Phosphanyl Methanimine (PCN) Ligands for the Selective Trimerization/Tetramerization of Ethylene with Chromium

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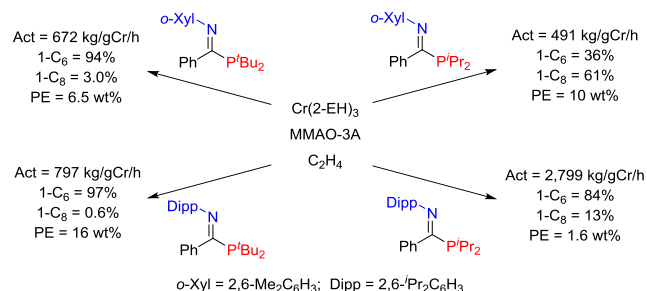
Supporting Information Placeholder

ABSTRACT: 1-Phosphanyl methanimine ligands, R_2P-$C(Ph)=NR'$, may be prepared *via* a modular, convergent synthesis in good overall yield. Coordination chemistry studies with chromium confirm they bind in a bidentate κ^2-*P,N* mode. In combination with chromium and an activator, these ligands promote the selective oligomerization of ethylene to 1-hexene and 1-octene with high activity. Notably, an exceptionally high liquid fraction selectivity to saleable products (1-hexene + 1-octene) is observed (>95%) along with a potent ligand dependence, such that selectivity can be varied from pure trimerization through to tri-/tetramerization with a 1-octene to 1-hexene (OTH) ratio of 1.7.

The selective oligomerization of ethylene to 1-hexene and 1-octene, commonly referred to as trimerization and tetramerization, has attracted considerable and sustained attention over the last 15 years.[1,2,3,4] These efforts have culminated in the construction of trimerization plants by CPChem, Axens and Mitsui,[5,6] and a tetramerization plant by Sasol,[5] with numerous other companies also active in the field.[2] From an industrial perspective, 1-hexene and 1-octene are in higher demand, and more profitable, relative to the rest of the broad product slate resulting from classical oligomerization technologies. Thus, the ability to target the production of these specific Linear Alpha Olefins (LAOs) remains highly desirable.[5,7] Simultaneously, academic interest has been fuelled by gaining an understanding of the origins of the unusual selectivity achieved in these catalytic transformations.[2,8] Although aspects of the general mechanism have been established,[2,8] most notably the role of a metallacyclic reaction manifold,[9] definitive answers relating to the oxidation state of chromium and specific aspects of ligand control remain elusive.[10,11] Furthermore, work is continuing apace to rationalize and expand the very narrow set of ligands that engender the high levels of chemo- and regio-selectivity required for the commercialization of trimerization and tetramerization processes.

Remarkably, despite the extensive work in the field of olefin oligomerization, less than twenty distinct initiator systems capable of selective trimerization and/or tetramerization are known, the majority of which are based upon chromium.[1-5] This is in stark contrast to the hundreds of systems known to deliver statistical distributions of olefinic products.[5,12] Furthermore, the number of catalysts capable of promoting ethylene tetramerization, in preference to trimerization, is yet more limited,[1-5] and a truly 1-octene-selective system remains unknown.[13] The first and most ubiquitous class of ligand for the promotion of tetramerization are PNP diphosphines used in combination with chromium.[14] Attempts to further enhance tetramerization performance have largely focused on the development of alternative diphosphines including PNNP,[14a] PCP,[15,16] PCCP,[14a,15] PCNCP,[17] and $PN(C)_nNP$ scaffolds,[18] but without success. Only recently have ligands other than diphosphines been located for this transformation, most notably reports of PNCN scaffolds from CPChem,[6] and various bidentate P,N systems described by Duchateau and Gambarotta.[19] To-date, PNP-based catalysts remain the best performing systems for tetramerization, giving the highest activities, lowest polymer formation and highest 1-octene to 1-hexene ratios.

Herein, we report the first use of 1-phospanyl methanimine (PCN) ligands for the selective oligomerization of ethylene (Scheme 1). Through judicious modification of the PCN framework, a wide range of product selectivities are achievable, from pure trimerization through to mixed tri-/tetramerization with 1-octene to 1-hexene (OTH) ratios well above one, with very high yields of 1-hexene + 1-octene.

Act = 672 kg/gCr/h
1-C_6 = 94%
1-C_8 = 3.0%
PE = 6.5 wt%

Act = 491 kg/gCr/h
1-C_6 = 36%
1-C_8 = 61%
PE = 10 wt%

$Cr(2\text{-}EH)_3$
MMAO-3A
C_2H_4

Act = 797 kg/gCr/h
1-C_6 = 97%
1-C_8 = 0.6%
PE = 16 wt%

Act = 2,799 kg/gCr/h
1-C_6 = 84%
1-C_8 = 13%
PE = 1.6 wt%

o-Xyl = $2,6\text{-}Me_2C_6H_3$; Dipp = $2,6\text{-}{}^iPr_2C_6H_3$

Scheme 1. The tunable oligomerization selectivity achievable with PCN ligands.

The target PCN ligands **1-8** are obtained through a new, modular, convergent approach (Scheme 2). Our strategy

involves the preparation of imidoyl chlorides, which are readily synthesized *via* condensation of the corresponding acyl chloride and primary amine, both of which are low cost and available with a wide variety of substitution patterns. Separately, trimethylsilylphosphines are prepared in a facile one-pot procedure from either phosphine or chlorophosphine precursors. Subsequent reaction of the chosen trimethylsilylphosphines with the desired imidoyl chlorides affords the target PCN ligands in high yields.[20] Although 1-phosphanyl methanimines and their coordination chemistry with Au, Rh and Ir have recently been described,[21] the ligands were prepared using a more complex, less flexible synthetic strategy.
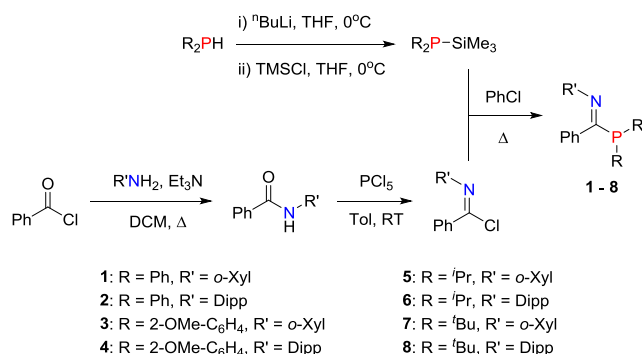

**Scheme 2.** The convergent, modular synthesis of PCN ligands.

PCN ligands **1-8** present a characteristic doublet resonance by ^{13}C NMR spectroscopy (δ ~177 – 180 ppm; $^2J_{PC}$ ~10 – 30 Hz), together with a distinctive C=N absorption in their infrared spectra in the range 1549 – 1636 cm^{-1}, indicative of conjugation of the backbone phenyl group with the C=N bond.[22] In solution, the PCN ligands bearing diarylphosphanyl groups (**1-4**) exist as slowly interconverting mixtures of *E* and *Z* isomers, something that is readily apparent from their ^{31}P NMR spectra, which show two resonances at 298 K; this is in accord with previous observations.[21a] In contrast, the dialkylphosphanyl derivatives **5-8**, each exhibit a single phosphorus resonance over the temperature regime 223 – 323 K consistent with no isomerization taking place.

An exploratory study of the coordination chemistry of selected PCN ligands with chromium has been undertaken (Scheme 3), with particular emphasis upon probing the ability of these scaffolds to attain a κ^2-*P,N* bidentate binding mode, akin to that for established Cr/PNP selective oligomerization systems. The chromium carbonyl complexes Cr(CO)$_4$(κ^2-*P,N*-iPr$_2$PC(Ph)N-Ar) (Ar = 2,6-Me$_2$-C$_6$H$_3$ (**9**), 27%; Ar = 2,6-iPr$_2$-C$_6$H$_3$ (**10**), 25%) were prepared *via* displacement of CO from Cr(CO)$_6$ by ligands **5** and **6** in toluene at reflux. Single-crystal X-ray structures of **9** and **10** (recrystallized from CH$_2$Cl$_2$/hexane) confirm distorted octahedral geometries with *cis* bidentate P,N coordination of the PCN ligands. Acute P-Cr-N bite angles of 65.64(14) [**9**] and 65.79(2)° [**10**] are comparable with the P-Cr-P angles of typical PNP tri-/tetramerization initiators (Figure 1).[14a,23] In a parallel study, the chromium(III) complexes of ligands **5** and **6** were prepared by reaction of CrCl$_3$(THF)$_3$ with 1.1 equivalents of ligand in CH$_2$Cl$_2$. Upon recrystallization from CH$_2$Cl$_2$/hexane the complexes CrCl$_3$(THF)(κ^2-*P,N*-iPr$_2$PC(Ph)N-Ar) (Ar = 2,6-Me$_2$-C$_6$H$_3$ (**11**); Ar = 2,6-iPr$_2$-C$_6$H$_3$ (**12**) were obtained in good yields (90 and 81%, respectively).

Consistent with paramagnetic d^3 complexes, neither ^1H nor ^{31}P NMR spectra could be obtained. The room temperature magnetic susceptibilities μ_{eff} for complexes **11** and **12**, 3.8 and 3.9 μ_B respectively, determined *via* Evans' method in CH$_2$Cl$_2$, are in accordance with the spin-only μ_{eff} value for S = 3/2 species.
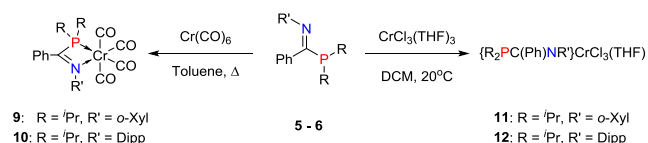
Scheme 3. The synthesis of chromium PCN complexes.
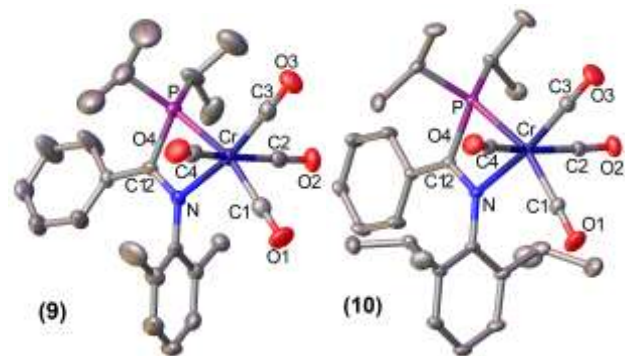
Figure 1. Molecular structures of complexes **9** (one of the two independent molecules) and **10** with thermal ellipsoids at the 50% probability level; H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): [**9**] Cr-P, 2.385(2); Cr-N, 2.162(5); P-C12, 1.837(6); N-C12, 1.290(8); P-Cr-N, 65.64(14); P-C12-N, 103.0(4). [**10**] Cr-P, 2.3829(3); Cr-N, 2.1425(9); P-C12, 1.869(1); N-C12, 1.305(1); P-Cr-N, 65.79(2); P-C12-N, 100.48(6).

Ligands **1-8**, when combined with Cr(2-EH)$_3$ {2-EH = 2-ethylhexanoate} and MMAO-3A in methylcyclohexane (MCH) as solvent and ZnEt$_2$ as additive,[24] prove to be highly active catalysts for the oligo-/polymerization of ethylene (Table 1). Dialkylphosphanyl derivatives **5-8** perform much better than their diaryl counterparts **1-4**; polymer formation is significantly lower and activity is much higher for the former. Within the product liquid fraction all ligands show good selectivity towards selective tri-/tetramerization, although the dialkylphosphanyl variants again perform the best. An overall consideration of the data for **5-8**, reveals that the OTH ratio obtained shows a strong dependence upon the ligand steric bulk, with less bulky ligands giving more tetramerization, as might be expected.[14,25] Ligands **3** and **4** with *ortho*-methoxyphenyl groups at phosphorus, both show a similar OTH ratio despite differing steric bulk. In this case a pendant coordination of the *ortho*-methoxy group most likely occurs to give tridentate coordination as has been observed previously in related systems,[14b,26] and this presumably overrides other steric factors. A second run is included using ligand **6** that demonstrates, for comparison, catalysis in the absence of ZnEt$_2$ as additive. It will be noted that whilst the liquid fraction selectivity remains essentially unchanged, the polymer formation doubles, whilst the activity is somewhat reduced.

Table 1. Ethylene oligomerization results.[a]

L	Rxn Time {min}	Prod. {kg/gCr}	Activity {kg/gCr/h}	1-C$_8$: 1-C$_6$	Total 1-C$_6$+1-C$_8$ {wt%}[a]	C$_4$ {wt%}[b] (% 1-C$_4$)	C$_6$ {wt%}[b] (% 1-C$_6$)	Cyc-C$_6$ {wt%}[b] (% C$_6$)	C$_8$ {wt%}[b] (% 1-C$_8$)	C$_{10-14}$ {wt%}[b]	C$_{15+}$ {wt%}[b]	PE {wt%}[c]
1[d]	60	84	84	1.0	65.6	0.9 (85.5)	50.8 (66.2)	13.8 (27.1)	34.4 (92.9)	3.6	10.3	72.2
2[d]	60	133	133	1.8	79.7	1.1 (68.2)	32.4 (87.4)	3.5 (10.7)	54.0 (95.2)	5.1	7.4	74.5
3[d]	64	93	87	0.7	87.2	1.0 (87.0)	54.1 (96.0)	0.9 (1.7)	38.5 (91.6)	2.7	3.7	84.4
4[d]	168	191	68	0.7	96.2	0.2 (100)	57.4 (98.5)	0.8 (1.4)	40.1 (99.0)	1.1	1.2	60.2
5	200	1,639	491	1.7	96.7	0.0 (100)	36.4 (97.9)	0.8 (2.1)	61.2 (99.8)	2.1	0.2	9.8
6[e]	64	2,950	2,799	0.2	96.2	0.0 (100)	83.8 (99.7)	0.2 (0.2)	12.6 (99.9)	3.5	0.0	1.6
6[f]	88	2,874	1,964	0.2	96.7	0.0 (100)	81.9 (99.6)	0.3 (0.3)	15.2 (99.8)	2.9	0.0	3.6
7	139	1,562	672	0.0	97.0	0.0 (100)	94.0 (99.9)	0.0 (0.0)	3.0 (99.6)	2.7	0.3	6.5
8	173	2,293	797	0.0	97.9	0.0 (100)	97.3 (99.9)	0.0 (0.0)	0.6 (98.0)	2.0	0.1	16.4

General conditions: Cr(2-EH)$_3$ (1.25 μmol); 1.0 eq PCN ligand **1-8**; MMAO-3A (500 eq); ZnEt$_2$ (100 eq); MCH (283 mL); p(C$_2$H$_4$) 40 barg; 60 °C. [a] Full details of catalysis procedures, including ethylene uptake data, are available in the SI. The catalyst was active for the full duration of the reaction time. [b] wt% of liquid fraction. [c] wt% of total product. [d] p(C$_2$H$_4$) 45 barg. [e] Average of two runs – see SI for details and analysis. [f] No ZnEt$_2$.

Focusing on specific examples, ligands **7** and **8** favor trimerization with liquid fraction selectivities to 1-hexene of 93.9 and 97.2 wt%, making them some of the most selective systems known, although the polymer formation is slightly high.[1-5] For ligand **6**, the activity and polymer formation are in the league of PNP-based catalysis; additionally the total formation of 1-hexene and 1-octene combined is exceptionally high at 96.2 wt% of the liquid fraction, which contrasts with the best PNP systems which deliver in the region of 80-89 wt%.[25] This high selectivity to saleable products results from a comparatively low level of formation of C$_6$-cyclic products and significantly reduced incorporation of primary products to form C$_{10-14}$ material.[25,27] All of the systems examined here gave active catalysis for periods from 1-3 hours, allowing operation to the high catalyst productivities essential for potentially economic commercial operation.

In summary, we have reported a facile and convergent synthesis for 1-phospanyl methanimine (PCN) ligands, which should allow more widespread utilization of these deceptively simple ligands for coordination chemistry and catalysis. Furthermore, we have demonstrated their coordination chemistry with chromium, whilst exemplifying their potential in facilitating the selective tri-/tetramerization of ethylene with high activity. Depending upon the choice of substituent, selectivity may be tuned from high selectivity towards trimerization, through to mixed tri-/tetramerization with exceptionally high selectivity to saleable 1-hexene and 1-octene products. Further studies to fully explore the potential of these ligands for selective oligomerization are in progress.

ASSOCIATED CONTENT

Supporting Information

Synthetic procedures, characterizing data, catalysis procedures, ethylene uptake data and crystallographic data in CIF format.
The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interests.

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excess of 95%. In contrast, even the best tetramerization catalysts give a yield of 1-octene in the region of 70 %, with the remainder being ~20% 1-hexene, and 10% other products. Typically, yields of 1-octene are lower, and any catalyst that produces more 1-octene than 1-hexene may be considered a tetramerization system.

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(27) The incorporation of 1-hexene and 1-octene into further tri-/tetramerization cycles to form branched C_{10-14} products is well documented. However, this incorporation is highly dependent upon the standing concentration of 1-hexene and 1-octene present in the reaction, and is hence strongly influenced by the product to solvent (P:S) ratio to which catalysis is operated. The catalysis herein, and that to which it is compared, was all operated to a P:S ratio in the region of 1:1.

1-Phosphanyl methanimine ligands, R_2P-C(Ph)=NR', may be prepared *via* a modular, convergent synthesis in good overall yield. Coordination chemistry studies with chromium confirm the ligands bind in a bidentate κ^2-*P,N* mode. In combination with a chromium source and an activator, these ligands promote the selective oligomerization of ethylene to 1-hexene and 1-octene with high activity. Notably, an exceptionally high liquid fraction selectivity to saleable products (1-hexene + 1-octene) is observed (>95%) along with a potent ligand dependence, such that selectivity can be varied from pure trimerization through tetramerization with a 1-octene to 1-hexene (OTH) ratio of 1.7.

OTH = 1-Octene to 1-Hexene