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N-Phosphanyl- and *N,N′*-Diphosphanyl-Substituted N-Heterocyclic Carbene Chromium Complexes: Synthesis, Structures, and Catalytic Ethylene Oligomerization

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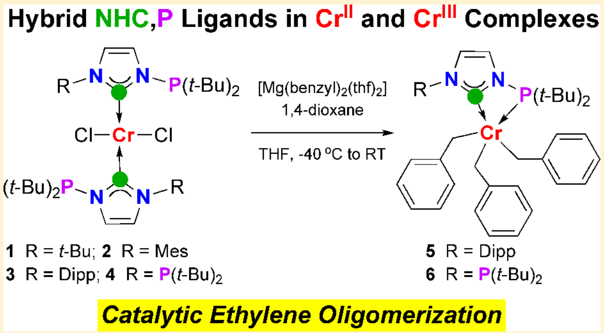
Supporting Information

ABSTRACT: The chromium(II) complexes [CrCl$_2$($^{t\text{-Bu}}$**NHC,P**-κC)$_2$] (**1**), [CrCl$_2$($^{\text{Mes}}$**NHC,P**-κC)$_2$] (**2**), [CrCl$_2$($^{\text{Dipp}}$**NHC,P**-κC)$_2$] (**3**), and [CrCl$_2$(**P,NHC,P**-κC)$_2$] (**4**) containing the *N*-phosphanyl- or *N,N′*-diphosphanyl-substituted N-heterocyclic carbene (NHC) hybrid ligands $^{t\text{-Bu}}$**NHC,P** (1-(di-*tert*-butylphosphino)-3-*tert*-butylimidazol-2-ylidene), $^{\text{Mes}}$**NHC,P** (1-(di-*tert*-butylphosphino)-3-mesitylimidazol-2-ylidene), $^{\text{Dipp}}$**NHC,P** (1-(di-*tert*-butylphosphino)-3-(2,6-diisopropylphenyl)imidazol-2-ylidene), and **P,NHC,P** (1,3-bis(di-*tert*-butylphosphino)imidazol-2-ylidene), respectively, were prepared from Cr$^{\text{II}}$ ([CrCl$_2$(thf)$_2$]) or Cr$^{\text{III}}$ ([CrCl$_3$(thf)$_3$] or [Cr(Me)Cl$_2$(thf)$_3$]) precursors. The solid-state structures of these four complexes show square-planar Cr$^{\text{II}}$ centers, with two trans chloride and two monodentate C$_{\text{NHC}}$ donors. Alkylation of **3** and **4** with [Mg(benzyl)$_2$(thf)$_2$] led to the formation of the σ complexes [Cr(benzyl)$_3$($^{\text{Dipp}}$**NHC,P**-$\kappa C,\kappa P$)] (**5**) and [Cr(benzyl)$_3$(**P,NHC,P**-$\kappa C,\kappa P$)] (**6**), respectively, with five-coordinate distorted-square-pyramidal Cr$^{\text{III}}$ coordination, comprising a chelating ligand through the C$_{\text{NHC}}$ and one P donor and three benzyl groups. These complexes were used as precatalysts in ethylene oligomerization, and it was found that the nature of the cocatalyst used and the metal oxidation state have a remarkable influence on the catalytic properties. The Cr$^{\text{III}}$/MAO systems displayed superior catalytic performance (TOF values up to 16320 mol of C$_2$H$_4$/((mol of Cr) h) for **6**) and gave mostly oligomers. Interestingly, the oligomers obtained with complex **3** were almost exclusively 1-hexene and 1-butene when the reaction was initiated at 30 °C. The overall activities and selectivities were also affected by the initial reaction temperature and the nature of the solvent. With AlEtCl$_2$ (EADC) as cocatalyst, polyethylene was predominately formed.



INTRODUCTION

Metal-catalyzed transformations for converting ethylene to linear α-olefins (LAO) or polyethylenes are of continuing interest, due to the industrial importance and value of the end products.[1] For example, LAOs are highly demanded industrial intermediates, in particular as comonomers for the production of linear low-density polyethylene (C4−C8), surfactants (C12−C20), and plasticizers (C6−C10). Chromium is at the core of these transformations, being the active center of the Phillips[2] and Union Carbide[3] SiO$_2$-supported Cr catalyst, responsible for 40%−50% of the annual world production of polyethylene,[4] or of a number of selective homogeneous oligomerization catalysts affording mainly 1-hexene or 1-octene (Phillips,[5] Mitsubishi,[6] BP Chemicals,[7] Sasol[8]). Since the influence of the Cr oxidation state, the ancillary ligands, and the cocatalyst on the oligomer selectivity has not yet been fully elucidated, considerable efforts have been devoted to the development of well-defined, catalytically active molecular systems, which lend themselves to mechanistic studies and rational tailoring.[1b,f,9]

Although N-heterocyclic carbenes (NHCs) have been established as efficient ancillary ligands in diverse topics of homogeneous catalysis,[10] they have not yet found wide applications in olefin oligomerization and polymerization reactions, in particular with electropositive metals. This may be due to the small metal−NHC bond dissociation energies but also due to the decomposition of the active species with alkyl−NHC−metal bonds via alkylimidazolium reductive elimination.[11] It is conceivable that the side reaction could be suppressed through the donor functionalization and chelation of the NHC functionality, by the introduction of steric bulk and the protection at the NHC, and/or by using early transition metals that are less susceptible to this type of deactivation (e.g. due to unavailable oxidation states etc.). Presently, only a few monodentate, bidentate (N,C; C,S; C,C), and tridentate (N,C,N; C,N,C; C,S,C) functionalized NHC ligands have been employed to prepare Cr complexes as precatalysts for ethylene polymerization or oligomerization.[11,12] Among them, the "pincer" pyridylbis(carbene)chromium(III) complexes of type **A** are the most active precatalysts for the oligomerization of ethylene, with activities up to 7.8 × 10^5 g/((g of Cr) h).[9a]

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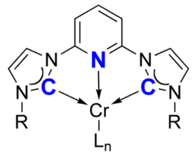
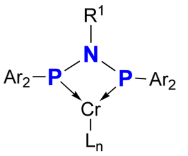


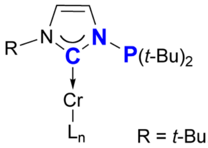
R = 2,6-*i*-Pr$_2$C$_6$H$_3$ (Dipp)

A



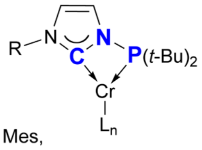
R^1 = Me, Ar = *o*-MeO-Ph
R^1 = *i*-Pr, Ar = Ph

B



C

R = *t*-Bu, Mes,
Dipp, (*t*-Bu)$_2$P



D

Recently, *N*-phosphanyl-functionalized NHC ligands[13] have received much attention, since they feature vicinal, strong σ donors in rigid, easily tunable sterically and electronically coordination environments. The chemistry that has been explored to date involves coinage, platinum-group, or late transition metals, where the ligands adopt bridging or chelating modes, in the last case giving distorted chelate rings and small bite angles.[14] In contrast, the coordination chemistry with the early and 3d metals is unknown.

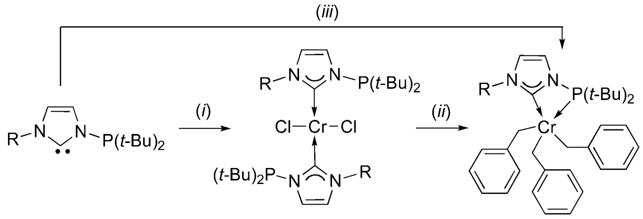
Of relevance to the origin of the present work were the versatile ethylene trimerization catalyst PNP-Cr (**B**, Ar = *o*-MeO-Ph), developed by BP Chemicals,[7a] and the analogous ethylene tetramerization catalyst PNP-Cr (**B**, Ar = Ph), developed by Sasol,[8c] both based on a bis(phosphanyl)amine-type (PNP) ligand. The recognition that the nature of the ancillary ligand clearly plays a major role in determining the catalytic activity and selectivity[1e−g] led us to consider the synthesis of complexes with a hybrid ligand containing NHC and phosphine donor groups, in view of the widely accepted similarity of their donor abilities[10b,g,15] and the often unique properties brought about by hybrid ligands.[16] Herein, we report the synthesis of Cr$^{\mathrm{II}}$ and Cr$^{\mathrm{III}}$ complexes based on a family of P-functionalized NHC ligands of types **C** and **D** and their evaluation in the catalytic oligomerization of ethylene.

RESULTS AND DISCUSSION

Synthesis of the Chromium Complexes. The new complexes [CrCl$_2$(**$^{t\text{-Bu}}$NHC,P**-κC)$_2$] (**1**), [CrCl$_2$(**$^{\mathrm{Mes}}$NHC,P**-κC)$_2$] (**2**), [CrCl$_2$(**$^{\mathrm{Dipp}}$NHC,P**-κC)$_2$] (**3**), and [CrCl$_2$(**P,NHC,P**-κC)$_2$] (**4**) were prepared by the addition of the known *N*-phosphanyl-substituted NHC ligands **$^{t\text{-Bu}}$NHC,P**, **$^{\mathrm{Mes}}$NHC,P**, **$^{\mathrm{Dipp}}$NHC,P**, and **P,NHC,P**, respectively,[13c,14a,17] to a suspension of 0.5 equiv of [CrCl$_2$(thf)$_2$] in THF at −78 °C (Scheme 1).

They were obtained as purple, paramagnetic, air-sensitive solids in good yields and characterized by X-ray diffraction (see below). Initial attempts to use the same methodology to prepare Cr$^{\mathrm{III}}$ complexes, i.e. by reacting excess ligand with [CrCl$_3$(thf)$_3$] or [Cr(Me)Cl$_2$(thf)$_3$], led unexpectedly to the reduction of Cr$^{\mathrm{III}}$ to Cr$^{\mathrm{II}}$ and the isolation of **1**−**4**. Similar redox reactions between a Cr$^{\mathrm{III}}$ complex and *N*,*N*′-diisopropylimidazol-2-ylidene have been observed previously, but their mechanisms were not fully elucidated.[18]

Scheme 1. Synthesis of Cr$^{\mathrm{II}}$ and Cr$^{\mathrm{III}}$ Complexes[a]



$^{t\text{-Bu}}$NHC,P: R = *t*-Bu
$^{\mathrm{Mes}}$NHC,P: R = Mes
$^{\mathrm{Dipp}}$NHC,P: R = Dipp
P,NHC,P: R = (*t*-Bu)$_2$P

1: R = *t*-Bu
2: R = Mes
3: R = Dipp
4: R = (*t*-Bu)$_2$P

5: R = Dipp
6: R = (*t*-Bu)$_2$P

[a] Reagents and conditions: (*i*) [CrCl$_2$(thf)$_2$], [CrCl$_3$(thf)$_3$] or [Cr(Me)Cl$_2$(thf)$_3$], THF, −78 °C to room temperature; (*ii*) [Mg(benzyl)$_2$(thf)$_2$] and 1,4-dioxane, THF, −40 °C to room temperature; (*iii*) [CrCl$_3$(thf)$_3$], [Mg(benzyl)$_2$(thf)$_2$], and 1,4-dioxane, THF, −78 to −40 °C to room temperature.

Further derivatization of **3** and **4** aiming at the introduction of reactive Cr−C σ bonds was attempted by the reaction with [Mg(benzyl)$_2$(thf)$_2$]. This led to the isolation of [Cr(benzyl)$_3$(**$^{\mathrm{Dipp}}$NHC,P**-κC,κP)] (**5**) and [Cr(benzyl)$_3$(**P,NHC,P**-κC,κP)] (**6**), respectively. Whereas substitution of the chlorides by the benzyl moieties was expected, we do not know at which stage the oxidation of Cr$^{\mathrm{II}}$ to Cr$^{\mathrm{III}}$ took place. One may speculate that disproportionation of an unstable Cr$^{\mathrm{II}}$ species has resulted in the formation of **5** and **6**. Subsequently, a more convenient and rational one-pot method was developed to access **5** and **6**, by the reaction of [CrCl$_3$(thf)$_3$] with **$^{\mathrm{Dipp}}$NHC,P** and **P,NHC,P**, respectively, and excess [Mg(benzyl)$_2$(thf)$_2$] under a carefully controlled temperature regime (see the Experimental Section). The reaction of [Cr(benzyl)$_3$(thf)$_3$] with the ligand **$^{\mathrm{Dipp}}$NHC,P** also led to **5**, and this procedure could probably be extended to the other NHC,P ligands. However, the difficulties associated with the synthesis of [Cr(benzyl)$_3$(thf)$_3$] made this route less attractive. Isolation and purification of the new benzyl complexes were carried out by extraction of the complex into toluene and layering the solution with pentane for crystallization; however, this resulted in lower isolated yields of **5** (8% based on Cr), which has reduced solubility in toluene, and **6** (56%). Attempts to isolate the complexes by extraction into more polar solvents, such as THF, gave impure products. The paramagnetic **5** and **6** are black, extremely air- and moisture-sensitive crystalline materials that were characterized by single-crystal X-ray diffraction.

Solid-State Structures of the Cr$^{\mathrm{II}}$ and Cr$^{\mathrm{III}}$ Complexes. The structures of **1**−**4** are shown in Figures S1 and S2 in the Supporting Information for **1** and **2** and Figures 1 and 2 for **3** and **4**, respectively. Selected bond lengths and angles are given in Table 1.

In all four complexes, the Cr$^{\mathrm{II}}$ center, at a center of molecular and crystallographic symmetry, features a perfect square-planar geometry with mutually trans C$_{\mathrm{NHC}}$ and chlorine donors. The coordination plane and the imidazole ring form a dihedral angle of 85.51° in **1**, 87.37° in **2**, 88.30° in **3**, and 85.58° in **4**. The Cr−C$_{\mathrm{NHC}}$ and Cr−Cl bond distances are in the ranges 2.152(6)−2.205(2) and 2.3432(6)−2.3525(5) Å, respectively, and are comparable with those in similar complexes.[12a,b,19] No interaction between the phosphine groups and the chromium can be deduced on the basis of the observed set of metrical data and conformations.

The structures of **5** and **6** are shown in Figures 3 and 4, respectively, and selected bond lengths and angles are given in Table 2.

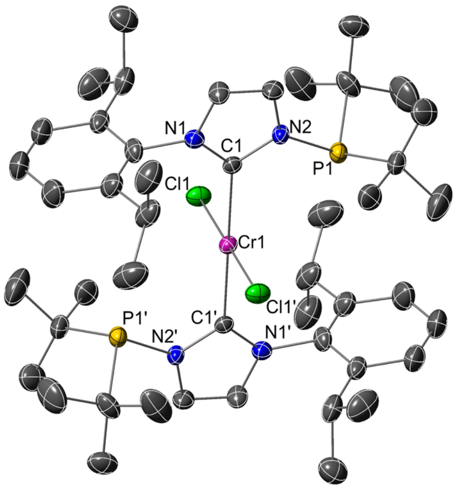


Figure 1. Thermal ellipsoid representation (30% probability level) of the structure of **3**. H atoms are omitted for clarity.

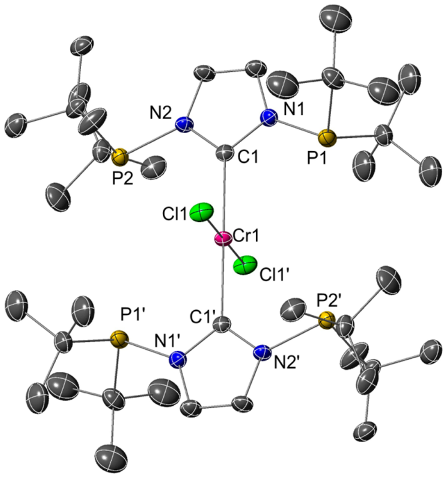


Figure 2. Thermal ellipsoid representation (30% probability level) of the structure of **4**. H atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in the Solid-State Structures of 1−4

	1	**2**	**3**	**4**
Cr1−C1	2.205(2)	2.169(2)	2.176(4)	2.152(6)
Cr1−Cl1	2.3525(5)	2.3432(6)	2.346(1)	2.349(2)
C1−N1	1.347(2)	1.347(3)	1.351(5)	1.363(8)
C1−N2	1.382(2)	1.370(3)	1.358(5)	1.370(8)
N2−P1(P2)	1.739(2)	1.755(2)	1.748(3)	1.753(5)
N1−P1				1.755(5)
C1−Cr1−Cl1	89.97(5)	89.98(6)	87.40(9)	87.2(1)
C1−Cr1−Cl1′	90.03(5)	90.02(6)	92.60(9)	92.8 (2)
Cr1- C1−N1	133.3(1)	133.0(2)	131.7(3)	127.4(4)
Cr1- C1−N2	122.6(1)	123.0(2)	123.1(2)	127.5(4)
N1−C1−N2	104.0(2)	103.9(2)	104.6(3)	104.4(5)
C1−N2−P1(P2)	120.9(1)	115.8(2)	117.6(2)	116.9(4)
C1−N1−P1				116.8(4)

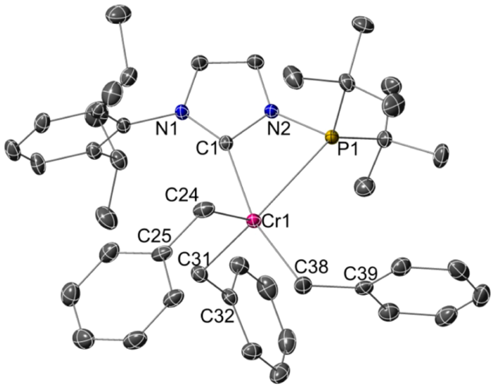


Figure 3. Thermal ellipsoid representation (30% probability level) of the structure of **5**. H atoms are omitted for clarity.

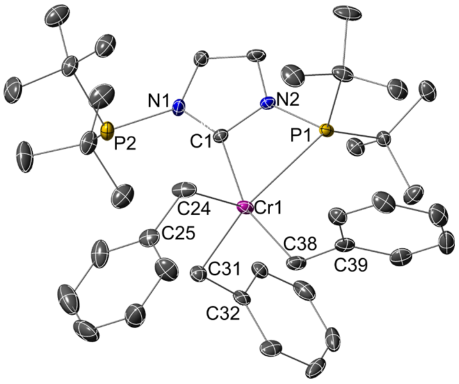


Figure 4. Thermal ellipsoid representation (30% probability level) of the structure of **6**. H atoms are omitted for clarity.

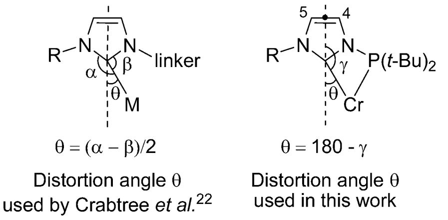
Complexes **5** and **6** constitute rare examples of five-coordinate Cr^{III} organometallics.[20] In both, the geometry at Cr^{III} is slightly distorted square pyramidal (τ^{21} 0.41 and 0.36 for **5** and **6**, respectively), with the two C_{benzyl} (C31 and C38), the C_{NHC}, and the P donors forming the basal plane. In contrast to the previously described Cr^{II} species, the phosphanyl NHC ligands in **5** and **6** adopt a chelating bonding mode that results in a strained four-membered ring with an acute bite angle of 60.64(3)° and 61.84(11)°, respectively. The sum of the bond angles within the chelate ring (358.8° for **5**, 360° for **6**) indicates planarity. The short-bite nature of the chelating ligand results in a significant value for the angle θ (Scheme 2), defined as the angle between the axis going through the carbene donor atom C1 and the middle of the imidazole C=C double bond and the C1−Cr bond (18.61 and 21.20°, respectively). This definition is slightly different from that of the yaw distortion angle used by Crabtree (Scheme 2),[22] which is based on a symmetrical imidazole ring (although the two N substituents are not the same), but the θ values obtained according to these two definitions are almost the same.

The Cr−C_{benzyl} bond distances in **5** and **6** (2.095(5)−2.149(1) Å) fall within the expected range[18,23] and are significantly shorter than the Cr−C_{NHC} bonds (2.216(1) Å for **5** and 2.227(4) Å for **6**). In both **5** and **6**, the three angles subtended at $C_{benzylic}$ show considerable differences: the C32−C31−Cr1 angle (107.20(8)° in **5**, 99.8(3)° in **6**) is more acute than the other two (C39−C38−Cr1 121.57(8), 124.7(3)° and C25−C24−Cr1 117.07(9), 118.1(3)° in **5** and **6**, respectively). Even more acute angles of 97.9(2) and 76.6(2)° have been found recently in a Cr^{II} complex of the type $[Cr(NHC)(benzyl)_2]$, the angular distortion at the benzylic carbon having been ascribed to intramolecular polarization-induced metal−arene interactions.[18] In the structure of **6** there is no interaction between the second P(*t*-Bu)$_2$ group and the metal. The lone

Table 2. Selected Bond Lengths (Å) and Angles (deg) in the Solid-State Structures of 5 and 6

	5	6
Cr1−C1	2.216(1)	2.227(4)
Cr1−P1	2.8014(3)	2.725(1)
Cr1−C24	2.100(1)	2.095(5)
Cr1−C31	2.080(1)	2.102(4)
Cr1−C38	2.149(1)	2.137(4)
C1−N1	1.358(1)	1.371(5)
C1−N2	1.376(1)	1.369(5)
N2−P1	1.7517(9)	1.740(3)
N1−P2		1.775(4)
C1−Cr1−P1	60.64(3)	61.8(1)
C31−Cr1−C24	96.41(5)	94.6(2)
C31−Cr1−C38	96.22(5)	94.0(2)
C31−Cr1−C1	96.34(5)	100.0(2)
C24−Cr1−C1	94.99(4)	95.4(2)
C38−Cr1−C1	164.02(4)	160.6(2)
C31−Cr1−P1	139.57(4)	139.2(1)
C24−Cr1−P1	116.98(4)	121.8(2)
C38−Cr1−P1	103.40(4)	98.8(2)
Cr1−P1−N2	77.84(3)	79.1(1)
Cr1−C1−N2	109.58(7)	107.5(3)
Cr1−C38−C39	121.57(8)	124.7(3)
Cr1−C31−C32	107.20(8)	99.8(3)
Cr1−C24−C25	117.07(9)	118.1(3)
C1−N2−P1	110.74(7)	111.6(3)
C1−N1−P2		120.0(3)
N1−C1−N2	103.85(9)	103.9(3)

Scheme 2. Distortion Angle *θ* Resulting from the Short-Bite Character of the NHC,P Chelating Ligands[a]



Distortion angle θ used by Crabtree *et al.*[22]

Distortion angle θ used in this work

[a] In our case (right), the dashed line goes through the middle of the double bond between C4 and C5 and the C_{NHC} atom.

pair at P2 is oriented toward the benzylic carbons C24 and C31.

Catalytic Ethylene Oligomerization and Polymerization. The complexes **1**−**6** were evaluated as precatalysts for the oligomerization of ethylene at 10 bar of ethylene with 400 equiv of methylaluminoxane (MAO) as cocatalyst. The results are compiled in Table 3. At 30 °C, **1**, **2**, and **4** with MAO as cocatalyst were only poorly active (less than 350 g/((g of Cr) h)) in comparison to the pyridylbis(carbene) Cr^{III} species of type **A** (7.8×10^5 g/((g of Cr) h))[9a] and mostly polyethylene (PE) was formed (entries 1, 2, and 5 in Table 3). The **3**/MAO system showed higher activity (1040 g/((g of Cr) h)) and gave smaller amounts of polymers (32 wt %) and mostly octenes (51%), of which 97% was 1-octene. The C6 fraction (17%) contained almost exclusively 1-hexene; only very small amounts of 3-*cis*-hexene and 2-*trans*-hexene were found in the liquid phase, but no methylcyclopentane and methylenecyclopentane, which are usually produced with other ethylene tetramerization catalysts. When the initial reaction temperature was set at 80 °C, the **3**/MAO system was more than twice as active (2390 g/((g of Cr) h)) and only oligomers were produced (entry 4 in Table 3). Under similar conditions, the Cr^{III} complexes **5** and **6** performed better than the Cr^{II} complexes, with activities of up to 8790 g/((g of Cr) h)) for **6**/MAO (entry 7 in Table 3).[24] The molecular mass distribution of the oligomerization products is of the Schulz−Flory type with a K value of 0.73 ($K = k_{prop}/(k_{prop} + k_{ch\ transfer})$ = (mol of C_{n+2})/(mol of C_n); Figure 5). The nature of the ligand N substituent can significantly affect the nature of the products obtained from catalytic ethylene oligomerization, as found for example in Cr complexes with the pyridine bis(carbene)[9a] and pyridine bis(imine)[21] ligands. The major oligomer produced by the **5**/MAO system was 1-octene, and 4 wt % of polymer was formed, whereas in the case of **6**/MAO, the major oligomers were 1-hexene and 1-octene and 9 wt % waxes were produced. Subsequently, the influence of the reaction conditions on the catalytic performance of **6**/MAO was investigated. The latter system was found to be still active after 35 min and lasted for 90 min, giving an activity of 5360 g/((g of Cr) h)) (entry 8 in Table 3). Methylcyclohexane has been reported to improve the catalytic activity of Cr^{III} complexes with a P,N donor ligand in ethylene oligomerization,[9e] whereas an adverse effect was noted recently with Cr^{III} systems containing dipyrrole-based ligands.[25] In our case, using methylcyclohexane as solvent for the **6**/MAO

Table 3. Oligomerization of Ethylene for Complexes 1−6 with MAO as Cocatalyst[a]

		overall selectivity (wt %)							
entry	cat.	C4 (1-C4)	C6 (1-C6)	C8 (1-C8)	C10 (1-C10)	> C10	PE	productivity[b]	TOF[c]
1	**1**	1 (97)	10 (100)	19 (65)	0	0	70	150	280
2	**2**	0	3 (89)	33 (71)	0	0	64	190	350
3	**3**	0	17 (99)	51 (97)	0	0	32	1040	1930
4[d]	**3**	15 (99)	18 (91)	15 (86)	16 (82)	36	0	2390	4440
5	**4**	0	2 (92)	2 0(96)	1 (12)	2	75	310	580
6	**5**	10 (99)	15 (91)	18 (84)	15 (76)	38	4	6110	11350
7	**6**	14 (95)	16 (95)	15 (91)	13 (85)	33	9[h]	8790	16320
8[e]	**6**	16 (100)	18 (95)	16 (90)	14 (83)	36	0	5360	9950
9[f]	**6**	15 (100)	17 (95)	16 (90)	14 (85)	37	1[h]	6040	11220
10[g]	**6**	12 (99)	15 (84)	16 (87)	14 (80)	33	10	6060	11250

[a] Conditions unless specified otherwise: temperature 30 °C, 10 bar of C_2H_4, reaction time 35 min, 4×10^{-5} mol of catalyst, solvent 9.33 mL of chlorobenzene and 10.66 mL of the cocatalyst solution (1.5×10^{-3} M) for 400 equiv of MAO. [b] In (g of C_2H_4)/((g of Cr) h). [c] In (mol of C_2H_4)/((mol of Cr) h). [d] Temperature 80 °C. [e] Reaction time 90 min. [f] In methylcyclohexane. [g] Temperature 45 °C. [h] Waxes.

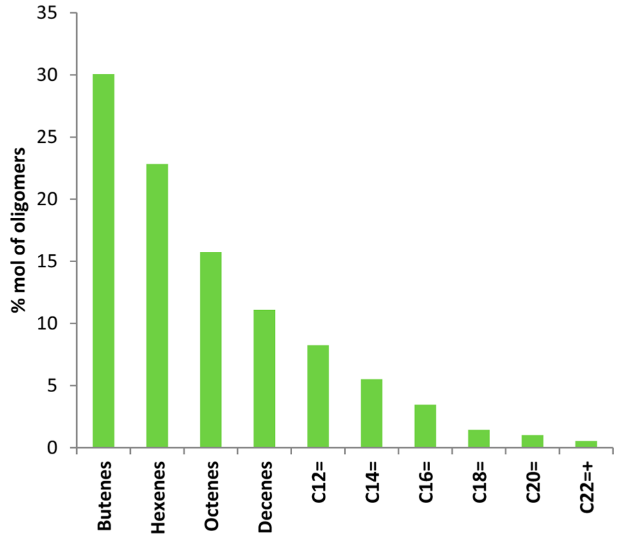


Figure 5. Oligomer distribution with precatalysts **6** (entry 7 in Table 3) using MAO as cocatalyst.

system also had an adverse effect on the activity, which may be ascribed to the poor solubility of **6** in this solvent, but led to a decreased formation of waxes (entry 9 in Table 3). After injection of the catalyst and cocatalyst, **6** consumed ethylene very slowly during the first 7 min. Acceleration of ethylene uptake only started when the reaction temperature reached 45 °C. Subsequently, the **6**/MAO system was tested at an initial temperature of 45 °C, but this resulted in a decreased activity (entry 10 in Table 3). This could be attributed to the rapid formation of polymers instead of waxes, which can encapsulate the catalyst and hamper further reaction.

The use of $AlEtCl_2$ (EADC) as cocatalyst for all of the complexes (**1**−**6**) led predominantly to the formation of polyethylene and less than 5% of oligomers (Table 4). When the R group was changed from *t*-Bu to $P(t\text{-}Bu)_2$ in the Cr^{II} complexes **1**−**4**, the activity gradually increased from 380 to 1690 g/((g of Cr) h). Increasing the reaction temperature to 80 °C for **3**/EADC (entry 4 in Table 4) and reducing the amount of cocatalyst (3 equiv) for **4**/EADC (entry 6 in Table 4) led to a dramatic decrease in activity. No obvious differences between the Cr^{III} complex **6** and the Cr^{II} complexes **3** and **4** were observed when EADC (entries 3, 5, and 7 in Table 4) was used as a cocatalyst, at variance with the MAO system.

Table 4. Polymerization of Ethylene for Complexes 1−4 and 6 with $AlEtCl_2$ as Cocatalyst[a]

entry	cat.	amt of PE (g)	amt of PE (wt %)	productivity[b]	TOF[c]
1	**1**	0.36	100	380	710
2	**2**	1.37	98	1370	2540
3	**3**	2.09	100	1650	3060
4[d]	**3**	0.26	96	490	910
5	**4**	2.05	97	1690	3140
6[e]	**4**	0.49	95	460	850
7	**6**	1.64	100	1670	3100

[a] Conditions unless specified otherwise: temperature 30 °C, 10 bar of C_2H_4, time 35 min, 4×10^{-5} mol of catalyst, solvent 10 mL of chlorobenzene and 5 mL of the cocatalyst solution (8×10^{-5} M) for 10 equiv of $AlEtCl_2$. [b] In (g of C_2H_4)/((g of Cr) h). [c] In (mol of C_2H_4)/((mol of Cr) h). [d] Temperature 80 °C. [e] 1.5 mL of the cocatalyst solution (8×10^{-5} M) for 3 equiv of $AlEtCl_2$ and 13.5 mL of chlorobenzene.

■ CONCLUSION

Motivated by their donor characteristics and bite angles, we studied the phosphanyl- and diphosphanyl-substituted NHC ligands $^{t\text{-Bu}}$**NHC,P**, $^{\text{Mes}}$**NHC,P**, $^{\text{Dipp}}$**NHC,P**, and **P,NHC,P** as mimics of the *N,N*′-bis(diarylphosphino)amines (PNP) used in Cr complexes for the catalytic oligomerization or polymerization of ethylene. In contrast to the chelating behavior of bis(phosphanyl)amine-type ligands, the functionalized NHC ligands behaved as monodentate C_{NHC} donors with dangling, coordination-inactive PR_2 groups in their Cr^{II} complexes **1**−**4**, obtained from either Cr^{II} or Cr^{III} chlorido precursors. The mechanism of the redox reaction responsible for the formation of the Cr^{II} complexes has not been elucidated but may be relevant to transformations occurring in situ in catalytic systems. In contrast, benzylation of either well-defined Cr^{II} complexes or $[CrCl_3(THF)_3]$/ligand mixtures with $[Mg(benzyl)_2(thf)_2]$ led to [Cr(NHC)(benzyl)$_3$] species with κ^2-phosphanyl-NHC ligand coordination. Upon activation with MAO, the Cr^{III} complexes were active in ethylene oligomerization, displaying catalytic performances superior to those of the Cr^{II} precursors. However, it is noteworthy that the oligomers obtained with complex **3** were almost exclusively 1-hexene and 1-butene when the reaction was initiated at 30 °C. At 80 °C, a broader mass distribution of oligomers was observed (from C4 to >C10) and polyethylene formation was suppressed. The use of EADC as cocatalyst led predominantly to the formation of polymers. The tri- and tetramerization observed in some cases validates further the idea that NHC-P can mimic the PNP ligands, although each ligand family possesses its own specific features. The significant differences in activities and selectivities observed with catalytic species generated from seemingly similar ligand designs demonstrate further the subtlety of the parameters that determine the catalytic features of metal complexes.

■ EXPERIMENTAL SECTION

General Methods. All manipulations involving organometallics were performed under nitrogen or argon in a Braun glovebox or using standard Schlenk techniques. Solvents were dried using standard procedures and distilled under nitrogen prior to use or passed through columns of activated alumina and subsequently purged with nitrogen or argon. The ligands $^{t\text{-Bu}}$**NHC,P**, $^{\text{Mes}}$**NHC,P**, $^{\text{Dipp}}$**NHC,P**, and **P,NHC,P** were prepared according to the literature.[13c,14a,17] $[Mg(benzyl)_2(THF)_2]$ was prepared as described,[26] and $[CrCl_2(THF)_2]$ and $[CrCl_3(THF)_3]$ were prepared by continuous Soxhlet extraction of commercial anhydrous $CrCl_2$ with THF under argon for 24−48 h.

Synthesis of the Chromium(II) Complexes 1−4. *Method a.* To a supension of $[CrCl_2(THF)_2]$ (0.133 g, 0.50 mmol) in THF (8 mL) was added a solution of the corresponding ligand (1.05 mmol) in THF (8 mL) at −78 °C. The reaction mixture was warmed slowly to room temperature and stirred overnight. After evaporation of the solvent under reduced pressure, the residue was washed with pentane (5 mL) to give a purple, air-sensitive powder. X-ray-quality crystals were obtained by slow diffusion of pentane into THF solution of the corresponding complex.

Complex **1**: yield 0.274 g, 83%. Anal. Found (calcd for $C_{30}H_{58}Cl_2CrN_4P_2$): C, 54.97 (54.62); H, 8.97 (8.86); N, 8.18 (8.49).

Complex **2**: yield 0.337 g, 86%. Anal. Found (calcd for $C_{40}H_{62}Cl_2CrN_4P_2$): C, 61.22 (61.29); H, 8.15 (7.97); N, 6.64 (7.15).

Complex **3**: yield 0.380 g, 88%. Anal. Found (calcd for $C_{46}H_{74}Cl_2CrN_4P_2$): C, 63.52 (63.65); H, 8.73 (8.59); N, 6.37 (6.46).

Complex **4**: yield 0.309 g, 74%. Anal. Found (calcd for $C_{38}H_{76}Cl_2CrN_4P_4$): C, 54.35 (54.60); H, 9.03 (9.16); N, 6.68 (6.70).

Method b. To a suspension of $[CrCl_3(THF)_3]$ (0.093 g, 0.25 mmol) or $[Cr(Me)Cl_2(THF)_3]$ (0.088 g, 0.25 mmol) in THF (8 mL) was added a solution of the corresponding ligand in excess (0.70 mmol) in THF (8 mL) at −78 °C. The reaction mixture was warmed slowly to room temperature and stirred for 4 h. The resulting brown suspension was filtered, and layering the filtrate with pentane afforded crystals of the corresponding Cr(II) complex **1**−**4**.

Synthesis of Chromium(III) Complexes 5 and 6. *Method a.* Solid $[CrCl_3(THF)_3]$ (0.068 g, 0.183 mmol), the corresponding carbene ligand (0.210 mmol), and $[Mg(benzyl)_2(THF)_2]$ (0.150 g, 0.428 mmol) were placed in a Schlenk tube in the glovebox. The tube was connected to the vacuum line and cooled to −78 °C. At this temperature, precooled THF (15 mL) and dioxane (2 mL) were added and the reaction mixture was stirred at −40 °C for 1 h. Then the dark brown reaction mixture was warmed to room temperature and was further stirred for 1 h. After evaporation of the solvent under reduced pressure, the residue was extracted with toluene (30 mL) and the solution was filtered. The filtrate was layered with pentane (60 mL) for 3 days to give a black and air-sensitive crystalline material. X-ray-quality crystals were obtained by slow diffusion of pentane into a dilute toluene solution of the complex.

Complex **5**: yield 0.010 g, 8% based on Cr.

Complex **6**: yield 0.070 g, 56% based on Cr. Due to the extreme sensitivity of **5** and **6**, satisfactory elemental analyses could not be obtained.

Method b. To a solution of **3** (0.174 g, 0.200 mmol) or a suspension of **4** (0.167 g, 0.200 mmol) in THF (10 mL) was added dioxane (2 mL), and the reaction mixture was cooled to −40 °C. At this temperature, a precooled solution of $[Mg(benzyl)_2(THF)_2]$ (0.210 g, 0.60 mmol) in THF (6 mL) was added and the reaction mixture was stirred at −40 °C for 1 h. The dark brown reaction mixture was then warmed to room temperature and was further stirred for 1 h. After evaporation of the solvent under reduced pressure, the residue was extracted with toluene (40 mL) and the solution filtered. The filtrate was layered with pentane (60 mL) for 3 days to give a black, air-sensitive crystalline material.

Complex **5**: yield 0.008 g, 6% based on Cr.

Complex **6**: yield 0.030 g, 22% based on Cr.

General Procedure for the Catalytic Ethylene Oligomerization. All catalytic reactions were performed in a magnetically stirred (1200 rpm) 145 mL stainless steel autoclave. A 125 mL glass container was used to avoid corrosion of the autoclave walls. The preparation of the catalytic solution of the precatalyst was dependent on the nature and the amount of the cocatalyst.

With MAO, 4×10^{-5} mol of Cr complex was dissolved in 9.33 mL of chlorobenzene or methylcyclohexane and the solution was injected into the reactor under an ethylene flux. Then 8 mL of a 1.5×10^{-3} M cocatalyst toluene solution, corresponding to 400 equiv of MAO, was added to the reactor to reach a total volume of 20 mL with the precatalyst solution.

With $AlEtCl_2$ (EADC), 4×10^{-5} mol of Cr complex was dissolved in 13.5 or 10 mL in chlorobenzene and the solution was injected into the reactor under an ethylene flux, followed by 1.5 or 5 mL of a 8×10^{-5} M cocatalyst solution corresponding to 3 or 10 equiv of EADC, respectively. The total volume of the solution inside the reactor was 15 mL.

The catalytic reaction was started at 30, 45, or 80 °C. No cooling of the reactor was applied during the reaction. After injection of the catalyst and cocatalyst solutions under a constant low flow of ethylene, which is considered as the t_0 time, the reactor was immediately pressurized to 10 bar of ethylene. The temperature increased, owing solely to the exothermicity of the reaction. The 10 bar working pressure was maintained through a continuous feed of ethylene from a bottle placed on a balance to allow continuous monitoring of the ethylene uptake. At the end of each test (35 or 90 min to facilitate comparisons with previous studies from this laboratory[1c,9d]), a dry ice bath was used to rapidly cool the reactor. When the inner temperature reached 0 °C, the ice bath was removed, allowing the temperature to slowly rise to 18 °C. The gaseous phase was then transferred into a 10 L polyethylene tank filled with water. An aliquot of this gaseous phase was transferred into a Schlenk flask, previously evacuated, for GC analysis. The amount of ethylene consumed was thus determined by differential weighing of the ethylene bottle (accuracy of the scale 0.1 g). From this amount of ethylene was subtracted the remaining ethylene (calculated using the GC analysis) in the gaseous phase. Although this method is of limited accuracy, it was used throughout and gave satisfactory reproducibility. The reaction mixture in the reactor was quenched in situ by the addition of ethanol (1 mL), transferred into a Schlenk flask, and separated from the metal complexes by trap-to-trap evaporation (20 °C, 0.8 mbar) into a second Schlenk flask previously immersed in liquid nitrogen in order to avoid loss of product for GC analysis. Each catalytic test was performed twice to ensure the reproducibility of the results. For GC analyses, 1-heptene was used as an internal reference.

X-ray Crystallography. A summary of the crystal data, data collection and refinement for structures of **1**−**6** are given in Table S1 in the Supporting Information. For **1** and **3**−**5**, X-ray diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo Kα radiation (λ = 0.71073 Å). The crystal−detector distance was 38 mm. The cell parameters were determined (APEX2 software)[27] from reflections taken from 3 sets of 12 frames, each at 10 s exposure. The structure was solved by direct methods using the program SHELXS-97.[28] The refinement and all further calculations were carried out using SHELXL-97.[29] The H atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least squares on F^2. A semiempirical absorption correction was applied using SADABS in APEX2.[27]

For **2** and **6**, X-ray diffraction data collection was carried out on a Nonius Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo Kα radiation (λ = 0.71073 Å). The crystal−detector distance was 36 mm. The cell parameters were determined (Denzo software)[30] from reflections taken from one set of 10 frames (1.0° steps in ψ angle), each at 20 s exposure. The structures were solved by direct methods using the program SHELXS-97.[28] The refinement and all further calculations were carried out using SHELXL-97.[29] The H atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least squares on F^2. A semiempirical absorption correction was applied using MULscanABS in PLATON.[31]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

This material is also available free of charge via the Internet at http://pubs.acs.org/. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00547. The Crystallographic information files (CIF) have been deposited with the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., and can be obtained on request free of charge, by quoting the publication citation and deposition numbers 1055511−1055516.

Structures of **1** and **2** and crystal data for **1**−**6** (PDF)

Crystal data for **1**−**6** (CIF)

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The authors declare no competing financial interest.

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