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N,N′-Bis(diphenylphosphino)diaminophenylphosphine Ligands for Chromium-Catalyzed Selective Ethylene Oligomerization Reactions

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Reaction of 1 or 2 equiv of Ph_2PCl with $PhP(N(H)R)_2$ (R = *n*-propyl) yields $Ph_2PN(R)P(Ph)N(R)H$ (**1**) or $Ph_2PN(R)P(Ph)N(R)PPh_2$ (**2**), respectively. In contrast, reaction of 1 or 2 equiv of Ph_2PCl with $PhP(N(H)R)_2$ (R = isopropyl) yields exclusively $Ph_2PN(R)P(Ph)N(R)H$ (**3**), even under more forcing conditions. Low-temperature NMR spectroscopy and a conformational analysis of $Ph_2PN(i\text{Pr})P(Ph)N(i\text{Pr})H$ (**3**) reveal the lowest energy conformer to have a close N−H···P interaction of 2.95 Å, which we speculate may hinder further reactivity of this molecule. Reaction of **3** with $[Cr(CO)_6]$ yields $[Cr(\mathbf{3})(CO)_4]$ (**5**), which has been structurally characterized. Coordination of ligand **3** facilitates its conversion to $Ph_2PN(i\text{Pr})P(Ph)N(i\text{Pr})PPh_2$ (**4**) while bound to chromium, yielding the complex $[Cr(\mathbf{4})(CO)_4]$ (**6**), which has also been structurally characterized. Ligands **1** and **2**, when reacted in situ with $[Cr(acac)_3]$ (acac = acetylacetonate) and modified methylalumoxane, and complexes **5** and **6**, when activated with $Ag[Al(OC_4F_9)_4]$ and triethylaluminum, are moderately active and selective catalysts for the selective oligomerization of ethene to 1-hexene and 1-octene.

Introduction

Catalysts capable of the selective trimerization or tetramerization of ethylene to 1-hexene or 1-octene via a distinctive metallacyclic mechanism have revolutionized olefin oligomerization.[1] In 2002, we reported catalysts based on chromium complexes of ligands of the type $Ar_2PN(Me)PAr_2$ (Ar = *o*-methoxy-substituted aryl group) with productivity figures over 1 order of magnitude better than for previous systems for selective ethylene trimerization.[2] This unprecedented performance led to interest both from a mechanistic viewpoint and in extending the range of substrates used in these reactions;[3] however, the most significant subsequent development has been the report from Bollmann and co-workers which demonstrated that relatively minor changes to ligand structure and reaction conditions can lead to ethylene tetramerization rather than trimerization.[4] A wider variety of diphosphine ligands has subsequently been investigated for these reactions with mixed results. Carbon-backboned diphosphines of the type 1,2-bis(diphenylphosphino)benzene[5] and $Ph_2PCH(R)PPh_2$ (R = alkyl group) have shown some promise.[6] However, in general, nitrogen-based backbone groups give the best results, including derivatives of the original *N,N*-bis(diarylphosphino)amines ("PNP") and *N,N′*-bis(diarylphosphino)hydrazines ("PNNP"). The reasons for this are yet to be fully defined, although in the case of PNP ligands delocalization of the nitrogen lone pair over the entire PNP chelate could be significant. We were interested in extending this series, not least to explore the role of increasing bite angle on catalysis. Longer chain phosphazane ligands such as *N,N′*-bis(diarylphosphino)diaminoarylphosphine ("PNPNP") are known and show some interesting coordination chemistry,[7] but their application in chromium-catalyzed ethylene oligomerization has been unexplored.[8] The synthesis and catalytic screening of such complexes are reported here.

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(1) (a) Dixon, J. T.; Green, M. J.; Hess, F. M.; Morgan, D. H. *J. Organomet. Chem.* **2004**, *689*, 3641. (b) Wass, D. F. *Dalton Trans.* **2007**, 816.

(2) Carter, A.; Cohen, S. A.; Cooley, N. A.; Murphy, A.; Scutt, J.; Wass, D. F. *Chem. Commun.* **2002**, 858.

(3) (a) Agapie, T.; Schofer, S. J.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2004**, *126*, 1304. (b) Blann, K.; Bollmann, A.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M. J. *Chem. Commun.* **2005**, 620. (c) Overett, M. J.; Blann, K.; Bollmann, A.; Dixon, J. T.; Hess, F.; Killian, E.; Maumela, H.; Morgan, D. H.; Neveling, A.; Otto, S. *Chem. Commun.* **2005**, 622. (d) Bowen, L. E.; Wass, D. F. *Organometallics* **2006**, *25*, 555. (e) Bowen, L. E.; Charernsuk, M.; Wass, D. F. *Chem. Commun.* **2007**, 2835. (f) Blann, K.; Bollmann, A.; De Bod, H.; Dixon, J. T.; Killian, E.; Nongodlwana, P.; Maumela, M. C.; Maumela, H.; McConnell, A. E.; Morgan, D. H.; Overett, M. J.; Pretorius, M.; Kuhlmann, S.; Wasserscheid, P. *J. Catal.* **2007**, *249*, 244. (g) McGuinness, D. S.; Overett, M.; Tooze, R. P.; Blann, K.; Dixon, J. T.; Slawin, A. M. Z. *Organometallics* **2007**, *26*, 1108. Hey, T. W.; Wass, D. F. *Organometallics* **2010**, *29* (16), 3676. Bowen, L. E.; Charernsuk, M.; Hey, T. W.; McMullin, C. L.; Orpen, A. G.; Wass, D. F. *Dalton Trans.* **2010**, *39*, 560.

(4) Bollmann, A.; Blann, K.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H; McGuiness, D. S.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M.; Slawin, A. M. Z.; Wasserscheid, P.; Kuhlmann, S. *J. Am. Chem. Soc.* **2004**, *126*, 14712.

(5) Overett, M. J.; Blann, K.; Bollmann, A.; de Villiers, R.; Dixon, J. T.; Killian, E.; Maumela, M. C.; Maumela, H.; McGuinness, D. S.; Morgan, D. H.; Rucklidge, A.; Slawin, A. M. Z. *J. Mol. Catal. A: Chem.* **2008**, *283*, 114.

(6) Dulai, A.; de Bod, H.; Hanton, M. J.; Smith, D. M.; Downing, S.; Mansell, S. M.; Wass, D. F. *Organometallics* **2009**, *28*, 4613.

(7) Appleby, T.; Woollins, J. D. *Coord. Chem. Rev.* **2002**, *235*, 121.

(8) Ligands with a "PNPN" framework have been disclosed: Müller, B. H., Fritz, P. M.; Bölt, H.; Wöhl, A.; Müller, W.; Winkler, F.; Wellenhofer, A.; Rosenthal, U.; Hapke, M.; Peulecke, N.; Al-Hazmi, M. H.; Aliyev, O. V.; Mosa, M. F. *PCT Pat. Appl.* WO09006979, 2009. Peitz, S.; Peulecke, N.; Aluri, B. R.; Hansen, S.; Müller, B. H.; Spannenberg, A.; Rosenthal, U.; Al-Hazmi, M. H.; Mosa, F. M.; Wöhl, A.; Müller, W. *Eur. J. Inorg. Chem.* **2010**, 1167. Peitz, S.; Peulecke, N.; Aluri, B. R.; Mueller, B. H.; Spannenberg, A.; Rosenthal, U.; Al-Hazmi, M. H.; Mosa, F. M.; Woehl, A.; Mueller, W. *Organometallics* **2010**, *29*, 5263.

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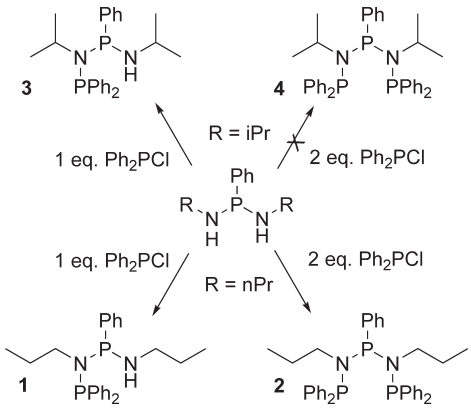
Scheme 1. Synthesis of 1−3 and Attempted Synthesis of 4



Results and Discussion

We focused on the synthesis of $Ph_2PN(R)P(Ph)N(R)PPh_2$ (R = *n*-propyl, isopropyl), using a methodology based on that reported by Keat and co-workers[9] for other derivatives (R = methyl, ethyl). This involves the initial synthesis of $PhP(N(H)R)_2$ from $PhPCl_2$ and 2 equiv of the desired primary amine, followed by further reaction with 1 equiv of Ph_2PCl in the presence of triethylamine to yield $Ph_2PN(R)P(Ph)N(R)H$ or further reaction with 2 equiv of Ph_2PCl in the presence of triethylamine to yield $Ph_2PN(R)P(Ph)N(R)PPh_2$ (Scheme 1).

This sequence proceeded smoothly when R = *n*-propyl to give **1** and **2**, albeit in poor to moderate (12 and 30%) yields. In contrast, when R = isopropyl, reaction with 1 or 2 equiv of Ph_2PCl gives only **3** in both cases. We reasoned that more forcing conditions might be needed to obtain the more bulky PNPNP compound **4** in this case, but **3** persists as the only product even with a 10-fold excess of Ph_2PCl, with more potent bases (MeLi, ^{n}BuLi, DBU), over extended reaction times (72 h), or at higher temperature (reflux in 1,1,2,2-tetrachloroethane). ^{31}P NMR spectroscopy also revealed differences between these derivatives; whereas **1** gives the expected pattern of two sets of sharp doublets (at 48.6 and 88.6 ppm) at room temperature, **3** gives a rather broad spectrum with two singlets (at 41.2 and 68.4 ppm). This is presumably due to the bulkier isopropyl groups causing restricted rotation about the P−N bonds, and in order to examine this further, the ^{31}P NMR spectra of **3** at lower temperatures were recorded (Figure 1).

To our surprise, when the sample is cooled, the expected pattern of two doublets is not observed; six doublets are observed, suggesting that there are three species present, each with two inequivalent phosphorus atoms. We speculated that these three species originate from different conformers of **3**, which interconvert on the NMR time scale at room temperature. Similar behavior is known for related systems; in a study of bis(isopropylamino)phenylphosphine, Eichorn and co-workers used ab initio calculations to determine its four lowest energy conformers.[10] In order to further examine the results of the variable-temperature NMR experiment, a molecular mechanics conformer search was carried out on the free ligand with geometry taken from the crystal structure of the chromium(0) complex **5** (see Figure 3). The eight lowest

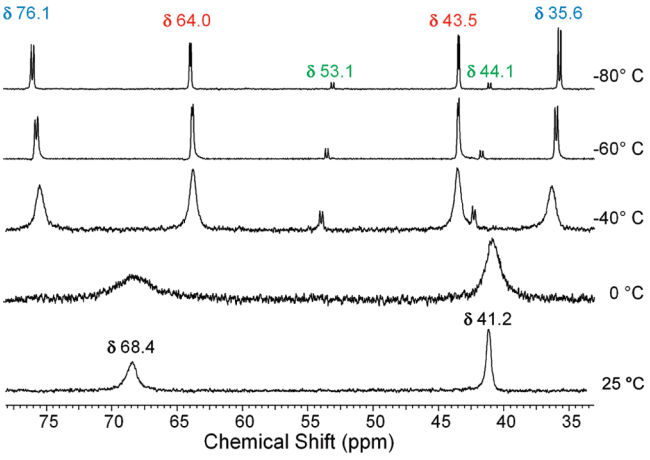


Figure 1. Variable-temperature ^{31}P NMR spectra of **3**.

energy unique structures from this conformer search were then optimized using density functional theory calculations (B3LYP/6-31G*)[11] to improve the predicted energetic ranking for each isomer. Two of the eight optimized conformer geometries were identical; the remaining seven geometries were labeled **3a**−**g** and evaluated further; we focus here on the three lowest energy conformers, and structural data for all are available in the Supporting Information.

The two lowest energy conformers (**3a**,**b**) are not preorganized for transition-metal complexation and have the lone pairs of the phosphorus atoms (P1 and P2) pointing in opposite directions; coordination as a chelate would require rotation about the P1−N1 bond. In conformer **3a**, the terminal nitrogen atom, N2, has a very planar geometry, with the angles around N2 totaling 349.5°. Inversion of this planar N2 and subsequent rotation of the isopropyl group about the N2−C1 bond gives rise to conformer **3b**, which has a slightly more pyramidal geometry around N2, with a smaller sum of angles around N2 at 344.0°. The extra stabilization of **3a** might arise from an anomeric effect,[12] where the lone pair (from a p orbital) of N2 delocalizes into the antibonding σ^* (P1−N1) orbital, while in **3b** the lone pair (sp^3 hybridized orbital) of N2 has poorer overlap with the antibonding orbital and a higher relative energy (by 2.5 kcal mol^{-1}). Due to the different N2 hybridization environments and energy differences between conformers **3a**,**b**, we suggest that these might be seen as two distinct conformers, which would give rise to different peak splittings in a ^{31}P NMR spectrum.

Conformer **3c** (also seen in Figure 2) has the same geometry as seen in the crystal structure for the complexed ligand (**5**·0.5CH_2Cl_2), with the lone pairs of each phosphorus atom pointing toward one another, ready for complexation.

An interesting feature of conformations **3a**,**b** is the close proximity of H1 to P2. The distances (2.95 and 2.82 Å) are significantly shorter for these conformers compared to those for the conformers **3c**−**g** (~4.5 Å). As can be seen in Figure 2, the orientation of conformers **3a**,**b** suggests the amine proton

(9) Keat, R.; Sim, W.; Payne, D. S. *J. Chem. Soc. A* **1970**, 2715.
(10) Eichhorn, B.; Nöth, H.; Seifert, T. *Eur. J. Inorg. Chem.* **1999**, 2355.
(11) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C.; Yang, W.; Parr, B. G. *Phys. Rev. B* **1988**, *37*, 785–789. (c) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200–1211. (d) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623–11627.
(12) Belyakov, A. V.; Haaland, A.; Shorokhov, D. J.; Sokolov, V. I.; Swang, O. *J. Mol. Struct.* **1998**, *445*, 303–309.

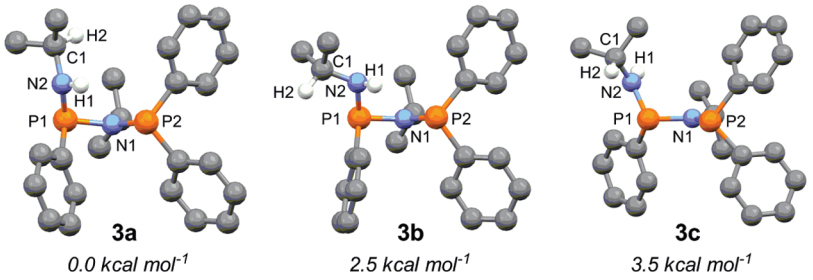


Figure 2. Geometries of ligand **3** suggested by conformer analysis as the three observed isomers at low temperature NMR, with hydrogens (except for H1 and H2) omitted for clarity. Relative energies are given in kcal mol^{-1}.

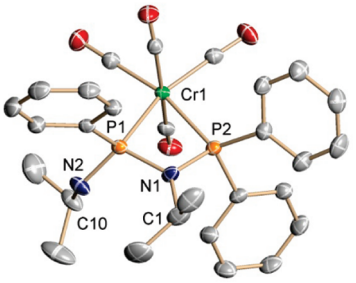


Figure 3. Thermal ellipsoid plot of **5**·0.5 CH_2Cl_2. Ellipsoids are drawn at the 50% probability level. All hydrogen atoms and the solvate have been omitted for clarity.

H1 is sterically shielded by the neighboring isopropyl group and the phenyl ring of the adjacent phosphorus atom, potentially making it less accessible. This may help to explain why reaction of **3** with another 1 equiv of Ph_2PCl to yield **4** proved so difficult.

A potential solution to these synthetic challenges presented itself by exploiting a metal templating strategy. We hypothesized that coordination of **3** in a chelating fashion to a transition metal would not allow a conformation in this ligand akin to that of **3a**,**b** but rather would reduce the steric shielding of H1, making it potentially reactive. We have previously used coordination of diphosphines to [$Cr(CO)_4$] fragments as a "protection" strategy in the synthesis of C-substituted bis(diphenylphosphino)methane derivatives;[6] this has a number of advantages, including ease of synthesis of the complexes, the utility of [(diphosphine)$Cr(CO)_4$] complexes as model compounds in which steric and electronic factors can be probed, and, perhaps most importantly, the fact that such complexes are precatalysts for selective oligomerization catalysis via a one-electron-oxidation method.[13]

Complex **5** was obtained by the reaction of **3** with chromium hexacarbonyl (Scheme 2).[14] The expected ^{31}P NMR spectrum is obtained with two sharp doublets, both shifted downfield compared to the free ligand, indicating rotation around the P−N bond is now frozen on the NMR time scale.

Crystals of complex **5**·0.5CH_2Cl_2 suitable for X-ray diffraction study were grown by slow diffusion of hexane into a concentrated CH_2Cl_2 solution of the complex at −20 °C, and the complex crystallized in the space group *Pbca*. The molecular structure of **5** is shown in Figure 3, with key bond lengths and angles being given in Table 1. Ligand **3** coordinates through the two phosphorus atoms to the octahedral chromium(0) metal center in a fashion similar to that for known PNP chelates. It has a bite angle, P1−Cr1−P2, of 67.95(2)°; the bite angle in the complex [$Cr(CO)_4(Ar_2PN(Me)PAr_2)$] is 68.44(3)°, where Ar is C_6H_4(*o*-OMe).[11b] In this sense the ligand can be seen as a simple asymmetric PNP ligand. The fold angle between the P1−Cr1−P2 plane and the P1−N1−P2 plane is 8.11(1)°, making the P1−Cr1−P2−N1 ring close to planar. The central carbon (C1) of the isopropyl substituent at N1 lies close to this plane; C1 is only 0.196(4) Å above the P1−N1−P2 plane. The P−N bonds in the chelate ring (P1−N1 = 1.719(2) Å and P2−N1 = 1.6932(19) Å) are slightly longer than the P1−NH^iPr bond (P1−N2 = 1.648(2) Å) due to the more planar nature of the bridging nitrogen atom (N1).

Scheme 2. Synthesis of 5 and 6

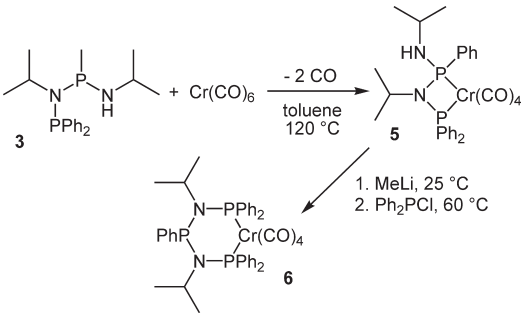


Table 1. Key Bond Lengths (Å) and Angles (deg) for 5·0.5CH_2Cl_2

Cr1−P1	2.3592(6)	P1−N2	1.648(2)
Cr1−P2	2.3380(7)	P1−N1	1.719(2)
		P2−N1	1.6932(19)
P1−Cr1−P2	67.95(2)	P1−N1−P2	100.57(10)

With compound **5** in hand, we were satisfied to observe that reaction with Ph_2PCl in the presence of MeLi base proceeded smoothly to give the PNPNP ligand complex [(**4**)$Cr(CO)_4$] (**6**) in good yield (51%) (Scheme 2). Simultaneous rearrangement gives a product in which the newly formed PNPNP ligand **4** coordinates through its terminal phosphorus atoms, as determined from its ^{31}P NMR spectrum, which displays the expected doublet and triplet.

Crystals of complex **6**·2.5CH_2Cl_2 suitable for X-ray diffraction study were grown by slow diffusion of hexane into a concentrated CH_2Cl_2 solution of the complex at −20 °C, and the complex crystallized in space group $P2_1/c$. The molecular

(13) (a) Rucklidge, A. J.; McGuinness, D. S.; Tooze, R. P.; Slawin, A. M. Z.; Pelletier, J. D. A.; Hanton, M. J.; Webb, P. B. *Organometallics* **2007**, *26*, 2782. (b) Bowen, L. E.; Haddow, M.; Orpen, A. G.; Wass, D. F. *Dalton Trans.* **2007**, 1160.

(14) (a) Balakrishna, M. S.; Prakasha, T. K.; Krishnamurthy, S. S.; Siriwardane, U.; Hosmane, N. S. *J. Organomet. Chem.* **1990**, *390*, 203. (b) Compound **5** was recently independently reported: Aluri, B. R.; Peulecke, N.; Peitz, S.; Spannenberg, A.; Mueller, B. H.; Schulz, S.; Drexler, H.-J.; Heller, D.; Al-Hazmi, M. H.; Mosa, F. M.; Woehl, A.; Mueller, W.; Rosenthal, U. *Dalton Trans.* **2010**, *39*, 7911.

structure of complex **6** is shown in Figure 4. Key bond lengths and angles are summarized in Table 2.

The structure of **6** has approximate mirror symmetry through the Cr1−P2 plane and bisecting the six-membered chelate ring, with a bite angle of 93.20(4)°. The chelate ring has a "boat-like" conformation, with Cr1 and P2 sitting above the P1−N1−N2−P3 plane by 0.530(4) and 0.687(6) Å, respectively.

Complexes **5** and **6** were investigated by cyclic voltammetry to ensure that the chromium(I) analogues of these complexes could be accessed using $Ag[Al(OC(CF_3)_3)_4]$. Values for $E_{1/2}$ of 0.75 and 0.72 V, respectively, at a scan rate of 250 mV s^{-1} versus a saturated calomel electrode (SCE) indicate that this is the case.

Ligands **1**−**3** and complexes **5** and **6** were all screened for ethylene oligomerization using established methods. The ligands were tested in conjunction with chromium tris(acetylacetonate) as the chromium source and MMAO as the activator;[2−5] the complexes were used in conjunction with $Ag[Al(OC(CF_3)_3)_4]$ as an in situ oxidizing agent and TEA as a carbonyl scavenger.[13] Results of the screening are summarized in Table 3.

Ligands **1** and **3** (runs 1 and 3), with a PNPN structure, give moderately productive catalysts that have good selectivity to 1-hexene and 1-octene.[8] Interestingly, for ligand **3** we observed more octene than hexene, in contrast to literature reports of high 1-hexene selectivity for this particular derivative. Selective olefin oligomerization catalysts are known to be highly sensitive to reaction conditions (pressure, temperature, activation method), and we attribute this surprising difference to the slightly different conditions employed. Comparison of runs 3 and 4, in which the same ligand **3** is tested using different activation methods, shows that MMAO activation of an in situ formed chromium complex (run 3) gives a higher productivity value; a similar trend is observed for PNP complex activation.[13] Within error, the selectivity is not influenced, suggesting that the same active species is formed with either method. The PNPNP ligand **2** and complex **6** (runs 2 and 5) yield catalysts with productivity values similar to those for these other systems. However, there is a marked influence on selectivity with the *N*-*n*-propyl substituted system **2** (run 2) favoring 1-hexene over 1-octene (60.0% to 31.3%) and the *N*-isopropyl-substituted system **6** (run 5) favoring 1-octene over 1-hexene (57.1% to 28.6%). Although we necessarily need to use different activation methods for these derivatives and cannot completely rule this out as the source of the observed difference in selectivity, the previous comparison of runs 3 and 4 in terms of selectivity gives us confidence this is a ligand-based structure−property relationship. The performance of these PNPNP ligands does not match that of the related PNP ligands (for example, $Ph_2PN(iPr)PPh_2$ tested under similar conditions[3g] gives a productivity of 139 800 g/((g of Cr) h) and over 70% selectivity to octene), suggesting that smaller bite angles are to be preferred. However, it is perhaps surprising that PNPNP still outperforms many carbon-backboned diphosphine ligands which initially seem to be closer analogues of the PNP ligands (for example, bis(diphenylphosphino)methane or bis(diphenylphosphino)ethane).[6]

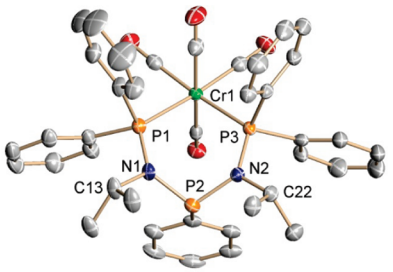


Figure 4. Thermal ellipsoid plot of $6\cdot 2.5CH_2Cl_2$. Ellipsoids are drawn at the 50% probability level. All hydrogen atoms and the solvate have been omitted for clarity.

Table 2. Key Bond Lengths (Å) and Angles (deg) for $6\cdot 2.5CH_2Cl_2$

Cr1−P1	2.3792(12)	P1−N1	1.710(4)
Cr1−P3	2.3797(13)	P2−N1	1.721(4)
N1−C13	1.522(6)	P2−N2	1.715(4)
N2−C22	1.517(5)	P3−N2	1.710(3)
P1−Cr1−P3	93.20(4)	P2−N2−P3	126.2(2)
N1−P2−N2	107.50(16)	N1−P1−Cr1	119.15(13)
P1−N1−P2	125.8(2)	N2−P3−Cr1	119.58(13)

Conclusions

We have synthesized $Ph_2PN(R)P(Ph)N(R)H$ (R = *n*Pr, *i*Pr) and $Ph_2PN(R)P(Ph)N(R)PPh_2$ (R = *n*Pr). Low-temperature NMR spectroscopy and a conformational analysis of the latter compound revealed the lowest energy conformer to have a close N−H···P interaction of 2.95 Å, which may explain the lack of further reactivity of this molecule. This problem was overcome by coordination of the ligand to chromium, allowing its conversion to $Ph_2PN(iPr)P(Ph)N(iPr)PPh_2$ while bound to the metal. The ligands and complexes are moderately active and selective catalysts for the selective oligomerization of ethene to 1-hexene and 1-octene.

Experimental Section

General Considerations. All procedures were carried out under an inert (N_2) atmosphere using standard Schlenk line techniques or in an inert-atmosphere (Ar) glovebox. Chemicals were obtained from Sigma Aldrich or Fisher Scientific and used without further purification unless otherwise stated. Modified

Table 3. Ethylene Oligomerization Results

				oligomers (wt % of total products)			
run	cat.	productivity (g/((g of Cr) h))	polymer (%)	C_4	C_6 (1-C_6)	C_8 (1-C_8)	C_{10+}
1[a]	**1**	6 460	2.7	6.2	34.6 (89.9)	54.1 (99.2)	2.2
2[a]	**2**	34 100	2.9	3.1	60.0 (89.6)	31.3 (98.2)	2.9
3[a]	**3**	78 930	2.2	5.4	34.3 (96.7)	44.9 (99.5)	13.2
4[b]	**5**	45 060	2.0	4.7	37.2 (96.4)	47.1 (99.8)	9.0
5[b]	**6**	37 850	1.0	6.1	28.6 (91.9)	57.1 (99.4)	7.2

[a]Run conditions: 10 μmol of $[Cr(acac)_3]$, 20 μmol of ligand, chlorobenzene diluent, 20 bar of ethylene, 60 °C, 500 equiv of MMAO. [b]Run conditions: 10 μmol of complex, 20 μmol of $Ag[AlO\{OC(CF_3)_3)_4]$, 300 equiv of TEA, chlorobenzene diluent, 20 bar of ethylene, 60 °C.

methylaluminoxane (MMAO) was obtained from Akzo-Nobel as a 7 wt % solution in hexane. 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 dichloromethane. NMR spectra were recorded on a JEOL ECP 300 spectrometer at 300 MHz (^{1}H) and 121 MHz (^{31}P{^{1}H}), a JEOL Delta 400 at 200.6 MHz (^{13}C{^{1}H}), and a JEOL Lambda 300 at 282 MHz (^{19}F), in deuterated solvent. ^{1}H and ^{13}C{^{1}H} NMR spectra are referenced with chemical shifts relative to the high frequency of residual solvent, ^{31}P NMR spectra are referenced relative to the high frequency of 85% H_3PO_4, and ^{19}F NMR spectra are referenced relative to the high frequency of CCl_3F. Mass spectrometry was carried out by the Mass Spectrometry Service at the School of Chemistry at the University of Bristol. Microanalyses were carried out by the Microanalytical Laboratory of the School of Chemistry at the University of Bristol. Electrochemical studies were carried out using an EG&G Model 273A potentiostat linked to a computer using EG&G Model 270 Research Electrochemistry software in conjunction with a three-electrode cell. The working electrode was a platinum disk (1.6 mm diameter) and the auxiliary electrode a platinum wire. The reference was an aqueous saturated calomel electrode separated from the test solution by a fine-porosity frit and an agar bridge saturated with KCl. Solutions were 1.0 mM in the test compound and 0.1 M in [^{n}Bu$_4$N][PF$_6$] as the supporting electrolyte. The solvent used was CH_2Cl_2. Under these conditions, $E_{1/2}$ values for the one-electron oxidation of [Fe(η^5-C_5H_5)$_2$] and [Fe(η^5-C_5(CH$_3$)$_5$)$_2$] are 0.47 and −0.08 V, respectively. In each experiment, one of these was added to the test solutions as an internal calibrant.

Bis(isopropylamino)phenylphosphine. This was prepared using a modification of the method of Eichhorn et al.[10] Isopropylamine (9.45 mL; 6.50 g; 0.11 mol) was dissolved in diethyl ether (100 mL) and cooled to 0 °C. Phenyldichlorophosphine (3.00 mL; 4.00 g; 0.02 mol) in diethyl ether (20 mL) was added to this dropwise over 10 min with stirring. A white precipitate formed almost immediately. The mixture was warmed to room temperature and stirred for 16 h. It was then filtered and the solid washed with diethyl ether (2 × 50 mL). The filtrate and washings were combined and the solvents removed under reduced pressure to give the desired compound as a viscous cream-colored liquid (3.70 g; 74%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.17 (d, 6H, $^3J_{H-H}$ = 6.4 Hz, CH_3), 1.21 (d, 6H, $^3J_{H-H}$ = 6.2 Hz, CH_3), 2.01 (d, 2H, $^2J_{P-H}$ = 7.7 Hz, NH), 3.30 (m, 2H, CH), 7.28 (m, 1H, ArH), 7.35 (m, 2H, ArH), 7.63 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ 26.6 (d, $^3J_{C-P}$ = 5.8 Hz, CH_3), 26.9 (d, $^3J_{C-P}$ = 2.9 Hz, CH_3), 46.2 (d, $^2J_{C-P}$ = 16.7 Hz, CH), 127.7 (s, CH), 128.0 (d, J_{C-P} = 3.5 Hz, CH), 130.7 (d, $^1J_{C-P}$ = 15.6 Hz, CP), 141. Six (d, J_{C-P} = 7.5 Hz, CH). ^{31}P NMR ($CDCl_3$, 121 MHz): δ 58.5 (s). Anal. Calcd for $C_{12}H_{21}N_2P$: C, 64.26; H, 9.44; N, 12.49. Found: C, 65.78; H, 10.01; N, 12.23.

Bis(*n*-propylamino)phenylphosphine. This compound was prepared as above using *n*-propylamine (11.20 mL; 8.00 g; 0.14 mol) and phenyldichlorophosphine (4.10 mL; 5.40 g; 0.03 mol) to give a viscous colorless liquid (3.20 g; 48%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.95 (t, 6H, $^3J_{H-H}$ = 7.4 Hz, CH_3), 1.55 (m, 4H, CH_2CH$_3$), 2.22 (br, m, 2H, NH), 2.88 (m, 4H, NCH_2), 7.29 (m, 1H, ArH), 7.37 (m, 2H, ArH), 7.63 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ 11.7 (s, CH_3), 26.4 (d, $^3J_{C-P}$ = 5.4 Hz, CH_2CH$_3$), 45.8 (d, $^2J_{C-P}$ = 11.5 Hz, NCH_2), 128.1 (d, J_{C-P} = 4.6, CH), 127.8 (s, CH), 130.7 (d, $^1J_{C-P}$ = 14.6 Hz, CP), 142.0 (d, J_{C-P} = 6.2 Hz, CH). ^{31}P NMR ($CDCl_3$, 121 MHz): δ 65.7 (s); Anal. Calcd for $C_{12}H_{21}N_2P$: C, 64.26; H, 9.44; N, 12.49. Found: C, 64.70; H, 9.03; N, 11.88.

Ph$_2$PN(*n*Pr)PPhN(*n*Pr)H (1). This compound was prepared using a modification of the method of Maumela et al.[15] Chlorodiphenylphosphine (1.21 mL; 1.49 g; 6.70 mmol) was dissolved in CH_2Cl_2 (60 mL) and cooled to 0 °C. To this was added dropwise a solution of bis(*n*-propylamino)phenylphosphine (1.50 g; 6.70 mmol) and triethylamine (0.94 mL; 0.68 g; 6.7 mmol) over 10 min with stirring. The mixture was warmed to room temperature and stirred for 3 h. The volatiles were removed under reduced pressure, and diethyl ether (80 mL) was added. The solution was then filtered, and the remaining solid was washed with diethyl ether (2 × 30 mL). The washings and filtrate were combined, and the solvent was removed under reduced pressure to give a tacky, cream-colored solid. The solid was triturated with hexane (50 mL), and the resulting cloudy solution was passed through a column of neutral alumina. Recrystallization from hot ethanol afforded **1** as a white solid (0.32 g; 12%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.59 (t, 3H, $^3J_{H-H}$ = 7.3 Hz, CH_3), 0.97 (t, 3H, $^3J_{H-H}$ = 7.4 Hz, CH_3), 1.20 (m, 2H, CH_2), 1.60 (m, 2H, CH_2), 2.62 (m, 1H, NH), 3.09 (m, 2H, NCH_2), 3.20 (m, 2H, NCH_2), 7.37 (m, 10H, ArH), 7.46 (m, 3H, ArH), 7.55 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ 11.4, 11.6 (s, CH_3), 25.8 (d, $^3J_{C-P}$ = 4.6 Hz CH_2), 26.5 (d, $^3J_{C-P}$ = 8.5 Hz, CH_2), 48.5 (d, $^2J_{C-P}$ = 26.2 Hz, NCH_2), 52.9 (d, $^2J_{C-P}$ = 21.3 Hz, NCH_2), 129.1 (s, CH), 130.7 (d, J_{C-P} = 16.9 Hz, CP), 131.8 (d, J_{C-P} = 19.2 Hz, CH), 133.6 (d, $^1J_{C-P}$ = 22.2 Hz, CP), 139.4 (d, J_{C-P} = 2.3 Hz, CH), 139. Six (d, J_{C-P} = 2.3 Hz, CH), 140.4 (d, J_{C-P} = 4.6 Hz), 144.2 (d, $^1J_{C-P}$ = 7.9 Hz, CH). ^{31}P NMR ($CDCl_3$, 121 MHz): δ 88.6 (d, $^2J_{P-P}$ = 50.2 Hz, PPh), 48.6 (d, $^2J_{P-P}$ = 50.2 Hz, PPh_2). Anal. Calcd for $C_{24}H_{30}N_2P_2$: C, 70.57; H, 7.40; N, 6.86. Found: C, 70.32; H, 7.37; N, 6.82.

Ph$_2$PN(*n*Pr)PPhN(*n*Pr)PPh$_2$ (2). Chlorodiphenylphosphine (2.78 mL; 3.39 g; 15.00 mmol) was dissolved in CH_2Cl_2 (60 mL) and cooled to 0 °C. To this was added a solution of bis(*n*-propylamino)phenylphosphine (1.68 g; 7.50 mmol) and triethylamine (2.62 mL; 1.90 g; 19.00 mmol) in CH_2Cl_2 (20 mL). The solution was warmed to room temperature and stirred for 3 h. After this time, the volatiles were removed under reduced pressure and diethyl ether (80 mL) was added. The mixture was filtered and the solid washed with diethyl ether (2 × 30 mL). The filtrate and washings were combined, and the solvent was removed under reduced pressure to give a tacky, pale pink solid. This was triturated with hexane (40 mL) and filtered. When the filtrate was cooled, a white solid was obtained (1.30 g; 30%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.47 (t, 6H, $^3J_{H-H}$ = 7.3 Hz, CH_3), 1.07 (m, 2H, CH_2), 1.41 (m, 2H, CH_2), 2.83 (m, 2H, NCH_2), 3.23 (m, 2H, NCH_2), 7.32 (m, 10H, ArH), 7.43 (m, 12H, ArH), 7.59 (m, 3H, ArH). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ 11.1 (s, CH_3), 22.8 (d, $^3J_{C-P}$ = 3.8 Hz CH_2), 25.3 (d, $^3J_{C-P}$ = 3.6 Hz, CH_2), 53.2 (t, $^2J_{C-P}$ = 5 Hz, CH_2), 53.4 (t, $^2J_{C-P}$ = 5 Hz, CH_2), 128.0 (t, J_{C-P} = 2.9 Hz, CH), 128.1 (t, J_{C-P} = 3.1 Hz, CH), 128.3 (d, J_{C-P} = 1.5 Hz, CH), 131.5 (d, $^1J_{C-P}$ = 18.5 Hz, CP), 132.9 (t, J_{C-P} = 15.6 Hz, CH), 133.4 (t, J_{C-P} = 16.1 Hz, CP), 139.9 (d, J_{C-P} = 2.3 Hz, CH), 140.6 (d, J_{C-P} = 5.4 Hz, CH). ^{31}P NMR ($CDCl_3$, 121 MHz): δ 106.3 (t, $^2J_{P-P}$ = 24.2 Hz, PPh), 53.8 (d, $^2J_{P-P}$ = 24.5 Hz, PPh_2). Anal. Calcd for $C_{36}H_{39}N_2P_3$: C, 72.96; H, 6.63; N, 4.73. Found: C, 72.74; H, 6.83; N, 4.67.

Ph$_2$PN(*i*Pr)PPhN(*i*Pr)H (3). This compound was synthesized by the same method as for **1** using chlorodiphenylphosphine (1.29 mL; 1.58 g; 7.20 mmol), bis(isopropylamino)phenylphosphine (1.53 g; 6.8 mmol), and triethylamine (1.00 mL; 0.73 g; 7.20 mmol) in CH_2Cl_2, The solvent was removed under reduced pressure to give a colorless, highly viscous liquid. Recrystallization from hot ethanol afforded **3** as a waxy, white solid (0.64 g; 23%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.21 (d, 3H, $^3J_{H-H}$ = 6.6 Hz, CH_3), 1.23 (d, 3H, $^3J_{H-H}$ = 6.5 Hz, CH_3), 1.25 (d, 3H, $^3J_{H-H}$ = 6.5 Hz, CH_3), 1.29 (d, 3H, $^3J_{H-H}$ = 6.4 Hz, CH_3), 2.59 (br, dd, 1H, $^2J_{P-H}$ = 10.9 Hz, $^3J_{H-H}$ = 6.1 Hz, NH), 3.25 (m, 1H, CH), 3.58 (m, 1H, CH), 7.34 (m, 5H, ArH), 7.42 (m, 10H, ArH). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ 25.2 (dd, $^3J_{C-P}$ = 11.2 Hz, 3.5 Hz, CH_3), 25.4 (t, $^3J_{C-P}$ = 6.1 Hz, CH_3), 26.1 (d, $^3J_{C-P}$ = 5.4 Hz, CH_3), 26.2 (d, $^3J_{C-P}$ = 6.2 Hz, CH_3), 46.9 (d, $^2J_{C-P}$ = 28.4 Hz, CH), 50.2 (dd, $^2J_{C-P}$ = 15.0 Hz, 5.0 Hz, CH), 130.7 (d, J_{C-P} = 17.7 Hz, CH), 132.8 (d, J_{C-P} = 19.9 Hz, CP), 133.2 (d, J_{C-P} = 2.3 Hz, CH), 133.4 (d, J_{C-P} = 1.5 Hz, CH), 139.7 (d, $^1J_{C-P}$ = 16.9 Hz, CP), 141.2 (d, J_{C-P} = 4.3 Hz, CH), 141.5

(15) Maumela, M. C.; Blann, K.; de Bod, H.; Dixon, J. T.; Gabrielli, W. F.; Williams, D. B. G. *Synthesis* **2007**, *24*, 3863.

(d, J_{C-P} = 3.8 Hz, *C*H), 144.9 (d, $^1J_{C-P}$ = 6.9 Hz, *C*H). ^{31}P NMR ($CDCl_3$, 121 MHz): δ 68.4 (br s, *P*Ph), 41.7 (br s, *P*Ph_2). Anal. Calcd for $C_{24}H_{30}N_2P_2$: C, 70.57; H, 7.40; N, 6.86. Found: C, 70.49; H, 7.25; N, 6.80.

[Cr(CO)$_4$(3)] (5). Compound **3** (0.20 g; 0.34 mmol) and chromium hexacarbonyl (0.15 g; 0.68 mmol) were dissolved in toluene (30 mL). The mixture was heated at reflux for 72 h. It was then cooled to room temperature and filtered, and the solvents were removed under reduced pressure. The resulting crude product was recrystallized from CH_2Cl_2 and hexane to give **5** as yellow plates (0.14 g; 74%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.60 (d, 3H, $^3J_{H-H}$ = 6.6 Hz, C*H*$_3$), 1.19 (d, 3H, $^3J_{H-H}$ = 6.8 Hz, C*H*$_3$), 1.43 (d, 3H, $^3J_{H-H}$ = 6.2 Hz, C*H*$_3$), 1.49 (d, 3H, $^3J_{H-H}$ = 6.4 Hz, C*H*$_3$), 3.64 (d, 1H, $^2J_{P-H}$ = 9.3 Hz, N*H*), 3.64 (m, 1H, C*H*), 4.12 (m, 1H, C*H*), 7.41 (m, 3H, Ar*H*), 7.48 (m, 3H, Ar*H*), 7.58 (m, 5H, Ar*H*), 7.64 (m, 2H, Ar*H*), 7.89 (m, 2H, Ar*H*). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ 20.9, 24.5 (s, *C*H$_3$), 26.2 (d, $^3J_{C-P}$ = 3.8 Hz, *C*H$_3$), 26.8 (d, $^3J_{C-P}$ = 3.8 Hz, *C*H$_3$), 47.7 (d, $^2J_{C-P}$ = 11.5 Hz, *C*H), 55.0 (t, $^2J_{C-P}$ = 6.3 Hz, *C*H), 128.3 (d, J_{C-P} = 9.9 Hz, *C*H), 128.5 (d, J_{C-P} = 9.2 Hz, *C*H), 128.7 (d, $^1J_{C-P}$ = 10.0 Hz, *C*P), 130.0 (d, J_{C-P} = 1.5 Hz, *C*H), 130.2 (d, J_{C-P} = 2.3 Hz, *C*H), 130.7 (d, J_{C-P} = 3.1 Hz, *C*H), 131.23 (d, J_{C-P} = 2.4 Hz, *C*H), 133.32 (d, $^1J_{C-P}$ = 14.6 Hz, *C*P). ^{31}P NMR ($CDCl_3$, 121 MHz): δ 102.2 (d, $^2J_{P-P}$ = 42.7 Hz, *P*Ph), 121.2 (d, $^2J_{P-P}$ = 42.7 Hz, *P*Ph_2); Mass spectrometry (EI, CH_2Cl_2): *m*/*z* 572.1 (M^+). Anal. Calcd for $C_{28}H_{32}CrNO_4P_2$: C, 58.33; H, 5.94; N, 4.86. Found: C, 58.65; H, 5.37; N, 4.65; IR (toluene): ν 1893 (C≡O), 1919 (C≡O), 1969 (C≡O), 2006 cm^{-1} (C≡O). $E_{1/2}$ = 0.75 V vs SCE.

[Cr(CO)$_4$(Ph$_2$PN(*i*Pr)P(Ph)N(*i*Pr)PPh$_2$)] (6). Compound **5** (0.06 g; 0.11 mmol) was dissolved in benzene (5 mL) to give a clear yellow solution. To this was added dropwise MeLi (1.6 M in diethyl ether; 0.07 mL; 0.11 mmol) over 10 min and the solution stirred at room temperature for 30 min. Chlorodiphenylphosphine (0.02 mL; 0.03 g; 0.11 mmol) was added and the solution stirred at 60 °C for 4 h. The solution was then cooled to room temperature and filtered, and the solvents were removed under reduced pressure. The crude product was recrystallized from a 1:1 mixture of CH_2Cl_2 and hexane to give **6** as a yellow solid (0.04 g; 51%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.80 (d, 6H, $^3J_{H-H}$ = 6.1 Hz, C*H*$_3$), 1.78 (d, 6H, $^3J_{H-H}$ = 6.2 Hz, C*H*$_3$), 4.18 (m, 2H, C*H*), 7.23 (m, 2H, Ar*H*), 7.35 (m, 10H, Ar*H*), 7.54 (m, 8H, Ar*H*), 7.94 (m, 5H, Ar*H*). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ 25.1 (d, $^3J_{C-P}$ = 6.2 Hz, *C*H$_3$), 25.3 (d, $^3J_{C-P}$ = 22.2 Hz, *C*H$_3$), 54.6 (t, $^2J_{C-P}$ = 3.8 Hz, *C*H), 54.9 (t, $^2J_{C-P}$ = 3.8 Hz, *C*H), 127.9 (t, J_{C-P} = 4.6 Hz, *C*H), 128.4 (d, J_{C-P} = 3.8 Hz, *C*H), 128.5 (d, J_{C-P} = 3.3 Hz, *C*H), 128.7 (d, J_{C-P} = 3.1 Hz, *C*H), 128.8, 129.0 (s, *C*H), 130.1 (d, $^1J_{C-P}$ = 19.2 Hz, *C*P), 130.9 (s, *C*H), 134.8 (br s, *C*H), 137.8 (d, $^1J_{C-P}$ = 14.3 Hz, *C*P), 142.3 (t, J_{C-P} = 6.5 Hz, *C*H), 145.9 (d, $^1J_{C-P}$ = 21.1 Hz, *C*P). ^{31}P NMR ($CDCl_3$, 121 MHz): δ 82.3 (t, $^2J_{P-P}$ = 31.4 Hz, *P*Ph), 108.8 (d, $^2J_{P-P}$ = 33.4 Hz, *P*Ph_2). Anal. Calcd for $C_{40}H_{39}CrN_2O_4P_3 \cdot 0.25CH_2Cl_2$: C, 61.82; H, 5.45; N, 3.99. Found: C, 61.83; H, 5.61; N, 3.58. IR (toluene): ν 1837 (C≡O), 1901 (C≡O), 1925 (C≡O), 2014 cm^{-1} (C≡O). $E_{1/2}$ = 0.72 V vs SCE.

Conformational Analysis of Ligand 3. A molecular mechanics conformer search was carried out on the free ligand, using geometry taken from the crystal structure of **5**·0.5CH_2Cl_2, by the PCModel program and forcefield MMX.[16] The eight lowest energy unique structures were taken from this search and optimized using DFT calculations to improve the relative energy ranking of each conformer, with the Jaguar program[17] using the standard hybridized functional B3LYP[11] and basis-set combination 6-31G*. We note that the computational methodology we have used here is quite simple, neglecting e.g. solvation and dispersion effects, and that this may affect the relative energies of the conformers of **3**, but since we are mainly interested in supporting the interpretation of NMR spectra here, we have not pursued further method improvements.

(16) *PCModel v9.0*; Serena Software, Bloomington, IN, 2004.
(17) Schrödinger, L. *Jaguar 6.0*; Schrödinger, LLC, New York, 2005.

Table 4. Crystallographic Data

	5·0.5CH_2Cl_2	**6**·2.5CH_2Cl_2
color, habit	yellow, plate	yellow, needle
size/mm	0.08 × 0.05 × 0.01	0.20 × 0.06 × 0.02
empirical formula	$C_{28.5}H_{31}ClCrN_2O_4P_2$	$C_{43}H_{45}Cl_6CrN_2O_4P_3$
M_r	1229.89	1011.42
cryst syst	orthorhombic	monoclinic
space group	*Pbca*	$P2_1/c$
a/Å	15.4028(2)	9.5183(9)
b/Å	17.6693(2)	26.520(2)
c/Å	21.5230(3)	20.3442(19)
β/deg	90.0	115.659(6)
V/Å^3	5857.63(1)	4629.0(7)
Z	8	4
μ/mm^{-1}	0.627	6.553
T/K	100	100
no. of rflns: total/indep	36 563/6725	74 266/7325
R_{int}	0.0582	[a]
final R1	0.0404	0.0516
largest peak, hole/e Å^{-3}	1.005, −0.450	0.659, −0.783
ρ_{calcd}/g cm^{-3}	1.395	1.451

[a] R_σ = 0.0389.

Crystallographic Details. X-ray diffraction experiments were carried out at 100 K on a Bruker Kappa Apex II CCD diffractometer using Mo Kα radiation (λ = 0.710 73 Å) for **5**·0.5CH_2Cl_2 and on a Bruker Microstar CCD diffractometer using Cu Kα radiation (λ = 1.541 78 Å) for **6**·2.5CH_2Cl_2. Single crystals were coated in inert oil and mounted on a glass fiber. Intensities were integrated[18] from several series of exposures in φ and ω calculated by the Apex II[19] or Proteum II[20] program after unit cell determination. Absorption corrections were based on equivalent reflections using SADABS,[21] and structures were refined against all F_o^2 data with hydrogen atoms riding in calculated positions using SHELXTL.[22] Crystal structure and refinement data are given in Table 4. The crystal used for **6**·2.5CH_2Cl_2 was nonmerohedrally twinned. The twin components of the diffraction data were assigned using the Bruker program CELL_NOW[23] and corrected for absorption with TWINABS.[24] Data completeness is at 92% for this 1:1 twinned structure.

Both solvate structures exhibit static disorder for the half-occupancy dichloromethane molecule to be 50%. For the disordered solvent in **6**·2.5CH_2Cl_2 further restraints were applied to the thermal ellipsoid parameters of the disordered central carbon atom (C43a and C43b), to mimic the other dichloromethane carbons present in the model (C41 and C42). Nine low-angle reflections were omitted from **5**·0.5CH_2Cl_2 and one from **6**·2.5CH_2Cl_2.

Ethylene Oligomerization. Runs were carried out in a 300 mL stainless steel Parr reactor with magnetic stirring. The oven-dried vessel was purged with nitrogen, charged with chlorobenzene (20 mL), and heated to the required temperature. The catalyst solution was prepared by dissolving the required amount of catalyst in chlorobenzene (5 mL) and adding the required amount of triethylaluminum ($AlEt_3$) in toluene or MMAO in heptanes. The catalyst solution was injected into the prepared autoclave, and the reactor was immediately charged with the required pressure of ethylene and maintained at this pressure for the duration of the reaction. After the run

(18) *SAINT v7.34A*; Bruker-AXS, Madison, WI, 2007.
(19) *Apex2*; Bruker-AXS, Madison, WI, 2007.
(20) *Proteum2*; Bruker-AXS, Madison, WI, 2007.
(21) Sheldrick, G. M. *SADABS V2008/1*; Bruker AXS, Madison, WI, 2008.
(22) *SHELXTL program system version V6.14*; Bruker AXS, Madison, WI, 2003.
(23) Sheldrick, G. M. *CELL NOW V2008/2*; Bruker AXS, Madison, WI, 2008.
(24) Sheldrick, G. M. *TWINABS V2008/2*, Bruker AXS, Madison, WI, 2008.

time, the reactor was cooled in an ice bath, the excess ethylene was vented, and an internal standard was added (mesitylene, 50 μL). After quenching with 10% HCl, the organic phase was separated, dried ($MgSO_4$), and analyzed by GC. The white solids were filtered, washed, dried, and weighed.

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Supporting Information Available: CIF files, text, tables, and a figure giving crystallographic data for **5**·0.5CH_2Cl_2 and **6**·2.5CH_2Cl_2 and Cartesian coordinates of the seven conformers of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added after ASAP Publication. This paper was published on the Web on Feb 16, 2011, and a pair of references to work by Rosenthal et al. were omitted. These have now been added to refs 8 and 14. The corrected version was reposted on Mar 7, 2011.