO)_6$] in toluene (Scheme 2). IR spectroscopy is unremarkable with CO stretching frequencies in the range of previous derivatives (see Experimental).



Scheme 2 Synthetic route to complexes **4**–**6**.

Crystals containing **8**–**11** were grown from saturated dichloromethane/methanol solutions, and each crystallised in the space group $P2_1/c$. The *ortho*-tolyl substituted diphosphines (**9** and **10**) crystallised as solvates: **9**·0.5MeOH has one methanol molecule per two crystallographically independent molecules of complex, with the solvent having 50% static disorder, whilst **10**·0.75CH_2Cl_2 has 75% occupancy of the dichloromethane.

The structures of the [$Cr(CO)_4${PNP}] complexes **8** and **9** are shown in Fig. 3 and 4 and selected bond lengths and angles given in Table 4. In these complexes the Cr(0) centre is coordinated by four CO ligands and chelated by the bidentate ligands **1** and **2**, which have bite angles of 68.37(2)° and 67.88(4)°/68.03(4)° respectively. The conformations of the *ortho* substituted aryls *o*-C_6H_4R (R = OMe, Me) can be helpfully described by their Cr–P–C_{ipso}–C_{ortho} torsion angles, which are either *gauche* (*ca.* ±50°) or *anti* (*ca.* 180°). In the asymmetric methoxy PNP ligand in **8** the *o*-anisyl substituents adopt *g*-*g*$^-$ conformations (Cr–P–C–C torsion angles −57.8(2)°, −58.4(2)°, see Fig. 1). The asymmetric *o*-tolyl PNP ligand in **9** has an *ag*$^-$ conformation (torsion angles 176.8(3)°, −79.1(3)° and 175.4(3)°, −80.0(3)° in the two independent molecules of **9** present).

The structures of the symmetrically *ortho*-substituted [$Cr(CO)_4${PNNP}] complexes **10** and **11** are shown in Fig. 5 and 6 and selected bond lengths and angles given in Table 5. In these complexes the Cr(0) centre is coordinated by four CO ligands

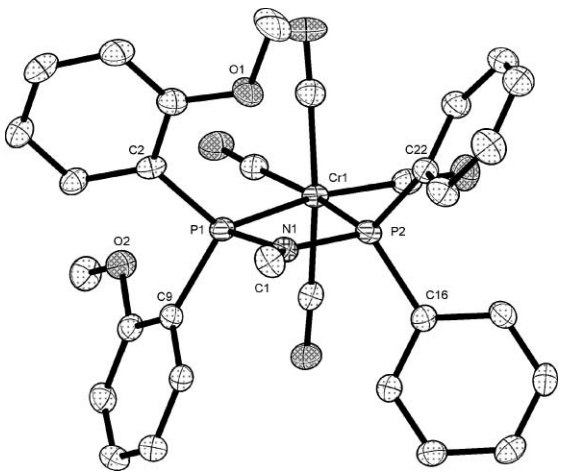


Fig. 3 Thermal ellipsoid plot of **8**. Displacement ellipsoids are shown at the 50% probability level and all hydrogen atoms have been removed for clarity.

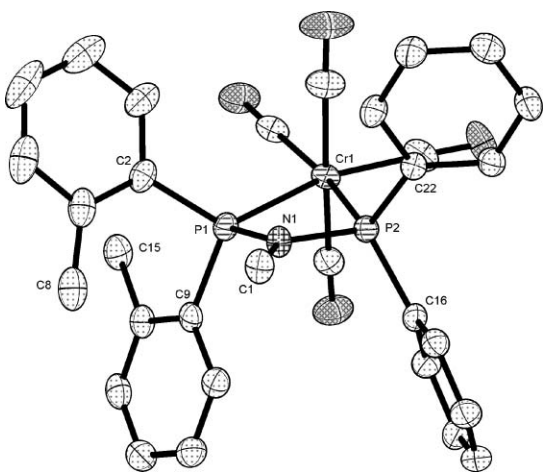


Fig. 4 Thermal ellipsoid plot of one of the 2 independent molecules of **9**. Displacement ellipsoids are shown at the 50% probability level and all solvent and hydrogen atoms have been removed for clarity.

and chelated by the bidentate ligands **6** and **7** which have bites angles of 79.87(2)° and 80.63(1)° respectively. Both the *o*-tolyl

Table 4 Selected bond distances (Å) and angles (°) for **8** and **9**·0.5MeOH

	8	**9**·0.5MeOH	
Cr1–P1	2.3535(6)	2.3756(11)	2.3753(11)
Cr1–P2	2.3328(7)	2.3405(11)	2.3429(11)
P1–N1	1.6972(19)	1.707(3)	1.709(3)
P2–N1	1.6992(19)	1.704(3)	1.697(3)
N1–C1	1.464(3)	1.466(5)	1.470(5)
P1–C2	1.821(2)	1.842(4)	1.839(4)
P1–C9	1.828(2)	1.829(4)	1.830(4)
P2–C16	1.827(2)	1.822(4)	1.831(4)
P2–C22	1.825(2)	1.815(4)	1.825(4)
P1–Cr–P2	68.37(2)	67.88(4)	68.03(4)
P1–N1–P2	101.66(10)	101.08(16)	101.58(15)

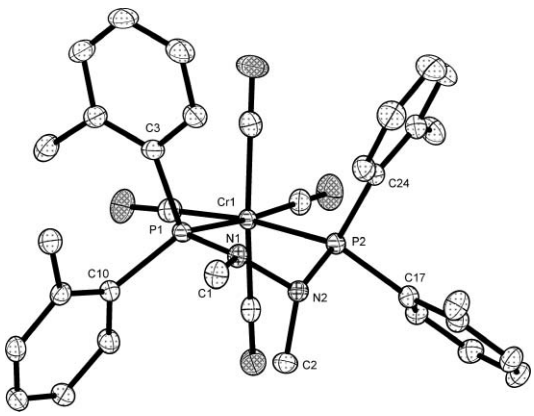


Fig. 5 Thermal ellipsoid plot of **10**. Displacement ellipsoids are shown at the 50% probability level and all solvent and hydrogen atoms have been removed for clarity.

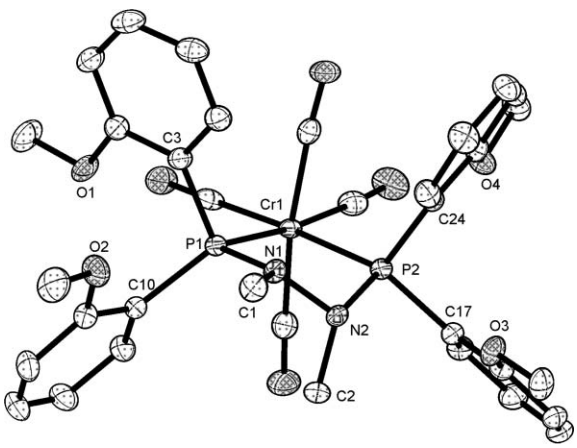


Fig. 6 Thermal ellipsoid plot of **11**. Displacement ellipsoids are shown at the 50% probability level and all hydrogen atoms have been removed for clarity.

(**10**) and *o*-anisyl (**11**) substituted diphosphines show $g^{+}aag^{-}$ conformations (torsion angles 68.9(2)°, 171.3(1)°, 167.8(1)°, –82.4(2)° and 82.2(1)°, –174.4(1)°, –170.1(1)°, –62.6(1)°). The backbone of the PNNP diphosphine has one planar nitrogen (N1), while the other (N2) has pyramidal geometry with the C2 methyl group axial. Combined with the conformation of the *ortho* substituents this reduces steric interaction between the aryl groups and the ligand backbone.

Table 5 Selected bond distances (Å) and angles (°) for **10**·0.75CH_2Cl_2 and **11**

	10·0.75CH_2Cl_2	**11**
Cr1–P1	2.3858(5)	2.3699(4)
Cr1–P2	2.3924(6)	2.3536(4)
P1–N1	1.7171(16)	1.7194(12)
P2–N2	1.7342(16)	1.7349(12)
N1–N2	1.438(2)	1.4427(16)
N1–C1	1.459(2)	1.4647(18)
N2–C2	1.475(2)	1.4723(18)
P1–C3	1.8472(19)	1.8292(15)
P1–C10	1.835(2)	1.8414(15)
P2–C17	1.8385(19)	1.8316(15)
P2–C24	1.837(2)	1.8276(15)
P1–Cr–P2	79.873(19)	80.627(14)
P1–N1–N2–P2	–51.34(14)	53.43(11)

What is clear from this study is that there is a very subtle interplay of factors which influence activity and selectivity in these systems. The expected larger bite angle of the PNNP derivatives is the obvious factor determining the excellent performance of these systems for isoprene trimerisation. However, why these systems are then less successful for ethene/styrene co-trimerisation is more difficult to rationalise. Similarly, the factors resulting in the unique selectivity of ligand **1** in co-trimerisation are not illuminated. Studies are ongoing to more fully map structure–activity relationships in this regard.

Conclusions

A series of symmetric and unsymmetric PNP and PNNP ligands have been synthesised. Catalytic screening for ethene/styrene co-trimerisation and isoprene trimerisation reveals a number of interesting trends. PNNP catalytic systems show a significant increase in activity and selectivity over previously reported PNP systems in isoprene trimerisation. Comparing the symmetric and unsymmetric variants in ethene and styrene co-trimerisation resulted in a switch in selectivity, an unsymmetric catalytic (o-anisyl)$_2$PN(Me)PPh$_2$ ligand system giving, for the first time, incorporation of two styrenic monomers into the cotrimer product distribution. Structural studies of model complexes of the type [(diphosphine)Cr(CO)$_4$] give some insights and are helping us to unravel the very subtle interplay of effects which determine performance in these systems.

Experimental

General comments

All procedures were carried out under an inert (N_2) atmosphere using standard Schlenk techniques or an inert atmosphere (Ar) glovebox. Chemicals were obtained from Sigma Aldrich, Fischer Scientific, Acros or Alfa Aesar and used without further purification unless otherwise stated. All solvents were purified using an anhydrous engineering Grubbs-type solvent system. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR Spectrometer in methylene chloride. Bands are characterised as strong (s), moderate (m), weak (w) and/or broad (br). ^{1}H, ^{13}C{^{1}H} and ^{31}P NMR spectra were recorded on a Jeol ECP 300, Lamda 300 or Varian 400 spectrometers at 400 or 300, 100.5

and 121 MHz respectively at room temperature. ^{1}H NMR and ^{13}C {^{1}H} chemical shifts are referenced relative to the residual solvent resonances in the deuterated solvent, and ^{31}P {^{1}H} NMR spectra are referenced to high frequency of 85% H_3PO_4. Mass spectra were recorded on a VG Analytical Autospec or Brüker Daltonics Apex IV spectrometers. Oligomerisation products were analysed by GC-FID and GC-MS, using a Varian L3800, using a Varian WC07 fused silica capillary column, 25 m × 0.25 mm, ID coating CP-Sil 5CB, DF = 0.25. Co-oligermerisation method: 40 °C to 80 °C at 2 °C min^{-1}, then 80 °C to 250 °C at 10 °C min^{-1}. Isoprene oligomerisation method: 40 °C to 80 °C at 2 °C min^{-1}, then 80 °C to 300 °C at 10 °C min^{-1}. Microanalyses were carried out by the Microanalytical Laboratory of the School of Chemistry at the University of Bristol. The syntheses of **4**[13] and **5**[3,7,14] were performed according to literature procedures. $Cl_2PN(Me)N(Me)PCl_2$ is commercially available but may be very conveniently prepared from low-cost starting materials as reported by Reddy and Katti.[15]

Synthesis of dichloro(diethylamine)phosphine. Diethylamine (100 mL, 0.96 mol) was added dropwise over 3 h to a stirred solution of PCl_3 (42 mL, 0.48 mol) in ether (800 mL) at −78 °C. The solution was then filtered *via* a cannula to give a colourless filtrate and white crystalline $Et_2NH{\cdot}HCl$. The ether was removed by distillation and the product was obtained by vacuum (60 °C at 0.6 Torr) distillation. ^{1}H NMR ($CDCl_3$): δ = 1.18 (t, $^{3}J_{HH}$ = 7.14 Hz, 6H, CH_3), 3.34 (dq,$^{2}J_{PH}$ = 14.0 Hz, $^{3}J_{HH}$ = 6.2 Hz, 4H, CH_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 162.9 (s, PCl_2).

Synthesis of {2-C_6H_4(OMe)}$_2$PN(Me)P(C_6H_5)$_2$ (1). A solution of *o*-bromoanisole (17 mL, 0.136 mol) in ether (60 mL) was added dropwise to magnesium turnings (5.27 g, 0.219 mol) in ether (20 mL). Once addition was complete, the mixture was heated under reflux for 2 h to give a brown solution. The Grignard reagent, *ortho*-methoxyphenylmagnesium bromide (0.136 mol) was transferred to a pressure equalising dropping funnel and added dropwise to a stirred solution of dichlorodiethylaminephosphine (9.89 mL, 68 mmol) in ether (30 mL). After 2 h the solution was filtered *via* a cannula and the filtrate was distilled to separate the ether. Hydrochloric acid (36 mL, 2.0 M in diethyl ether) was added and the solution filtered *via* a cannula. Diethyl ether was removed under reduced pressure resulting in pure chlorodi(*ortho*-methoxy)phenylphosphine as a pale yellow solid (5.25 g, 18.72 mmol, 27.5%). Chlorodi(*ortho*-methoxy)phenylphosphine (2 g, 6.6 mmol) was dissolved in DCM (20 mL) and the solution added dropwise to a stirred solution of triethylamine (20 mL) and methylamine (3.3 mL, 2.0 M solution in tetrahydrofuran) at 0 °C. This resulted in a white precipitation of $HCl{\cdot}Et_3N$ salt and a colourless solution. Chlorodiphenylphosphine (1.19 mL, 6.6 mmol) was dissolved in dichloromethane (40 mL) and added dropwise to the (di(*ortho*-methoxy)phenylphosphino)methylamine solution resulting in further precipitation of $HCl{\cdot}NEt_3$. The solution was allowed to stir for 30 min. The solution was then filtered *via* a cannula and the solvent was removed under reduced pressure resulting in an oily product. The product was dissolved in diethyl ether (60 mL) and passed through a neutral alumina plug under nitrogen to remove contaminates. Removal of diethyl ether under reduced pressure and drying *in vacuo* yielded **1** as a white powder (1.02 g, 2.22 mmol, 36.3%). CI mass spectrum: m/z = 460 [M + H]$^+$, 459 [M]$^+$. CI HR mass spectrum: m/z = 460.1592 [M + H]$^+$ (calcd 460.1595). ^{1}H NMR ($CDCl_3$): δ = 2.45 (dd, $^{3}J_{HP}$ = 4.13 Hz, $^{3}J_{HP}$ = 2.66 Hz, 3H, NCH_3), 3.69 (s, 6H, OCH_3), 7.33–7.47 (m, 18H, ArH). ^{13}C NMR ($CDCl_3$): δ = 32.62 (d, $^{2}J_{CP}$ = 7.79 Hz, NCH_3), 54.1 (s, OCH_3), 108.9 (s, *C*H), 119.3 (s, *C*H), 126.9 (d, $^{1}J_{CP}$ = 6.23 Hz, *C*P), 127.5 (s, *C*H), 129.1 (s, *C*H), 131.4 (s, *C*H), 131.7 (s, *C*H), 131.9 (s, *C*H), 138.0 (dd, $^{1}J_{CP}$ = 18.68 Hz, $^{3}J_{CP}$ = 11.68 Hz, *C*P), 159.6 (d, $^{2}J_{CP}$ = 17.3 Hz, *C*OCH$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 55.7 (d, $^{2}J_{PNP}$ = 284 Hz, *P*Ar$_2$), 69.5 (d, $^{2}J_{PNP}$ = 284 Hz, *P*Ar$_2$).

Synthesis of {2-C_6H_4(Me)}$_2$PN(Me)P(C_6H_5)$_2$ (2). This was synthesised in the same way as **1** only using *ortho*-tolyl magnesium bromide in place of *ortho*-anisyl magnesium bromide. The product was obtained as a white powder (2.48 g, 5.8 mmol, 22.3%). ESI mass spectrum: m/z = 428 [M + H]$^+$, 450 [M + Na]$^+$. ^{1}H NMR ($CDCl_3$): δ = 2.32 (s, 6H, ArCH_3), 2.49 (dd, $^{3}J_{HP}$ = 3.39 Hz, $^{3}J_{HP}$ = 2.48 Hz, 3H, NCH_3), 6.98–7.44 (m, 18H, ArH). ^{13}C NMR ($CDCl_3$): δ = 21.3 (d, $^{3}J_{CP}$ = 20.7 Hz, *C*H$_3$), 33.0 (s, N*C*H$_3$), 125.5 (s, *C*H), 128.2 (d, $^{1}J_{CP}$ = 5.2 Hz, *C*P), 128.9 (s, *C*H), 130.6 (s, *C*H), 131.8 (s, *C*H), 132.6 (s, *C*H),132.9 (s, *C*H), 136.6 (s, *C*H), 136.8 (s, *C*H), 138.6–138.9 (m, *C*H), 141.3 (d, $^{1}J_{CP}$ = 27.1 Hz, *C*P). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 58.6 (d, $^{2}J_{PNP}$ = 297 Hz, *P*Ar$_2$), 72.5 (d, $^{2}J_{PNP}$ = 296 Hz, *P*Ar$_2$). Elemental analysis: $C_{27}H_{27}NP_2$ calcd (%) C 75.86, H 6.37, N 3.28, found (%) C 75.93, H 6.50, N 3.30.

Synthesis of {2-C_6H_4(ethyl)}$_2$PN(Me)P(C_6H_5)$_2$ (3). Again, the same method as for **1** was followed, only using *ortho*-ethylphenyl magnesium bromide in place of *ortho*-anisyl magnesium bromide. In this case an oily product was initially obtained, which only after repeated trituration with methanol yielded **3** as a white powder (1.70 g, 3.72 mmol, 31%).

ESI mass spectrum: m/z = 456 [M + H]$^+$, 478 [M + Na]$^+$. ^{1}H NMR ($CDCl_3$): δ = 1.22 (t, $^{3}J_{HH}$ = 6.97 Hz, 6H, CH_3), 2.56–3.04 (m, 4H, CH_2), 2.46 (dd, $^{3}J_{HP}$ = 3.30 Hz, $^{3}J_{HP}$ = 2.57 Hz, 3H, NCH_3), 7.23–7.42 (m, 18H, ArH). ^{13}C NMR ($CDCl_3$): δ = 15.2 (d, $^{3}J_{CP}$ = 20.7 Hz, *C*H$_3$), 27.3 (d, $^{3}J_{CP}$ = 20.7 Hz, *C*H$_2$), 33.0 (s, N*C*H$_3$), 125.4 (s, *C*H), 127.9–129.9 (m, *C*H), 132.1–132.9 (m, *C*H), 136.5–136.9 (m, *C*H), 138.4–138.8 (m, *C*H), 147.2 (d, $^{1}J_{CP}$ = 25.7 Hz, *C*P). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 57.6 (d, $^{2}J_{PNP}$ = 300 Hz, *P*Ar$_2$), 72.5 (d, $^{2}J_{PNP}$ = 301 Hz, *P*Ar$_2$). Elemental analysis: $C_{29}H_{31}NP_2{\cdot}CH_3OH$ calcd (%) C 74.84, H 7.80, N 2.64, found (%) C 74.24, H 7.52, N 2.91.

Synthesis of {2-C_6H_4(Me)}$_2$PN(Me)N(Me)P{2-C_6H_4(Me)}$_2$ (6). *N*,*N*′-bis(dichlorophosphino)dimethylhydrazine (0.68 mL, 3.8 mmol) was dissolved in ether (25 mL) and added dropwise to *ortho*-tolyl magnesium bromide (60 mL in ether, 0.159 mol, prepared as before). After 24 h of stirring, water (25 mL) was slowly added and stirred for a further hour. The reaction mixture was transferred to a separatory funnel and the layers separated. The organic layer was dried over anhydrous magnesium sulfate and the drying agent was removed *via* Büchner filtration. The filtrate was evaporated to dryness *in vacuo* to give a colourless oil. The product was then washed with light petroleum ether and then dissolved in ether (60 mL) and filtered through a short neutral alumina plug. Removal of diethyl ether and drying *in vacuo* gives **6** as a white powder (0.34 g, 0.705 mmol, 19%). EI mass spectrum: m/z = 484.3 [M]$^+$. CI HR mass spectrum: m/z = 485.2272 [M + H]$^+$ (calcd 485.2276). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 47.3. ^{1}H NMR ($CDCl_3$): δ = 2.34 (s, 12H, ArCH_3), 2.83 (s, 6H, NCH_3), 7.11–7.27

(m, 16H, Ar*H*). ^{13}C NMR ($CDCl_3$): $\delta = 21.4$ (d, $^3J_{CP} = 23.08$ Hz, Ar*C*H$_3$), 37.7 (s, N*C*H$_3$), 125.7 (s, *C*H), 128.6 (s, *C*H), 130.2 (s, *C*H), 131.8 (s, *C*H), 138.3 (d, $^2J_{CP} = 20.8$ Hz, *C*CH$_3$), 141.3 (d, $^1J_{CP} = 28.27$ Hz, *C*P).

Synthesis of {2-C$_6$H$_4$(OMe)}$_2$PN(Me)N(Me)P{2-C$_6$H$_4$-(OMe)}$_2$ (7). The same method as for **6** was followed only using *ortho*-anisyl magnesium bromide in place of *ortho*-tolyl magnesium bromide. In this case an oily product was initially obtained, methanol trituration yielding **7** as a white powder (1.10 g, 2.01 mmol, 52%). ESI mass spectrum: $m/z = 549$ [M + H]$^+$, 571 [M + Na]$^+$. ^{1}H NMR (C_6D_6): $\delta = 2.70$ (s, 12H, OC*H*$_3$), 2.83 (s, 6H, NC*H*$_3$), 6.18–6.86 (m, 16H, Ar*H*). ^{13}C NMR (C_6D_6): $\delta = 36.0$ (d, $^2J_{CP} = 6.23$ Hz, N*C*H$_3$), 53.2 (s, ArO*C*H$_3$), 108.7 (s, *C*H), 109.0 (d, $^1J_{CP} = 1.56$ Hz, *C*P), 119.7 (s, *C*H), 128.5 (s, *C*H), 131.6 (s, *C*H), 159.6–160.8 (m, *C*OCH$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 27.6$. Elemental analysis: $C_{30}H_{34}N_2O_4P_2 \cdot 2CH_3OH$ calcd (%) C 62.74, H 6.91, N 4.57, found (%) C 62.51, H 6.62, N 4.75.

Chromium carbonyl complexation

The same general method was followed for all complexes, described here for the synthesis of **8**. Toluene (40 mL) was added to chromium hexacarbonyl, [Cr(CO)$_6$], (350 mg, 1.6 mmol) and **1** (500 mg, 1.2 mmol) and the stirred mixture was heated under reflux for 48 h. The solution was cooled to 0 °C and filtered to remove excess [Cr(CO)$_6$]. Solvent was removed under reduced pressure and the product extracted into dichloromethane (10 mL). Methanol (20 mL) was added to precipitate the product, which was isolated by filtration and dried *in vacuo* to yield a yellow solid (287 mg, 0.46 mmol, 44%). X-Ray-quality crystals were formed from a concentrated dichloromethane solution layered with methanol at 0 °C.

[Cr(CO)$_4${2-C$_6$H$_4$(OMe)}$_2$PN(Me)P(C$_6$H$_5$)$_2$] (8). 34%, CI mass spectrum: $m/z = 623$ [M]$^+$, 511 [M – 4 C≡O]$^+$. CI HR mass spectrum: $m/z = 623.0724$ (calcd 623.0719). ^{1}H NMR ($CDCl_3$): $\delta = 2.70$ (t, $^3J_{HP} = 8.19$ Hz, 3H, NC*H*$_3$), 3.40 (s, 6H, OC*H*$_3$), 6.81–7.47 (m, 18H, Ar*H*). ^{13}C NMR ($CDCl_3$): $\delta = 23.94$ (s, N*C*H$_3$), 54.0 (s, O*C*H$_3$), 109.8 (s, *C*H), 119.4 (s, *C*H), 119.5 (s, *C*P), 127.3 (s, *C*H), 127.4 (s, *C*H), 129.18 (s, *C*H), (m, 130.8–131.5, *C*H), 158.7 (s, *C*OCH$_3$), 204.1 (s, *C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 100.36$ (d, $^2J_{PNP} = 27.3$ Hz, *P*Ar$_2$), 111.2 (d, $^2J_{PNP} = 27.3$ Hz, *P*Ar$_2$). Elemental analysis: $C_{31}H_{27}CrNO_6P_2 \cdot 2CH_3OH$ calcd (%) C 57.64, H 5.13, N 2.04, found (%) C 57.45, H 4.61, N 2.37. IR ($CHCl_2$): = 1876 (s) (C≡O), 1893 (s), 1918 (C≡O), 2005 (s) (C≡O).

[Cr(CO)$_4${2-C$_6$H$_4$(Me)}$_2$PN(Me)P(C$_6$H$_5$)$_2$] (9). 31%, ESI mass spectrum: $m/z = 591$ [M + Na – C≡O]$^+$, 577 [M – 4 C≡O]$^+$. ^{1}H NMR ($CDCl_3$) (MeOH of crystallisation observed but omitted here for clarity): $\delta = 1.93$ (s, 6H, ArC*H*$_3$), 2.72 (t, $^3J_{HP} = 3.39$ Hz, 3H, NC*H*$_3$), 7.10–7.47 (m, 18H, Ar*H*). ^{13}C NMR ($CDCl_3$): $\delta =$ 15.4 (s, *C*H$_3$), 34.7 (s, N*C*H$_3$), 126.5–132.3 (m, *C*H). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 109.9$ (d, $^2J_{PNP} = 29.8$ Hz, *P*Ar$_2$), 114.1 (d, $^2J_{PNP} = 29.8$ Hz, *P*Ar$_2$). Elemental analysis: $C_{31}H_{27}CrNO_4P_2$ calcd (%) C 62.95, H 4.60, N 2.37, found (%) C 62.19, H 4.85, N 2.32. IR ($CHCl_2$): = 1877 (s) (C≡O), 1895 (s), 1916 (C≡O), 2008 (s) (C≡O).

[Cr(CO)$_4${2-C$_6$H$_4$(Me)}$_2$PN(Me)N(Me)P{2-C$_6$H$_4$(Me)}$_2$] (10). ^{1}H NMR (C_6D_6): $\delta = 1.93$ (s, 12H, C*H*$_3$), 2.53 (s, 6H, NC*H*$_3$), 6.97–7.13 (m, 20H, Ar*H*). ^{13}C NMR ($CDCl_3$): $\delta = 21.0$ (s, *C*H$_3$), 56.2 (s, N*C*H$_3$), 125.5–132.7 (m, *C*H), 211.1 (s, *C*O). ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 147.4$ (s, *P*Ph$^{o\text{-tolyl}}$). Satisfactory elemental analysis could not be obtained; accurate ESI MS for $C_{34}H_{34}CrN_2O_4P_2$ calcd m/z 649.140, found 649.138. IR (*n*-hexane): $\nu = 1897$ (s) (C≡O), 1932 (s), 1955 (C≡O), 2015 (s) (C≡O).

[Cr(CO)$_4${2-C$_6$H$_4$(OMe)}$_2$PN(Me)N(Me)P{2-C$_6$H$_4$(OMe)}$_2$] (11). 28%, ESI mass spectrum: $m/z = 713$ [M + H]$^+$, 735 [M + Na]$^+$. ^{1}H NMR ($CDCl_3$): $\delta = 2.11$ (s, 6H, NC*H*$_3$), 2.63 (s, 12H, C*H*$_3$), 6.64–7.25 (m, 20H, Ar*H*). ^{13}C NMR ($CDCl_3$): $\delta = 56.4$ (s, N*C*H$_3$), 54.0 (s, O*C*H$_3$), 109.4–131.8 (m, *C*H), 160.7 (s, *C*OCH$_3$), 208.1 (s, *C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 135.7$ (s, *P*Ph^{OMe}). Elemental analysis: $C_{34}H_{34}N_2O_4P_2 \cdot 2CH_3OH$ calcd (%) C 55.67, H 5.45, N 3.61, found (%) C 55.20, H 5.09, N 3.61. IR ($CHCl_2$): = 1883 (br) (C≡O), 1895 (s), 1916 (C≡O), 2005 (s) (C≡O).

Catalytic testing

Isoprene trimerisation. Our previously reported method was followed.[4] The ligand (20 μmol) and chromium(III) chloride tetrahydrofuran complex, [$CrCl_3(THF)_3$], (8 mg, 20 μmol) were dissolved in tetrahydrofuran (3 mL) and stirred at room temperature in a round bottomed Schlenk fitted with a condenser under nitrogen for 10 minutes. The solvent was removed and toluene (10 mL) was added to give a pink mixture. Methylaluminoxane (MAO, 10% wt solution in toluene, 4 mL, 300 equivalents, 6 mmol) was then added, to give a green solution. Freshly distilled isoprene (30 mL) was added and the solution was vigorously stirred at 70 °C for 1 h. The Schlenk tube was then opened to air and a dilute solution of hydrochloric acid (10% solution) in water was slowly added to quench the reaction. The organic layer was separated and dried over anhydrous magnesium sulfate, giving a colourless solution of products in toluene. A sample of the solution was analysed by GC-FID.

Ethene and styrene co-trimerisation. Our previously reported method was followed.[5] The ligand (20 μmol) and chromium(III) chloride tetrahydrofuran complex, [$CrCl_3(THF)_3$], (8 mg, 20 μmol) were dissolved in tetrahydrofuran (3 mL) and stirred at room temperature in a Schlenk tube under nitrogen for 10 minutes. The solvent was removed and toluene was added (10 mL) to give a pink mixture. Methylaluminoxane (MAO, 10% wt solution in toluene, 4 mL, 300 equivalents, 6 mmol) was then added, to give a green solution and the Schlenk tube was weighed. Next, the Schlenk tube was put under an ethene (1 bar) atmosphere and styrene (30 mL) was added. The solution was vigorously stirred at room temperature for 1 h. After 1 h the ethene feed was stopped and the Schlenk tube was re-weighed. The Schlenk tube was opened to air and a dilute solution of hydrochloric acid (10% solution) in water was slowly added to quench the reaction. The organic layer was separated and dried over anhydrous magnesium sulfate, giving a colourless solution of products in toluene. A sample of the solution was analysed by GC-FID.

Crystal structure determinations

X-Ray diffraction experiments on **8**, **10**·0.75CH_2Cl_2 and **11**, were carried out at 100 K on a Bruker Kappa Apex II CCD diffractometer, using Mo Kα radiation ($\lambda = 0.71073$ Å). A single crystal was coated in inert oil and mounted on a glass fibre.

Table 6 Crystallographic data

Compound	**8**	**9**·0.5MeOH	**10**·0.75CH_2Cl_2	**11**
Colour, habit	Yellow block	Yellow block	Yellow block	Yellow block
Size/mm	0.196 × 0.156 × 0.052	0.042 × 0.028 × 0.026	0.94 × 0.85 × 0.45	0.28 × 0.12 × 0.10
Empirical formula	$C_{31}H_{27}CrNO_6P_2$	$C_{31.5}H_{28.5}CrNO_{4.5}P_2$	$C_{34.75}H_{35.5}Cl_{1.5}CrN_2O_4P_2$	$C_{34}H_{34}CrN_2O_8P_2$
M	623.48	607.02	712.27	712.57
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	14.712(1)	9.944(1)	11.825(1)	20.708(1)
b/Å	13.357(1)	15.875(1)	16.615(1)	10.778(1)
c/Å	20.732(1)	38.828(2)	20.683(1)	15.910(1)
β/°	134.635(1)	101.416(1)	121.267(1)	110.343(1)
V/A^3	2898.95(7)	6008.5(4)	3473.6(3)	3329.28(11)
Z	4	8	4	4
μ/mm^{-1}	0.550	0.525	0.577	0.494
T/K	100	120	100	100
Reflections: total/independent	34 319/6627	51 936/13 757	29 654/7919	34 988/7573
R(int)	0.0636	0.0897	0.0269	0.0264
Final *R*1, w*R*2	0.0419, 0.0989	0.0694, 0.1654	0.0374, 0.1004	0.096, 0.0744

Intensities were integrated[16] from several series of exposures in *φ* and *ω* calculated by the Apex II[17] program after unit cell determination.

X-Ray diffraction experiments on **9**·0.5MeOH, were carried out at 120 K on a Bruker-Nonius KappaCCD diffractometer, also using Mo Kα radiation (λ = 0.71073 Å) generated by a Bruker-Nonius FR591 rotating anode. All data collections were performed using a single crystal coated in perfluoroalkylether and mounted on a glass fibre. Intensities were integrated[18] from several series of exposures in *φ* and *ω* calculated by the COLLECT[19] and DENZO[20] programs after unit cell determination by the DirAx[21] program.

Absorption corrections were based on equivalent reflections using SADABS,[22] and structures were refined against all F_o^2 data with hydrogen atoms riding in calculated positions using SHELXTL.[23] Crystal structure and refinement data are given in Table 6. Ten low angle disagreeable reflections were omitted from **9**, **10** and **11**. To improve the disordered solvent model for structure **9** the anisotropic displacement parameters for the carbon of the methanol molecule were restrained to match the attached oxygen atom. Attempts to model the disorder of the co-crystallised CH_2Cl_2 molecule in structure **10**·0.75CH_2Cl did not improve the final model, and instead an occupancy of 75% was assigned to the solvate after refinement.

Acknowledgements

We would like to thank the EPSRC, CCDC and University of Bristol for funding. Thanks to the National Crystallographic Service at Southampton for collecting diffraction data for **9**·0.5MeOH.

References

1 J. T. Dixon, M. J. Green, F. M. Hess and D. H. Morgan, *J. Organomet. Chem.*, 2004, **689**, 3641; D. F. Wass, *Dalton Trans.*, 2007, 816.
2 A. Carter, S. A. Cohen, N. A. Cooley, A. Murphy, J. Scutt and D. F. Wass, *Chem. Commun.*, 2002, 858.
3 A. Bollmann, K. Blann, J. T. Dixon, F. M. Hess, E. Killian, H. Maumela, D. McGuinness, D. H. Morgan, A. Neveling, S. Otto, M. Overett, A. M. Z. Slawin, P. Wasserscheid and S. Kuhlmann, *J. Am. Chem. Soc.*, 2004, **126**, 14712.
4 L. E. Bowen, M. Charernsuk and D. F. Wass, *Chem. Commun.*, 2007, 2835.
5 L. E. Bowen and D. F. Wass, *Organometallics*, 2006, **25**, 555.
6 J. R. Briggs, *J. Chem. Soc., Chem. Commun.*, 1989, **11**, 674.
7 M. J. Overett, K. Blann, A. Bollmann, J. T. Dixon, F. Hess, E. Killian, H. Maumela, D. H. Morgan, A. Neveling and S. Otto, *Chem. Commun.*, 2005, 622.
8 A. M. Slawin, M. Wainwright and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 2002, 513.
9 D. F. Wass, *PCT patent* appl. WO 0204119, 2002, (to BP).
10 S. Akutagawa, T. Taketomi, H. Kumobayashi, K. Takayama, T. Someya and S. Otsuka, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1158.
11 S. Akutagawa, T. Taketomi and S. Otsuna, *Chem. Lett.*, 1976, 485.
12 L. E. Bowen, M. Haddow, A. G. Orpen and D. F. Wass, *Dalton Trans.*, 2007, 1160.
13 N. Cooley, S. M. Green and D. F. Wass, *Organometallics*, 2001, **20**, 4769.
14 K. Blann, A. Bollmann, J. T. Dixon, F. M. Hess, E. Killian, H. Maumela, D. H. Morgan, A. Neveling, S. Otto and M. J. Overett, *Chem. Commun.*, 2005, 620.
15 V. S. Reddy and K. V. Katti, *Inorg. Chem.*, 1994, **33**, 2695.
16 SAINT v7.34A, Bruker-AXS, 2007.
17 Apex2, Bruker-AXS, 2007.
18 HKL package (DENZO, XDisplayF and Scalepack), HKL Research Inc, Z. Otwinowski & W. Minor, *Methods in Enzymology*, Vol. 27, Macromolecular Crystallography, part A, 307-326, 1997.
19 R. W. W. Hooft & B. V. Nonius, COLLECT data collection software, 1998.
20 Z. Otwinowski and W. Minor, *Methods in Enzymology*, Vol. 27, Macromolecular Crystallography, part A, 307–326, 1997.
21 A. J. M. Duisenberg, *J. Appl. Crystallogr.*, 1992, **25**, 92–96.
22 G. M. Sheldrick (2007), *SADABS V2007* (2, Bruker AXS Inc., Madison, Wisconsin, USA.
23 *SHELXTL program system version V 6.14*, Bruker AXS Inc., Madison, Wisconsin, USA, 2000-3.