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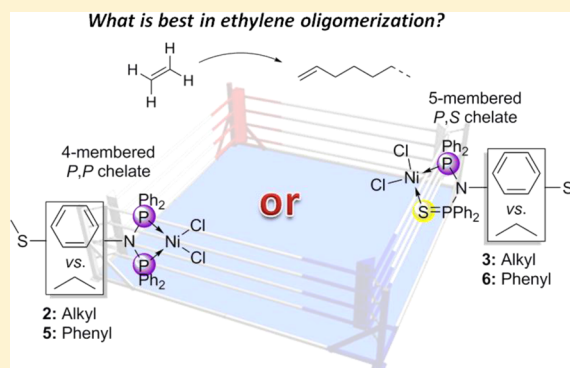
Combined Experimental and Theoretical Study of Bis(diphenylphosphino)(*N*-thioether)amine-Type Ligands in Nickel(II) Complexes for Catalytic Ethylene Oligomerization

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S Supporting Information

ABSTRACT: Starting from the new ligands bis-(diphenylphosphino)(*N*-4-(methylthio)phenyl)amine (**4**, $N-(PPh_2)_2(p-C_6H_4)SMe$) and its monosulfide derivative $(Ph_2P)N\{P(S)Ph_2\}(p-C_6H_4)SMe$ (**4S**), we have prepared and characterized, including by X-ray crystallographic studies, their Ni(II) complexes $[NiCl_2\{(Ph_2P)_2N(p-C_6H_4)SMe-P,P\}]$ (**5**) and $[NiCl_2\{(Ph_2P)N\{P(S)Ph_2\}(p-C_6H_4)SMe-P,S\}]$ (**6**), respectively. The bis-sulfide compound $N\{P(S)Ph_2\}_2(p-C_6H_4)SMe$ (**4S₂**) was also prepared and structurally characterized. Computational studies showed that the combined influence of stronger P donors and a four-membered-ring *P,P* chelate leads to complex **5** being thermodynamically more stable than **6**, which contains one weaker P=S donor group but a five-membered *P,P*=S chelate ring. For comparison, the bis-chelate complex $[Ni\{(Ph_2P)N\{P(S)Ph_2\}(p-C_6H_4)SMe-P,S\}_2](BF_4)_2$ (**7**), the monochelate complexes $[NiBr_2\{(Ph_2P)N\{P(S)Ph_2\}(p-C_6H_4)SMe-P,S\}]$ (**8**) and the Pd(II) analogue of **6**, $[PdCl_2\{(Ph_2P)N\{P(S)Ph_2\}(p-C_6H_4)SMe-P,S\}]$ (**9**), were synthesized and structurally characterized and their solution behavior was investigated. The catalytic activity and selectivity in ethylene oligomerization of the Ni(II) complexes **5** and **6** and their known *N*-(methylthio)propyl analogues $[NiCl_2\{(Ph_2P)_2N(CH_2)_3SMe-P,P\}]$ (**2**) and $[NiCl_2\{(Ph_2P)N\{P(S)Ph_2\}(CH_2)_3SMe-P,S\}]$ (**3**), which were obtained from the bis(diphenylphosphino)(*N*-(methylthio)propyl)amine ligand $N(PPh_2)_2(CH_2)_3SMe$ (**1**) and its monosulfide derivative $(Ph_2P)N\{P(S)Ph_2\}(CH_2)_3SMe$ (**1S**), respectively, revealed a significant influence of the nature of the *N*-substituent (aryl vs alkyl thioether) and of the chelate ring size (*P,P* vs *P,P*=S). DFT calculations showed that the trend in ΔE_{rel} , $[NiCl_2(P,P)] > [NiCl_2(P,P=S)] > [NiCl_2(P=S,P=S)]$, results from the stronger covalent character of the Ni–P vs Ni–S bond. Using $AlEtCl_2$ as cocatalyst, mostly ethylene dimers were produced, with significant amounts of trimers (selectivity in the range 11–36%). Productivities up to 40400 and 48200 g of $C_2H_4/((g \text{ of Ni}) h)$, with corresponding TOF values of 84800 and 101100 mol of $C_2H_4/((mol \text{ of Ni}) h)$, were obtained with precatalysts **2** and **3**, respectively.



INTRODUCTION

Short-bite ligands, such as bis(diphenylphosphino)methane-type (DPPM) and bis(diphenylphosphino)amine-type (DPPA) ligands, offer a diversity of coordination modes (monodentate, bidentate chelating, or bridging), which is reflected in their rich coordination chemistry. While their neutral forms, $Ph_2PCH_2PPh_2$ and $Ph_2PNHPPPh_2$, respectively, act as four-electron donors on coordination to a metal center through both phosphines, an additional X-type donor function is available in their deprotonated forms $(Ph_2PCHPPPh_2)^-$ and $(Ph_2PNPPPh_2)^-$, respectively.¹ Furthermore, various *N*-substituents can be readily introduced in DPPA-type ligands, which may facilitate the formation of polymetallic complexes² or the anchoring of coordination compounds into mesoporous materials³ or on metallic surfaces.⁴ Metal complexes of such short-bite ligands are involved in various catalytic reactions,⁵ and chromium derivatives in particular have been intensely studied for the selective catalytic tri- and tetramerization of ethylene.⁶ Four-

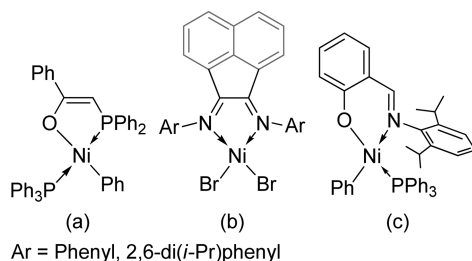
membered-ring nickel(II) complexes with chelating short-bite ligands have also been successfully used as precatalysts in ethylene oligo- or polymerization, although they do not display the selectivity of the analogous Cr complexes.⁷ The presence of a cocatalyst, such as an organoaluminum compound, is generally required and the characterization of the active species formed remains challenging.⁸ To date, no Ni(PNP)/Al system could be isolated, and only one bimetallic Cr(II)/Al complex supported by a DPPA-type ligand, resulting from the reaction of $[CrCl_3\{(Ph_2P)_2N(Cy)-P,P\}]$ with $AlMe_3$ as activator, could be structurally characterized.⁹

Five- and six-membered-ring Ni(II) complexes have been successfully applied to ethylene oligomerization, and typical examples are shown in Chart 1.^{10–12}

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Chart 1. Examples of “Post-Metallocene” Nickel Catalysts for Olefin Oligo-/Polymerization^{10–12}

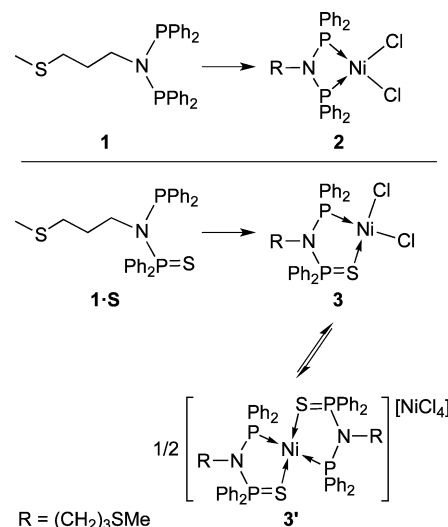


Our interest in catalytic ethylene oligomerization has led us *inter alia* to prepare various Ni complexes with mixed *P,L* ligands (*L* = N, O) (Chart 2).¹³ The association within a functional ligand of donor sets of different hard–soft properties leads to so-called hybrid ligands,¹⁴ which have been of longstanding interest to us.^{14a,b} Hybrid ligands bring about stereoelectronic differentiation within the metal coordination sphere, in particular in the positions *trans* to these donor atoms. Their metal complexes can exhibit in solution a hemilabile behavior resulting from the reversible coordination–decoordination of the weaker donor. This feature allows stabilization of potentially coordinatively unsaturated species and facilitates substrate coordination for improved catalytic performance.¹⁴

Starting from short-bite ligands, one can readily obtain a hybrid ligand by selective mono-oxidation of one *P*-donor group into a phosphorus oxide or sulfide, which can potentially form a five-membered-ring chelate upon metal coordination. Oxidation of both *P*(III) centers would of course restore a symmetrical bidentate ligand, suitable for the formation of six-membered-ring metal complexes. Starting from bis-(diphenylphosphino)(*N*-(methylthio)propyl)amine (**1**, *N*-(PPh_2)₂(CH_2)₃SMe), we recently prepared its monosulfide (Ph_2P) $\text{N}\{\text{P}(\text{S})\text{Ph}_2\}(\text{CH}_2)_3\text{SMe}$ (**1·S**) and obtained their corresponding Ni(II) complexes $[\text{NiCl}_2\{(\text{Ph}_2\text{P})_2\text{N}(\text{CH}_2)_3\text{SMe-P,P}\}]$ (**2**) and $[\text{NiCl}_2\{(\text{Ph}_2\text{P})\text{N}\{\text{P}(\text{S})\text{Ph}_2\}(\text{CH}_2)_3\text{SMe-P,S}\}]$ (**3**), which contain a *P,P* (**2**) or a *P,P=S* (**3**) chelate, respectively. These complexes exhibit very different reactivities in solution.¹⁵ In contrast to the symmetrical chelate complex $[\text{NiCl}_2(\text{P,P})]$ (**2**), which is stable in solution at various temperatures and in the presence of MeOH, a solvent-dependent reversible ligand exchange was found to be remarkably easy in the unsymmetrical chelate complex $[\text{NiCl}_2(\text{P,P=S})]$ (**3**) (Scheme 1).

An equilibrium was established in CH_2Cl_2 at room temperature between the neutral diamagnetic complex $[\text{NiCl}_2(\text{P,P=S})]$ (**3**) and the paramagnetic ion pair $[\text{Ni}(\text{P,P=S})_2][\text{NiCl}_4]$ (**3'**), which involves the reversible transfer

Scheme 1. Bis(diphenylphosphino)(*N*-(methylthio)propyl)amine Ligand **1** and Its Chelate Complex $[\text{NiCl}_2(\text{P,P})]$ (**2**) (Top) and Equilibrium between the Neutral Diamagnetic Complex $[\text{NiCl}_2(\text{P,P=S})]$ (**3**) and the Paramagnetic Ion Pair $[\text{Ni}(\text{P,P=S})_2][\text{NiCl}_4]$ (**3'**) Containing the Monosulfide Derivative Ligand **1·S** (Bottom)

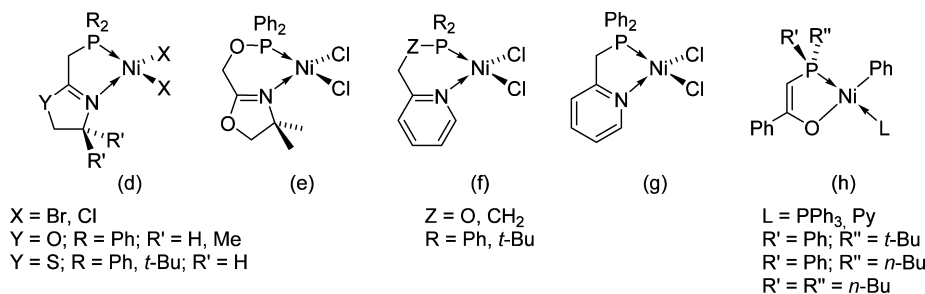


of the chelating ligand **1·S**, accompanied by chloride migration. This equilibrium was studied by multinuclear NMR, UV–visible, and FTIR spectroscopic methods and density functional theory (DFT) calculations.¹⁵ After identifying the factors responsible for the equilibrium, we have isolated, characterized, and produced selectively one isomer or the other.

The coordination chemistry of the Ni(II) ion with other hybrid ligands, of the *P,N* type, was recently shown to lead to high versatility and facile structural modifications.¹⁶ These included (i) the pressure-induced fragmentation of a tetranuclear complex with 20-electron Ni centers into mononuclear complexes $[\text{NiCl}_2(\text{P,N})]$ with 16-electron Ni centers,¹⁷ (ii) the formation of mono- or dinuclear isomers as a function of the crystallization temperature,^{13a,18} and (iii) the equilibrium in solution between the two formula isomers $[\text{Ni}(\text{P,N})_2][\text{NiCl}_4]$ and $[\text{NiCl}_2(\text{P,N})]$.¹⁹

Starting from short-bite ligands, we were interested in studying how small changes in the metal catalyst design may modify their catalytic properties. We examined first the influence of the *N*-substituent in DPPA-type ligands (type **1** vs type **4** ligands with a flexible or more rigid tail, respectively) and then that of the size of the chelate ring in the complex,

Chart 2. Examples of Ni(II) Precatalysts with Phosphorus-Based *P,L* Chelates for Ethylene Oligomerization from Our Laboratory¹³



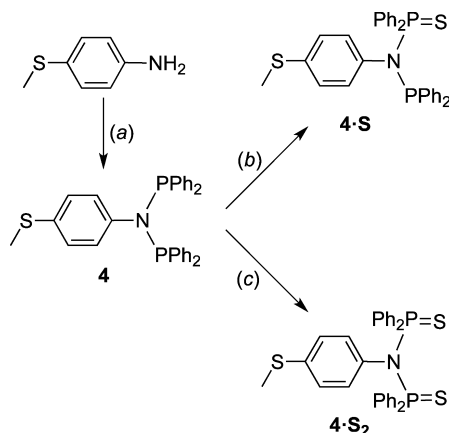
although we realize that this is accompanied by a change in the nature of one of the donor groups (four-membered ring in P,P chelates vs five-membered ring in the corresponding $P,P=S$ chelates). One objective was to provide unambiguous characterization, preferably both in the solid state and in solution, of precatalysts to be used in ethylene oligomerization.

We report here the synthesis, characterization, and DFT calculations of the Ni(II) complexes $[\text{NiCl}_2\{(\text{Ph}_2\text{P})_2\text{N}(p\text{-C}_6\text{H}_4\text{SMe})\text{-}P,P\}]$ (**5**) and $[\text{NiCl}_2\{(\text{Ph}_2\text{P})\text{N}\{P(S)\text{Ph}_2\}(p\text{-C}_6\text{H}_4\text{SMe})\text{-}P,S\}]$ (**6**), prepared from the ligand bis-(diphenylphosphino)(*N*-4-(methylthio)phenyl)amine (**4**) and its monosulfide derivative **4**·S, respectively. These complexes are *N*-aryl thioether analogues of complexes **2** and **3** obtained with *N*-alkyl thioether DPPA-type ligands. We also discuss the catalytic activities of the corresponding NiCl₂ complexes (**2**, **3** and **5**, **6**) in ethylene oligomerization, with ethylaluminum dichloride as cocatalyst, as a function of the influence of the *N*-substituent (aryl vs alkyl function) in the chelating diphosphine ligand and of the size of the chelate ring formed upon coordination to the Ni(II) center.

RESULTS AND DISCUSSION

Synthesis and Spectroscopic Characterization of the *N*-Arylthioether DPPA-Type Ligands. The preparation of bis(diphenylphosphino)(*N*-4-(methylthio)phenyl)amine (**4**) was readily achieved by reaction of the corresponding amines with 2 equiv of PPh₂Cl in the presence of excess NEt₃ as HCl scavenger (Scheme 2, reaction a).²⁰

Scheme 2. Synthesis of (*P,P*), (*P,P=S*), and (*P=S,P=S*) Ligands **4**, **4**·S, and **4**·S₂.^a



^aLegend; (a) PPh₂Cl (2 equiv), NEt₃ (2.5 equiv), THF, room temperature, 3 h; (b) S₈ (1.5 equiv), CH₂Cl₂, room temperature, 30 min; (c) S₈ (2.2 equiv), toluene, 115 °C, 3 h.

The ligand **4** was obtained in good yield (71%) as an air- and moisture-sensitive white powder. Its ³¹P{¹H} NMR spectrum contains a singlet resonance at 69.4 ppm for the two equivalent

phosphorus atoms (Table 1). This chemical shift is in agreement with the values observed for *N*-aryl-substituted DPPA-type ligands (62.2–71.1 ppm), higher values being found for compounds with aryl groups substituted at the *para* position (66.1–71.1 ppm).²¹ The monosulfide derivative **4**·S could not be obtained in pure form, owing to the concomitant formation of the bis-sulfide byproduct **4**·S₂ in a ca. 70:30 ratio (Scheme 2, reactions b and c). A similar situation was observed in the case of ligand **1**·S, which like **4**·S was prepared and used in situ for the synthesis of the desired Ni(II) complexes. The undesired compound **4**·S₂ can easily be removed by successive washings of its Ni(II) complexes with toluene (see below). However, the bis-sulfide derivative **4**·S₂ can be quantitatively obtained, as an air-stable white powder, using a slight excess of elemental sulfur, but its coordination properties will not be discussed here (Scheme 2, reaction c). Both **4**·S and **4**·S₂ were fully characterized, and their ³¹P{¹H} NMR spectra exhibit the expected patterns: i.e., two doublets (55.3 (P^{III}) and 72.4 (P^V) ppm; ²J_{P,P} = 104.5 Hz) for the mixed *P,P=S* ligand **4**·S and a singlet (69.0 ppm) for the two equivalent phosphorus atoms of **4**·S₂ (Table 1). These chemical shifts are comparable to those reported for other mono- and bis-sulfide DPPA-type ligands, which were found in the respective ranges: 51.5–54.5 (P^{III}) and 67.5–73.5 (P^V)^{21g,h,22} (monosulfide derivatives) and 67.5–73.6 ppm (bis-sulfide derivatives).^{21a–d,g,23} The experimental ³¹P{¹H} NMR chemical shifts of the *N*-thioether-functionalized *P,P=S* and *P=S,P=S* ligands (**1**·S, **1**·S₂, **4**·S, and **4**·S₂) measured in CDCl₃ and CD₂Cl₂ solutions were well reproduced by NMR calculations on the BP86/TZ2P minimum-energy gas-phase structures of **1**·S^{DFT}, **1**·S₂^{DFT}, **4**·S^{DFT}, and **4**·S₂^{DFT} (Supporting Information, Tables S4–S8).

The molecular structures of ligands **4** and **4**·S₂ were determined by single-crystal X-ray diffraction studies and are depicted in Figures 1 and 2, respectively. To the best of our knowledge, only four other bis(diarylphosphino)(*N*-4-(*R*)-phenyl)amine ligands have been structurally characterized (**A–D**),^{3a,21a,24,25} and interesting structural differences with ligand **4** were observed (Scheme 3 and Figure S-1 (Supporting Information)).

While in the reported compounds **A**,^{3a} **B**,²⁴ and **C**,^{21a} as well as in ligand **1**,²⁰ the P lone pairs display a *syn* conformation (pointing in the same direction, a typical chelating coordination orientation), those of ligand **4** and the *P*-benzyl derivative **D**²⁵ present an *anti* orientation (pointing in opposite directions; Scheme 3, bottom). The structure of **4** also exhibited a stronger tilt of the angle (α) between the aryl ring and the PNP plane (α = 62.1°) in comparison to **A** (α = 82.4°), **B** (α = 80.5°), **C** (α = 81.7°), and **D** (α = 78.3°) (Scheme 3, top). In view of the structures of ligands **A**^{DFT} (α = 84.4°), **B**^{DFT} (α = 83.5°), and **4**^{DFT} (α = 61.7°) calculated in the gas phase, one can say that the conformational difference associated with the α angle is rather “intrinsic” to **4** instead of being caused by packing effects (Supporting Information, Table S9). The other possible

Table 1. ³¹P{¹H} NMR Data of Ligands **4**, **4**·S₂, and **4**·S and Complexes **5–9**

	4 ^a	4 ·S ₂ ^a	4 ·S ^a	5 ^b	6 ^a	7 ^b	8 ^{a,d}	9 ^{a,d}
δ (ppm)	69.4	69.0	55.3; 72.4	45.4	83.8	84.6; 105.8	83.7	80.1; 106.7
mult	s	s	d; d	s	br s	t; t	br s	d; d
J (Hz)			² J _{P,P} = 104.5			^{2,2+3,3,4} J _{P,P} ^c		²⁺³ J _{P,P} = 59.9

^aNMR solvent CDCl₃. ^bNMR solvent CD₂Cl₂. ^cDetailed in the Experimental Section. ^dSee the Supporting Information.

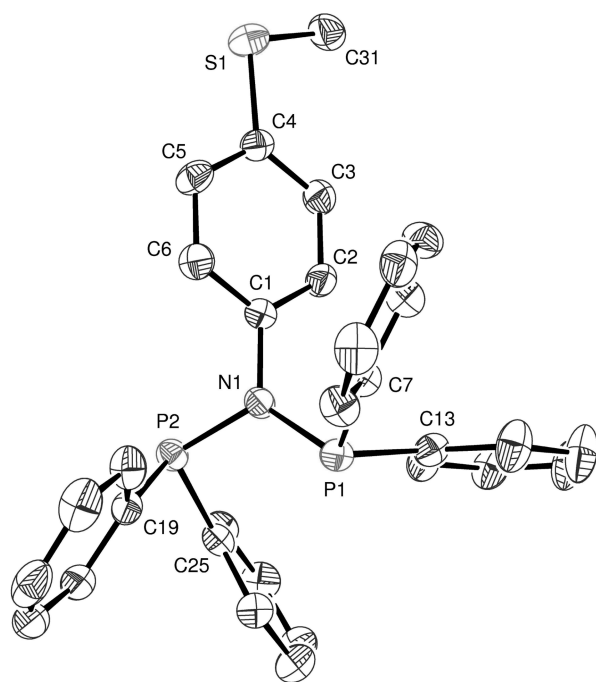


Figure 1. ORTEP drawing of the molecular structure of $N(PPh_2)_2(p\text{-}C_6H_4)SMe$ (**4**). Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): P1–N1 1.732(2), P2–N1 1.728(2), C1–N1 1.452(3); P1–N1–P2 120.8(1).

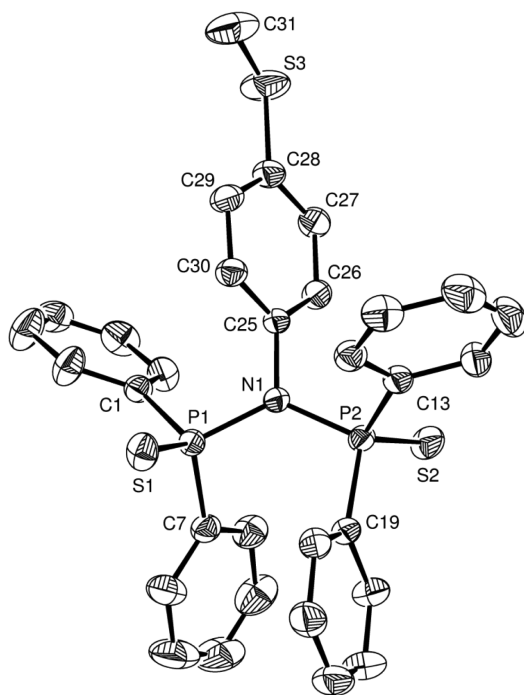
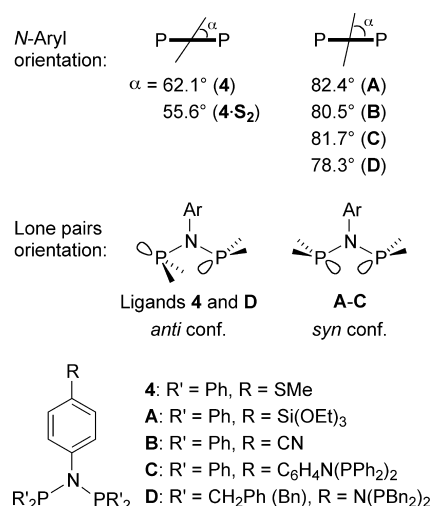


Figure 2. ORTEP drawing of the molecular structure of $N\{P(S)Ph_2\}_2(p\text{-}C_6H_4)SMe$ (**4·S₂**). Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): P1–N1 1.708(1), P2–N1 1.717(1), P1–S1 1.9452(6), P2–S2 1.9350(6), N1–C25 1.457(2); P1–N1–P2 127.11(7), S1–P1–N1 115.16(5), S2–P2–N1 114.82(5).

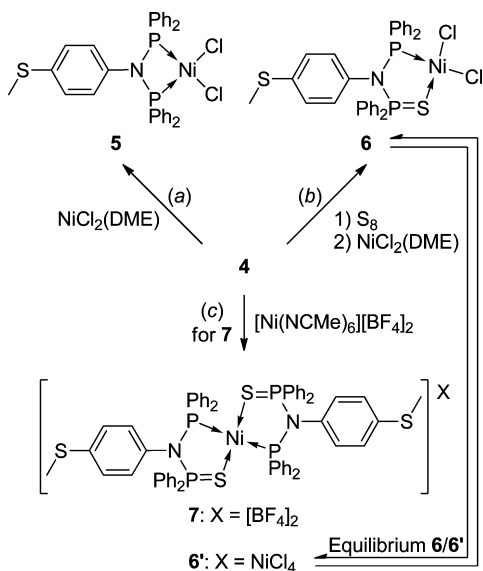
relationships between the orientation of P lone pairs and the α angle were not explored further.

Scheme 3. Main Structural Differences between Ligand **4** and the known Ligands **A–D**



The solid-state structure of **4·S₂** revealed characteristic P=S, P–N, and C–N bond lengths and a P–N–P angle in the usual range.^{21c,22d,23a,26} All attempts to obtain suitable crystals of ligand **4·S** for X-ray diffraction were unsuccessful, which may explain the relatively small number of structures of mono-sulfide-DPPA derivatives reported.^{22d,e} Interestingly, the oxidation of the P centers and the formation of the bis-sulfide ligand **4·S₂** result in only slight structural differences in comparison to **4**. The P–N and C–N bond lengths are almost similar (average 1.73 Å (**4**) vs 1.71 Å (**4·S₂**)), while the most affected parameters are the PNP angle (120.8(1)° (**4**) vs 127.1(7)° (**4·S₂**)) and the angle between the PNP moiety²⁷ and the phenyl ring ($\alpha = 62.1^\circ$ (**4**) vs 55.6° (**4·S₂**)) (Scheme 3). The BP86/TZ2P calculations provide values for the angles α comparable to those determined experimentally. Thus, the α angle between the planes of the PNP moiety and the N-aryl ring was calculated to be 61.7° for **4**^{DFT}, 57.6° for **4·S₂**^{DFT}, and 79.3° for the hypothetical structure **4·S**^{DFT}. The calculated PNP angles in **4**^{DFT}, **4·S₂**^{DFT}, and **4·S**^{DFT} are 120.8, 129.0, and 117.2°, respectively. As a result, a correlation between the α and PNP angles was observed: the greater the α angle (**4·S₂**^{DFT} < **4**^{DFT} < **4·S**^{DFT}), the smaller the PNP angle (**4·S₂**^{DFT} > **4**^{DFT} > **4·S**^{DFT}).

Synthesis of the Ni(II) Complexes. With the objective of developing new (pre)catalysts for ethylene oligomerization and evaluating the influence of the ligand properties (P,P vs P,P=S, chelate ring size, nature of the N-substituent), we prepared nickel(II) complexes with ligands **4** and **4·S** by analogy with complexes of the type [NiX₂(LL')] (e.g. LL' = P,N, P,O, or P,P ligand and X = Cl, Br).^{13a,b,28} Reaction of **4** with [NiCl₂(DME)] (DME = 1,2-dimethoxyethane) in a 1:1 ratio in dichloromethane at room temperature afforded [NiCl₂{(Ph₂P)₂N(p-C₆H₄SMe)-P,P}] (**5**) in high yield (83%) as a red crystalline powder (Scheme 4, reaction a). This color is consistent with the square-planar structure and diamagnetic nature of Ni(II) complex **5**, which could therefore be fully characterized by multinuclear NMR spectroscopic methods. Its ³¹P{¹H} NMR spectrum exhibits a singlet at 45.4 ppm, shifted upfield with respect to the free ligand **4** (s, 69.4 ppm, Table 1). This value compares well with those found for the other [NiX₂(P,P)] (X = Cl, Br, I and P,P = N-functionalized DPPA-type ligand) complexes reported (38.6–58.3 ppm).^{7b,c,e,15,23c,29}

Scheme 4. Synthesis of the Ni Complexes 5–7^a

^aLegend: (a) 1 equiv of [NiCl₂(DME)], CH₂Cl₂, room temperature, 4 h; (b) 1.5 equiv of S₈, CH₂Cl₂, room temperature, 30 min and 0.55 equiv of [NiCl₂(DME)], CH₂Cl₂, room temperature, 4 h; (c) 1.5 equiv. of S₈, CH₂Cl₂, room temperature, 30 min followed by 0.25 equiv of [Ni(NCMe)₆][BF₄]₂, CH₂Cl₂, room temperature, 4 h. Note: complexes 6 and 6' are in equilibrium in solution. DME = 1,2-dimethoxyethane.

Since 4·S could not be isolated in pure form, it was prepared in situ (see above), and subsequent addition of 0.5 equiv of [NiCl₂(DME)] led to the formation of [NiCl₂{(Ph₂P)N{P(S)Ph₂}(p-C₆H₄SMc)-P,S}] (6) in good yield (82%) as a crystalline solid, after removal of the undesired 4·S₂ by successive washings with toluene (Scheme 4, reaction b). Its purple color, both in the solid state and in solution, contrasts with that of the diamagnetic complex 5 (red). The ³¹P{¹H} NMR spectrum of a solution of 6 exhibited a broad singlet centered at 83.8 ppm (Table 1) instead of the expected pattern of two doublets for the nonequivalent P^{III} and P^V donors, as observed for the free ligand. A similar ³¹P{¹H} NMR spectrum was obtained for the complex [NiBr₂(4·S)] (8), which suggests no significant influence of the halide nature on the solution behavior of such P,P=S-chelate Ni(II) complexes (see Table 1 and the Supporting Information). The paramagnetic character of the solution prevented the recording of well-resolved ¹H and ¹³C NMR spectra. We recently showed in the case of complex 3 (Scheme 1), which is the analogue of 6 with the N-alkyl thioether ligand 1·S, that this broad signal observed in the NMR is due to a fast equilibrium in solution between the neutral diamagnetic [NiCl₂(1·S)] (3) species and its paramagnetic ion pair formula isomer [Ni{(1·S)₂}[NiCl₄] (3').¹⁵ This equilibrium was found to be dependent on the temperature and the solvent polarity and could be unambiguously characterized by ³¹P VT-NMR and UV–vis (variable temperature and polarity gradient) spectroscopic techniques and rationalized by computational studies. On the basis of this previous work, we reasonably assume that a similar equilibrium between the anticipated [NiCl₂(4·S)] structure and the ion pair formula isomer [Ni{(4·S)₂}[NiCl₄] (6') (Scheme 4), as well as for its NiBr₂ analogue 8, can be envisaged. Furthermore, the ESI-MS spectrum of a CH₂Cl₂ purple solution of complex 6 confirmed this hypothesis by revealing peaks at *m/z* 632.01 and

1298.99, which can be attributed to {[NiCl₂(4·S)] – Cl}⁺ and {[Ni{(4·S)₂}[NiCl₄] – Cl}⁺, respectively. Unfortunately, direct comparison of NMR data with literature values was not possible since, as far as we know, no other NiCl₂ complex of monosulfide N-functionalized DPPA-type ligands has been reported. Only PdCl₂ and PtCl₂ complexes have been described, which of course exhibit well-resolved signals, such as [PdCl₂(4·S)] (9) (see Table 1 and the Supporting Information).^{21g,h,22b,c,e} It is worth noting that no change in the ³¹P{¹H} NMR spectrum of 9 was observed, even by modification of the solvent polarity or recording temperature, in contrast to its Ni(II) analogues 6 and 8, reflecting the higher kinetic stability in solution of Pd derivatives. While isomer 6 could be isolated in pure form, all attempts to isolate the hypothetical isomer 6' by increasing the solvent polarity upon addition of MeOH (as for 3')¹⁵ led to a metal-induced dismutation-type reaction of the phosphorus atoms, resulting in the formation of the non-P=S-containing complex 5 and the bis-sulfide ligand 4·S₂ in a 1:1 ratio (NMR evidence). This transformation, from 6 to 5 and 4·S₂, was also observed when pure 6 was dissolved in *d*₆-DMSO, an aprotic but polar solvent. The latter characteristic thus appears decisive for the occurrence of this ligand transformation.

Since the paramagnetic component of 6' is [NiCl₄]²⁻, we prepared the diamagnetic bis-chelated complex [Ni{(Ph₂P)N{P(S)Ph₂}(p-C₆H₄SMc)-P,S}]₂(BF₄)₂ (7), containing the same dication as the hypothetical complex 6', using [Ni(NCMe)₆][BF₄]₂ as precursor instead of [NiCl₂(DME)] (Scheme 4, reaction c). Complex 7 was obtained in good yield (85%) as a crystalline solid, its red color (yellow in diluted solution) being characteristic of a square-planar arrangement of the ligands around the metal center. Its diamagnetic nature therefore allowed its full characterization by multinuclear NMR experiments, and its ³¹P{¹H} NMR spectrum exhibited two tripletlike resonances (AA'BB' spin system) at 105.8 (P^V) and 84.6 (P^{III}) ppm (Table 1).

An NMR experiment consisting of the addition of Cl⁻ anions (from HNEt₃Cl) to a solution of 7 showed an evolution of the NMR spectrum, from two well-resolved “triplets” to one broad singlet centered at 83.8 ppm, similar to that of 6, and the liberation of uncoordinated ligand 4·S (see the Experimental Section and Figure S2 (Supporting Information)). This reaction is accompanied by a significant color change from yellow (7) to the familiar purple of complex 6. These observations are reminiscent of the behavior of analogous complexes containing the N-alkyl thioether ligand 1·S (Scheme 1).¹⁵ From the unambiguously characterized equilibrium between 3 and 3', we conclude the existence of a similar process between 6 and 6'.

The chemical shifts observed for the methyl protons in complexes 5 and 7 (2.32 and 2.26 ppm, respectively) remain very close to that for the free diphosphines 4 and 4·S (2.35 and 2.23 ppm, respectively), indicating no S···Ni interaction in solution.

Solid-State Structure of the Ni(II) Complexes. Single crystals of complexes 5–7 suitable for X-ray diffraction studies were obtained as described in the Experimental Section. Their solid-state structures are depicted in Figures 3–5, and selected bond lengths and angles are reported in Table 2. In all three complexes, the Ni center displays a distorted-square-planar coordination geometry, with the P,P (4) and P,P=S (4·S) ligands acting as chelates, forming four- (5) and five-membered (6, 7) metallacycles. The metal coordination sphere in

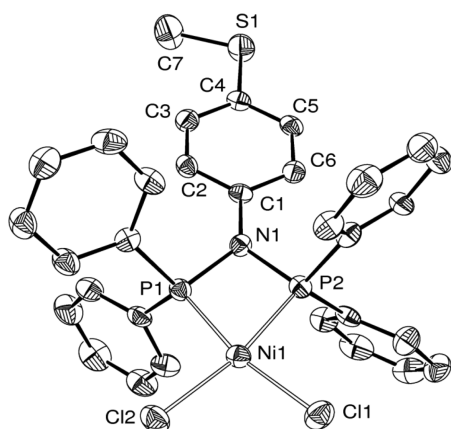


Figure 3. ORTEP drawing of the molecular structure of $[\text{NiCl}_2\{(\text{Ph}_2\text{P})_2\text{N}(p\text{-C}_6\text{H}_4)\text{SMe-}P,P\}]$ (**5**) in $5 \cdot 2\text{CH}_2\text{Cl}_2$. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

complexes **5** and **6** is completed by two chlorine ligands, while in the centrosymmetric structure of **7**, a second $P,P=S$ ligand is found in an *anti* arrangement.

The characteristic bond lengths and angles in **5** are similar to those found in related $[\text{NiCl}_2(P,P)]$ ($P,P = N$ -functionalized DPPA-type ligand) complexes.^{6c,29b,e,30} With the exception of complex **3**, which was recently described,¹⁵ no other example of a $[\text{NiCl}_2(P,P=S)]$ complex is available for comparison, to the best of our knowledge.

Interestingly, while the two $N-P$ bond lengths are similar in the (P,P) -Ni(II) complex **5**, the difference between the $\text{N1-P1}^{\text{III}}$ and the N1-P2^{V} distances in the $(P,P=S)$ -Ni(II) complexes **6** and **7** is more pronounced (1.731(3) and 1.678(3) Å (**6**) and 1.716(1) and 1.680(1) Å (**7**), respectively).

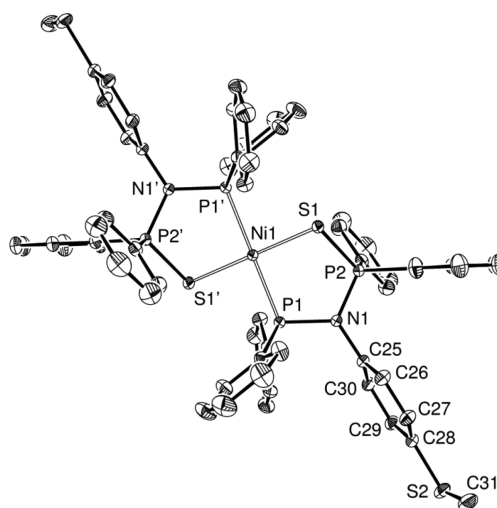


Figure 5. ORTEP drawing of the molecular structure of $[\text{Ni}\{(\text{Ph}_2\text{P})\text{-N}\{P(\text{S})\text{Ph}_2\}(p\text{-C}_6\text{H}_4)\text{SMe-}P,S\}_2](\text{BF}_4)_2$ (**7**) in $7 \cdot 4\text{CH}_2\text{Cl}_2$. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms, BF_4 anions, and solvent molecules are omitted for clarity.

This could be related to the electronegativity of the sulfur atom, which strengthens the $P-N$ bond, as observed in related complexes with $P=S$, $P=O$, and $P=Se$ groups.^{15,21g,22,22e,31}

The $P-N-P$ angle of the ligand is strongly affected by the presence of the sulfur donor (96.7° (**5**) vs 118.0° (**6**) and 114.7° (**7**)). In the $[\text{NiCl}_2(P,P)]$ complex **5**, the rectangular distortion of the coordination geometry around the metal is due to the four-membered chelate ring, which imposes a $P-Ni-P$ angle of 74.2° , while in the $[\text{Ni}(P,P=S)]$ -type complexes, the $P-Ni-S$ angle is closer to the preferred 90° (94.3° (**6**), 93.2° (**7**)).

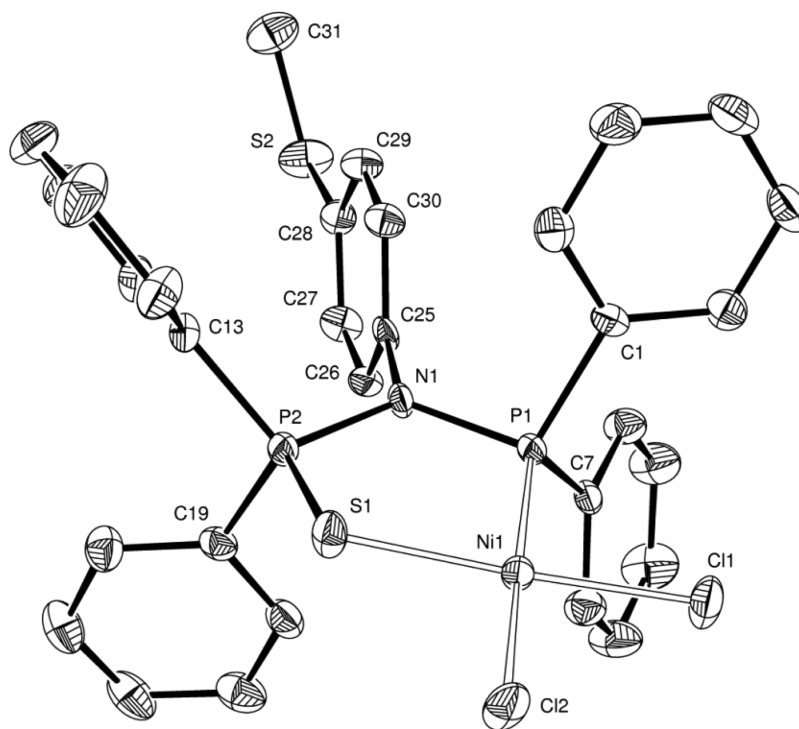


Figure 4. ORTEP drawing of the molecular structure of $[\text{NiCl}_2\{(\text{Ph}_2\text{P})\text{N}\{P(\text{S})\text{Ph}_2\}(p\text{-C}_6\text{H}_4)\text{SMe-}P,S\}]$ (**6**) in $6 \cdot \text{C}_3\text{H}_6\text{O}$. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in the Solid-State Structures of **5**·2CH₂Cl₂, **6**·C₃H₆O, and **7**·4CH₂Cl₂

	5	6	7
N1–P1	1.706(5)	1.731(3)	1.716(1)
N1–P2	1.716(5)	1.678(3)	1.680(1)
P2–S1		2.004(1)	2.020(4)
P1–Ni1	2.110(2)	2.138(1)	2.198(3)
P2(S1)–Ni1	2.128(2)	2.163(1)	2.180(3)
Ni1–Cl1	2.183(2)	2.173(1)	
Ni1–Cl2	2.202(2)	2.211(1)	
Cl1–Ni1–Cl2	99.26(6)	94.91(4)	
P1–Ni1–P2(S1)	74.20(6)	94.26(4)	93.16(1)
P1–Ni1–P2	96.70(2)	118.0 (2)	114.7(6)

However, the Cl–Ni–Cl angle is only slightly affected (99.3° (**5**) vs. 94.9° (**6**)).

As expected, the two P–Ni bond lengths in complex **5** are nearly equivalent (average 2.12 Å) and similar to the P1–Ni bond (2.14 Å) in complex **6**. The slightly stronger *trans* influence of the P donor compared to S in the mixed (P,P=S) nickel complex **6**, results in a longer Ni–Cl2 bond compared to Ni–Cl1, as also observed in related PdCl₂ and PtCl₂ complexes with (P,P=S) or (P,P=Se) DPPA-type ligands.^{21g,22c,e} In the bis-chelated dicationic complex of **7**, both L–Ni bonds (L = P, S) were found to be 0.2–0.6 Å longer than in complex **6**. The solid-state molecular structures of [NiBr₂(**4**·S)] (8·CH₂Cl₂) and [PdCl₂(**4**·S)] (**9**) are very similar to that of complex **6** (see the Supporting Information, Figure S3 and Table S3).

The DFT relative energies (ΔE_{rel}) calculated for the reaction processes associated with the formation of the Ni(II) complexes of the *N*-alkyl thioether functionalized DPPA-type ligands **1**^{DFT}, **1**·S^{DFT}, and **1**·S₂^{DFT} (type A) and those of their *N*-aryl thioether counter parts **4**^{DFT}, **4**·S^{DFT}, and **4**·S₂^{DFT} (type B) show that the presence of sulfur atoms at P significantly influences the energetics of the nickel–ligand bonding, thus resulting in decreased thermodynamic stability of the optimized Ni(II) complexes with the (P,P=S) and (P=S,P=S) ligands

(Figure 6). The trend in ΔE_{rel} is thus as follows: [NiCl₂(P,P)] > [NiCl₂(P,P=S)] > [NiCl₂(P=S,P=S)]. From these data, we may expect that the overall stability of the compounds, which in the case of [NiCl₂(P,P=S)] is the combined result of a modification in the chelate ring size (five-membered chelates are usually more stable than four-membered chelates) and the associated change in the nature of the donor groups (a P=S moiety is a poorer donor for Ni(II) than P) may influence the catalytic properties of the Ni(II) complexes in ethylene oligomerization.

Catalytic Ethylene Oligomerization. The nickel(II) complexes with *N*-(methylthio)propyl (**2**, **3**) or *N*-4-(methylthio)phenyl (**5**, **6**) functionalized PNP or P(S)NP-type ligands, containing a four- (**2**, **5**) or five-membered chelate (**3**, **6**), were evaluated as precatalysts in the oligomerization of ethylene with AlEtCl₂ as cocatalyst. Various amounts of cocatalyst and different concentrations of precatalysts were tested, and the catalytic results are presented in Table 3. To allow comparisons with previous studies, we kept the reaction time constant at 35 min and the ethylene consumption during catalysis progressively decreased but was retained up to at least 60 min (entries 2 and 9, Table 3). The reaction products did not follow a Schulz–Flory distribution of their chain length, since mostly dimers and significant amounts of trimers (selectivity in the range 11–36%) were obtained. The percentages of C8 and C10 measured are in the ranges 0–3.4% and 0–2.7%, respectively, and no longer chains were observed.

Comparison between [NiCl₂(P,P)]- and [NiCl₂(P,P=S)]-Type Complexes. Such a comparison, made with a constant *N*-substituent, allows us to examine the combined effect of a change in the chelate ring size and of the resulting difference in the nature of the donor atoms on the catalytic activity and/or the selectivity. In the *N*-(methylthio)propyl series, the activity of the P,P=S complex **3** was found to be higher than that of its P,P counterpart **2** at high Al/Ni ratios (10 and 40, entries 1–3 and 6, 7, respectively), with turnover frequencies (TOFs) of 47400 and 101100 mol of C₂H₄/((mol of Ni) h) for **3** and 35800 and 84800 mol of C₂H₄/((mol of Ni) h) for **2**,

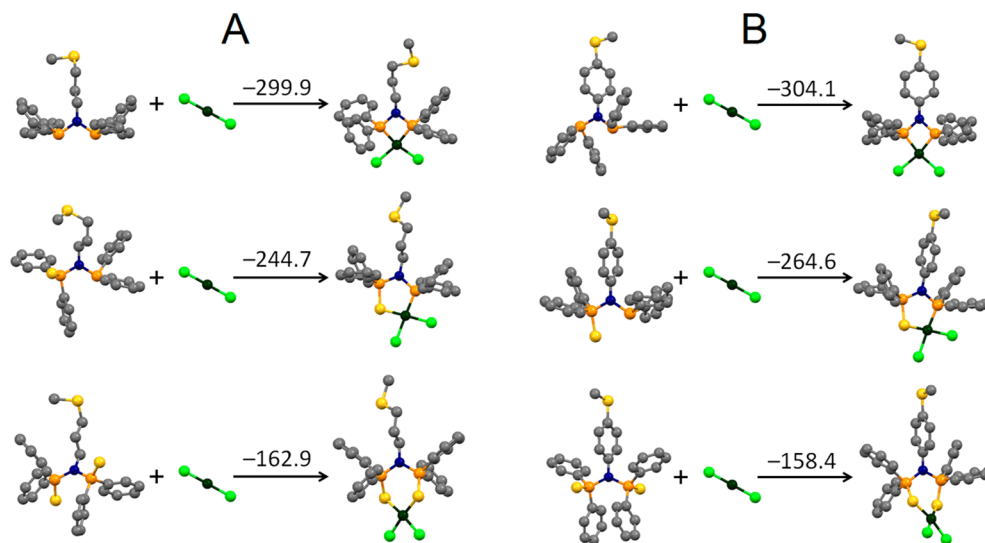


Figure 6. BP86/TZ2P relative energies (ΔE_{rel} in kJ mol^{−1}, including zero-point energy corrections) calculated for the gas-phase reaction processes involving minimum energy structures of the ligands analyzed herein and their Ni(II) complexes of types A and B. Color code: C, gray; N, blue; P, orange; S, yellow; Cl, light green; Ni, dark green. For more details on the computational methodology, see the Supporting Information.

Table 3. Pairwise Comparison of the Catalytic Data for Complexes 2, 3, 5, and 6 in the Oligomerization of Ethylene with AlEtCl₂ as Cocatalyst^a

entry no.	complex	n_{complex} (10 ⁻⁵ mol)	AlEtCl ₂ (equiv)	selectivity (%)				productivity ^{b,d}	TOF ^{c,d}	1-butene ^e (%)
				C4	C6	C8	>C8			
1	2	4	10	77	20	2	1	17100	35800	17
2 ^f	2	2	10	64	31	4	1	23000	48300	8.4
3	3	4	10	71	26	2	<1	22600	47400	7
4	2	4	3	77	21	2	0	3100	6600	16
5	3	4	3	70	21	7	2	2300	4800	35
6	2	1	40	70	26	3	1	40400	84800	16
7	3	1	40	66	26	5	2	48200	101100	25
8	5	4	10	69	27	3	<1	23100	48400	4
9 ^f	5	2	10	68	26	3	2	32800	68800	9
10	6	4	10	82	16	1	<1	12700	26700	9
11	5	4	3	58	36	5	1	12900	27100	9
12	6	4	3	87	11	1	<1	3900	8200	15
13	5	1	40	79	20	1	0	20000	41900	26
14	6	1	40	73	23	3	1	32200	67400	13

^aConditions: $T = 28-30^\circ\text{C}$, 10 bar of C₂H₄, time 35 min, solvent 10 mL chlorobenzene and 5 mL of the cocatalyst solution (8×10^{-5} M) for 10 and 40 equiv of AlEtCl₂ or 13.5 mL of chlorobenzene and 1.5 mL of the cocatalyst solution (8×10^{-5} M) for 3 equiv of AlEtCl₂. ^bIn g of C₂H₄/((g of Ni) h)). ^cIn mol of C₂H₄/((mol of Ni) h). ^dValues rounded off to the lower hundred. ^eWithin the C₄ fraction. ^fReaction time 60 min.

respectively. The chain-length selectivity was only slightly affected on going from 2 and 3 (entries 1–7), but a higher selectivity for C₄ oligomers was observed for the *P,P* derivative 2 at all precatalyst concentrations and Al/Ni ratios examined. Although modest, the best selectivity for 1-butene within the C₄ cut was achieved with complex 3, using 3 equiv of AlEtCl₂ and 4×10^{-5} mol catalyst loading and reached 35% (entry 5).

In the *N*-(4-methylthio)phenyl series, complex 6 exhibited TOF values between 8200 and 26700 mol of C₂H₄/((mol of Ni) h), while for 5, values between 27100 and 48400 mol of C₂H₄/((mol of Ni) h) (entries 12 and 10 (6) and entries 11 and 8 (5), respectively) were obtained. At higher Al/Ni ratios, the trend was reversed, since with 40 equiv of AlEtCl₂ and 1×10^{-5} mol catalyst loading, complex 6 exhibited a higher TOF (67400 vs 41900 mol of C₂H₄/((mol of Ni) h)) than 5. The selectivity in C₄ oligomers was generally improved, with 3 or 10 equiv of AlEtCl₂, by the introduction of the S donor and the associated increase in the chelating ligand ring size, since it reached 58 and 69% (entries 11 and 8) for complex 5 and 87 and 82% (entries 12 and 10), for complex 6, respectively. The lower activity of 6 in comparison to that of 5 was associated with an higher selectivity in C₄ oligomers (73 vs 79%) (entries 14 and 13).

Influence of the *N*-Substituent. Let us now compare the results obtained as a function of the *N*-substituent of the ligand, keeping the chelate ring size constant: i.e., comparing 2/5 and 3/6. While complex 2 (*P,P*; *N*-alkyl thioether) showed similar C₄ selectivities when different amounts of Ni and Al cocatalyst were used (70–77%, entries 1, 4, and 6), the C₄ selectivity observed for complex 5 (*P,P*; *N*-aryl thioether) varied much more (58–79%, entries 8, 11, 13) and remained generally lower than for 2. A greater difference in selectivity was observed for the *P,P*=S-containing Ni(II) complexes 3 and 6, and the latter always exhibited a higher selectivity, up to 87% for C₄ oligomers (entry 12), than its *N*-alkyl thioether counterparts 3 (70% under the same conditions, entry 5).

Within the *P,P* derivatives, we found better activities for the *N*-aryl complex 5 than for the *N*-alkyl complex 2 at lower Al/Ni ratios, with TOFs of 27100 (3 equiv of AlEtCl₂) and 48400 (10 equiv of AlEtCl₂) mol of C₂H₄/((mol of Ni) h) (entries 11 and

8, respectively) and 6600 (3 equiv of AlEtCl₂) and 35800 (10 equiv of AlEtCl₂) mol of C₂H₄/((mol of Ni) h) (entries 4 and 1), respectively. However, at higher Al/Ni ratios, using 40 equiv of AlEtCl₂, complex 2 led to TOF values more than twice those of 5 (84800 vs 41900 mol of C₂H₄/((mol of Ni) h), entries 6 and 13, respectively). For the *P,P*=S systems, however, the *N*-alkyl complex 3 was found to be more active than its *N*-aryl analogue 6 at high Al/Ni ratios (10 and 40 equiv of AlEtCl₂, entries 3 and 7 vs entries 10 and 14), and a lower TOF was observed for 3 (4800 mol of C₂H₄/((mol of Ni) h), entry 4) in comparison to 6 (8200 mol of C₂H₄/((mol of Ni) h), entry 12) when only 3 equiv of AlEtCl₂ was used.

Under the different conditions studied, the selectivity for α -olefins remained modest (4–35%) due to the typical fast isomerization process in Ni(II)-catalyzed oligomerization of ethylene.^{11c,32} No saturated hydrocarbons were produced during the catalytic process. The C₆ and C₈ oligomers produced contained a small percentage of linear chains in a larger distribution of branched olefins, which is indicative of the occurrence of both stepwise chain growth and of codimerization reactions (C₄ + ethylene).

CONCLUSION

The selective oligomerization of ethylene remains an active field of research, and the present work highlights, via a combination of experimental and computational studies, how subtle changes in the ligand design of the well-known (PNP)-NiCl₂ (pre)catalyst strongly influence their catalytic activity and selectivity. Our synthesis and characterization of the new bis(diphenylphosphino)(*N*-(4-methylthio)phenyl)amine ligand 4, its monosulfide derivative 4·S, and their Ni(II) complexes 5 and 6 follow our recent report on similar NiCl₂ derivatives (2 and 3) of the bis(diphenylphosphino)(*N*-(methylthio)propyl)-amine ligand 1 and its monosulfide derivative 1·S.¹⁵ The DFT geometry optimizations and relative binding energy calculations indicated that the [NiCl₂(*P,P*)] complexes have enhanced thermodynamic stability in comparison to the [NiCl₂(*P,P*=S)] and [NiCl₂(*P*=S,*P*=S)] complexes, and this is due to the stronger covalent character of the Ni–P vs the Ni–S bond. The series of NiCl₂ complexes (2, 3 and 5, 6) of *N*-thioether-

functionalized DPPA-type ligands (**1**, **1·S** and **4**, **4·S**) was applied to the catalytic oligomerization of ethylene. Using AlEtCl₂ as cocatalyst, mostly ethylene dimers were produced, with significant amounts of trimers (selectivity in the range 11–36%). Productivities up to 40400 and 48200 g of C₂H₄/((g of Ni) h), with corresponding TOF values of 84800 and 101100 mol of C₂H₄/((mol of Ni) h), were obtained with precatalysts **2** and **3**, respectively. It was clearly shown that both factors, (i) the chelate ring size formed upon coordination of the P,P and the P,P=S ligands to the Ni(II) center and (ii) the nature of the N-substituent, by comparison of the N-alkyl thioether and N-aryl thioether species, are important molecular characteristics, at constant cocatalyst, that should be considered in the development of active and selective (pre)catalysts for ethylene oligomerization. However, there is currently no clear explanation for the different catalytic performances as a function of the P,P or P,S donors and associated change in chelate ring size, of the N-substituent, and of the excess of cocatalyst used. It would be interesting in future work to examine to what extent interactions between the S atom of the N-substituent and the cocatalyst has an impact on its properties and also, perhaps, by bringing it closer to the nickel center.

EXPERIMENTAL SECTION

General Procedures. All operations were carried out using standard Schlenk techniques under an inert atmosphere. Solvents were purified and dried under nitrogen by conventional methods. CD₂Cl₂ and CDCl₃ were dried over 4 Å molecular sieves, degassed by freeze–pump–thaw cycles, and stored under argon. NMR spectra were recorded at room temperature on a Bruker AVANCE 300 spectrometer (¹H, 300 MHz; ¹³C, 75.47 MHz; ³¹P, 121.49 MHz) and referenced using the residual proton solvent (¹H) or solvent (¹³C) resonance. Chemical shifts (δ) are given in ppm. IR spectra were recorded in the region 4000–100 cm^{−1} on a Nicolet 6700 FT-IR spectrometer (ATR mode, SMART ORBIT accessory, Diamond crystal). Elemental analyses were performed by the “Service de microanalyses”, Université de Strasbourg. Electrospray mass spectra (ESI-MS) were recorded on a microTOF (Bruker Daltonics, Bremen, Germany) instrument using nitrogen as drying agent and nebulizing gas. Gas chromatographic analyses were performed on a Thermoquest GC8000 Top series gas chromatograph using a HP Pona column (50 m, 0.2 mm diameter, 0.5 μm film thickness). The complexes [NiCl₂(DME)],³³ [Ni(NCMe)₆](BF₄)₂,³⁴ [PdCl₂(COD)],³⁵ **2**,¹⁵ and **3**¹⁵ were prepared according to literature methods. All other reagents were used as received from commercial suppliers. All iteration-fitting calculations and simulations of the ³¹P{¹H} NMR spectra were performed by using the Bruker WIN-DAISY program.³⁶

Synthesis of the Ligands. **Ligand 4.** An excess of chlorodiphenylphosphine (6.342 g, 28.73 mmol) was added dropwise to a solution of 4-(methylthio)aniline (2.000 g, 14.37 mmol) and triethylamine (3.631 g, 35.91 mmol) in 150 mL of THF under an inert atmosphere. The reaction mixture was stirred for 3 h. After filtration, the volatiles were removed under reduced pressure and the residue was washed twice with pentane to give **4** as a colorless solid. Yield: 5.178 g, 71%. Anal. Calcd for C₃₁H₂₇NP₂S (507.57): C, 73.36; H, 5.36; N, 2.76. Found: C, 72.98; H, 5.48; N, 2.51. FTIR: ν_{max}(solid)/cm^{−1} 3050 w, 3022 vw, 2983 vw, 2922 vw, 1489 m, 1477 m, 1432 s, 1398 w, 1327 vw, 1308 w, 1266 vw, 1217 m, 1174 m, 1110 w, 1093 ms, 1070 w, 1024 w, 1012 w, 996 w, 974 w, 954 w, 941 w, 916 w, 886 vs, 807 m, 741 vs, 707 vw, 691 vs. ¹H NMR (CD₂Cl₂, 300 MHz): δ 7.40–7.27 (m, 20H, Ar), 6.84 (AA' part of a AA'BB' spin system, d, 2H, ³J_{H,H} = 8.6 Hz, N(C₆H₄)S, H_{meta/N}), 6.56 (BB' part of a AA'BB' spin system, d, 2H, ³J_{H,H} = 8.6 Hz, N(C₆H₄)S, H_{ortho/N}), 2.35 (s, 3H, SCH₃) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz): δ 145.00 (t, ²J_{C,P} = 2.1 Hz, N(C₆H₄)S, C_{ipso/N}), 139.54 (virtual t, ¹⁺³J_{C,P} = 13.6 Hz, Ar, C_{ipso}), 135.50 (t, ⁵J_{C,P} = 0.9 Hz, N(C₆H₄)S, C_{ipso/S}), 133.65 (virtual t, ²⁺⁴J_{C,P} = 23.1 Hz, Ar, C_{ortho}), 129.94 (t, ³J_{C,P} = 3.0 Hz, N(C₆H₄)S, C_{ortho/N}),

129.52 (s, Ar, C_{para}), 128.46 (virtual t, ³⁺⁵J_{C,P} = 6.5 Hz, Ar, C_{meta}), 126.77 (s, N(C₆H₄)S, C_{meta/N}), 16.34 (s, SCH₃) ppm. ³¹P{¹H} NMR (CDCl₃, 121.5 MHz): δ 69.36 (s) ppm.

Ligand 4·S₂. To a solution of **4** (0.300 g, 0.59 mmol) in 15 mL of toluene was added elemental sulfur (0.038 g, 1.18 mmol). The solution was heated to 115 °C for 3 h. After the mixture was cooled to room temperature, pentane was added to the solution and a microcrystalline white powder of **4·S₂** precipitated. Colorless crystals suitable for single-crystal X-ray diffraction were grown from a toluene/pentane mixture. Yield: 0.300 g, 89%. Anal. Calcd for C₃₁H₂₇NP₂S₃ (571.70): C, 65.13; H, 4.76; N, 2.45. Found: C, 65.18; H, 4.90; N, 2.36. FTIR: ν_{max}(solid)/cm^{−1} 3053 w, 2923 vw, 2858 vw, 2827 vw, 2682 vw, 2581 vw, 2364 w, 2344 w, 2324 w, 1586 w, 1560 w, 1491 m, 1480 m, 1437 s, 1405 w, 1308 mw, 1197 m, 1178 m, 1094 s, 1018 w, 999 w, 968 w, 953 s, 916 s, 880 s, 816 m, 746 w, 732 w, 715 vs, 697 vs, 686 vs, 645 vs, 631 w, 613 m. ¹H NMR (CDCl₃, 300 MHz): δ 8.07–8.03 (m, 8H, Ar), 7.54 (AA' part of a AA'BB' spin system, 2H, ³J_{H,H} = 8.4 Hz, N(C₆H₄)S, H_{meta/N}), 7.28–7.25 (m, 4H, Ar), 7.20–7.17 (m, 8H, Ar), 6.71 (BB' part of a AA'BB' spin system, 2H, ³J_{H,H} = 8.4 Hz, N(C₆H₄)S, H_{ortho/N}), 2.23 (s, 3H, SCH₃) ppm. ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 137.59 (t, ²J_{C,P} = 2.0 Hz, N(C₆H₄)S, C_{ipso/N}), 135.83 (s, N(C₆H₄)S, C_{ipso/S}), 133.61–133.48 (five-line multiplet of a simulated AXX' spin system, ²⁺⁴J_{C,P} = 11.1 Hz (⁴J_{AX'} ≈ 0 Hz), Ar, C_{ortho}), 132.73 (t, ³J_{C,P} = 3.0 Hz, N(C₆H₄)S, C_{ortho/N}), 131.61 (d, ¹J_{C,P} = 101.5 Hz, Ar, C_{ipso}), 131.46 (virtual t, ⁴⁺⁶J_{C,P} = 1.2 Hz, Ar, C_{para}), 127.69–127.53 (five line multiplet of a simulated AXX' spin system, ³⁺⁵J_{C,P} = 13.9 Hz (⁵J_{AX'} ≈ 0 Hz), Ar, C_{meta}), 125.59 (t, ⁴J_{C,P} = 1.5 Hz, N(C₆H₄)S, C_{meta/N}), 15.54 (s, SCH₃) ppm. ³¹P{¹H} NMR (CDCl₃, 121.5 MHz): δ 69.03 (s) ppm.

Ligand 4·S. To a solution of **4** (0.220 g, 0.43 mmol) in 15 mL of CH₂Cl₂ was added elemental sulfur (0.021 g, 0.65 mmol). The solution was stirred at room temperature for 30 min. Evaporation of the volatiles led to the formation of a pale yellow oil that was dissolved in 10 mL of toluene. Addition of pentane to this solution led to the precipitation of a white crystalline powder of **4·S₂**. After filtration and evaporation of the volatiles, a colorless oil was obtained. Its examination by ³¹P{¹H} NMR spectroscopy revealed the presence of **4·S** (ca. 70%) and **4·S₂** (ca. 30%). We could not isolate pure **4·S**, and in the subsequent complexation reactions, **4·S** was thus prepared in situ. Purification of the complexes with **4·S** and **4·S₂** was readily achieved (see below). ¹H NMR (CD₂Cl₂, 300 MHz): δ 8.11–8.05 (m, 4H, Ar), 8.02–7.05 (m, 4H, Ar), 7.43–7.31 (m, 12H, Ar), 6.68 (AA' part of a AA'BB' spin system, d, 2H, ³J_{H,H} = 8.6 Hz, N(C₆H₄)S, H_{meta/N}), 6.59 (BB' part of a AA'BB' spin system, d, 2H, ³J_{H,H} = 8.6 Hz, N(C₆H₄)S, H_{ortho/N}), 2.27 (s, 3H, S-CH₃) ppm. ³¹P{¹H} NMR (CDCl₃, 121.5 MHz): δ 72.38 (d, ²J_{P,P} = 104.5 Hz, P^V), 55.34 (d, ²J_{P,P} = 104.5 Hz, P^{III}) ppm.

Synthesis of the Ni(II) Complexes. **Complex 5.** To a suspension of [NiCl₂(DME)] (0.130 g, 0.59 mmol) in CH₂Cl₂ (10 mL) was added a solution of **4** (0.300 g, 0.59 mmol) in CH₂Cl₂ (20 mL). The solution quickly turned orange-red and was stirred at room temperature for 4 h. The solvent was removed under reduced pressure, and the red solid obtained was washed with pentane. Red crystals suitable for single-crystal X-ray diffraction were grown from a CH₂Cl₂/pentane mixture. Yield: 0.312 g, 83%. Anal. Calcd for C₃₁H₂₇Cl₂NNiP₂S (637.16): C, 58.44; H, 4.27; N, 2.20. Found: C, 58.48; H, 4.19; N, 2.31. FTIR: ν_{max}(solid)/cm^{−1} 3053 w, 2919 w, 1589 m, 1492 ms, 1480 m, 1433s, 1332 vw, 1309 w, 1255 vs, 1182 w, 1162 vw, 1105 vs, 1096 vs, 1023 vw, 1007 vw, 997 w, 951 s, 907 vs, 852 vw, 824 m, 749 w, 736 s, 720 w, 694 vw, 686 vs, 562 w, 548 s, 508 m, 495 m, 483 vs, 448 vw, 439 vw, 415 w, 343 w, 326 vs, 269 w, 236 w, 214 w, 172 vw, 157 vw, 142 w. ¹H NMR (CD₂Cl₂, 300 MHz): δ 8.01 (q, 8H, ³J_{H,H} = 7.0 Hz, H_{meta} of Ar), 7.71 (t, 4H, ³J_{H,H} = 7.0 Hz, H_{para} of Ar), 7.57 (t, 8H, ³J_{H,H} = 7.0 Hz, H_{ortho} of Ar), 6.84 (AA' part of a AA'BB' spin system, 2H, ³J_{H,H} = 8.4 Hz, N(C₆H₄)S, H_{meta/N}), 6.38 (BB' part of a AA'BB' spin system, 2H, ³J_{H,H} = 8.4 Hz, N(C₆H₄)S, H_{ortho/N}), 2.32 (s, 3H, SCH₃) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz): δ 137.59 (s, N(C₆H₄)S, C_{ipso/S}), 136.17 (t, ²J_{C,P} = 5.6 Hz, N(C₆H₄)S, C_{ipso/N}), 133.66 (virtual t, ²⁺⁴J_{C,P} = 11.2 Hz, C_{ortho} of Ar), 133.24 (virtual t, ⁴⁺⁶J_{C,P} = 1.5 Hz, C_{para} of Ar), 129.28 (virtual t, ³⁺⁵J_{C,P} = 11.9 Hz, C_{meta} of Ar),

126.80 (virtual t , $^{1+3}J_{C,P} = 50.8$ Hz, C_{ipso} Ar), 126.63 (s, $N(C_6H_4)_2S$, $C_{meta/N}$), 124.55 (t , $^3J_{C,P} = 3.4$ Hz, $N(C_6H_4)_2S$, $C_{ortho/N}$), 15.15 (s, SCH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2 , 121.5 MHz): δ 45.38 (s) ppm. MS (ESI): m/z 600.00 $[M - Cl]^+$.

Complex 6. To a solution of **4** (0.300 g, 0.59 mmol) in CH_2Cl_2 (20 mL) was added elemental sulfur (0.028 g, 0.88 mmol). The solution was stirred at room temperature for 30 min and then added to a suspension of $[NiCl_2(DME)]$ (0.065 g, 0.29 mmol) in CH_2Cl_2 (20 mL). The mixture quickly turned bright purple and was stirred at room temperature for 4 h. After filtration, the solvent was removed under reduced pressure and the bright purple solid was washed with toluene. Purple single crystals suitable for X-ray diffraction were grown by slow evaporation of an acetone/pentane mixture. Yield (based on **4**·**S** formed in situ and estimated by ^{31}P NMR): 0.132 g, 82%. Anal. Calcd for $C_{28}H_{29}Cl_2NNiP_2S_2$ ·(acetone) (727.31): C, 55.31; H, 4.65; N, 1.95. Found: C, 54.96; H, 4.54; N, 1.88. FTIR: $\nu_{max}(solid)/cm^{-1}$ 3057 w, 2921 w, 2682 w, 2584 w, 1706 s, 1583 w, 1560 w, 1483 s, 1432 vs, 1400 vw, 1359 m, 1309 w, 1222 w, 1201 s, 1179 m, 1161 w, 1098 vs, 1010 w, 998 w, 973 s, 937 m, 918 w, 897 vs, 745 m, 731 w, 709 w, 688 vs, 646 m, 557 w, 524 s, 513 vs, 489 w, 480 w, 455 vw, 440 w, 415 vw, 393 vw, 382 m, 339 s, 315 w, 309 m, 291 m, 271 w, 233 w, 210 vw, 179 m, 150 s, 139 vw, 134 vw, 121 vw, 108 w. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 83.81 (br s, see text). MS (ESI): m/z 632.01 $[M - Cl]^+$, 1298.99 $[Ni(4\cdot S)_2][NiCl_3]^+$.

Complex 7. To a solution of **4** (0.200 g, 0.40 mmol) in CH_2Cl_2 (20 mL) was added elemental sulfur (0.019 g, 0.60 mmol). The solution was stirred at room temperature for 30 min and then added to a suspension of $[Ni(NCMe)_6](BF_4)_2$ (0.039 g, 0.10 mmol) in CH_2Cl_2 (20 mL). The mixture quickly turned yellow-orange, and stirring at room temperature was maintained for 4 h. After filtration, the solvent was removed under reduced pressure and the orange solid was washed with toluene. Red crystals suitable for single-crystal X-ray diffraction were grown from a CH_2Cl_2 /pentane mixture. Yield (based on **4**·**S** formed in situ and estimated by ^{31}P NMR): 0.105 g, 85%. Anal. Calcd for $C_{62}H_{54}N_2NiP_4S_4BF_4$ (1131.56): C, 56.78; H, 4.15; N, 2.13. Found: C, 56.64; H, 4.24; N, 2.00. FTIR: $\nu_{max}(solid)/cm^{-1}$ 3048 vw, 2920 vw, 2679 vw, 1583 w, 1480 m, 1437 s, 1400 vw, 1318 w, 1286 vw, 1202 m, 1095 m, 1048 vs, 1037 w, 1024 vw, 996 w, 960 w, 933 w, 925 w, 890 m, 812 vw, 756 w, 744 w, 733 m, 705 w, 689 s, 634 w, 620 m, 598 s, 558 w, 521 s, 509 s, 493 s, 458 m, 432 w, 395 w, 382 m, 364 m, 353 vw, 320 w, 255 w, 235 w, 221 w, 194 m, 179 m, 140 vw, 125 w, 117 vw, 106 vs. 1H NMR ($CDCl_3$, 300 MHz): δ 7.72–7.56 (m, 40H, Ar), 6.64 (AA' part of a AA'BB' spin system, 4H, $^3J_{H,H} = 8.6$ Hz, $N(C_6H_4)_2S$, $H_{meta/N}$), 6.06 (BB' part of a AA'BB' spin system, 4H, $^3J_{H,H} = 8.6$ Hz, $N(C_6H_4)_2S$, $H_{ortho/N}$), 2.26 (s, 6H, SCH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 142.10 (s, $N(C_6H_4)_2S$, $C_{ipso/S}$), 135.64 (d, $^4J_{C,P} = 2.6$ Hz, C_{para} Ar–P^V), 134.29 (s, C_{para} Ar–P^{III}), 134.00 (virtual t , $^{2+4+5}J_{C,P} = 13.0$ Hz, C_{ortho} of Ar–P^{III}), 133.03 (d, $^2J_{C,P} = 11.6$ Hz, C_{ortho} Ar–P^V), 131.53 (s, $N(C_6H_4)_2S$, $C_{ortho/N}$), 130.31–130.20 (m, C_{meta} Ar–P^{III} + Ar–P^V), 129.96 (t , $^2J_{C,P} = 2.1$ Hz, $C_{ipso/N}$), 125.86 (s, $N(C_6H_4)_2S$, $C_{meta/N}$), 124.53 (virtual t , $^{1+3+4}J_{C,P} = 56.7$ Hz, C_{ipso} Ar–P^{III}), 125.35 (d, $^1J_{C,P} = 96.3$ Hz, C_{ipso} Ar–P^V), 14.73 (s, SCH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2 , 121.5 MHz): δ two triplets of a AA'BB' spin system (Scheme 5): δ_A 105.80 ppm, δ_B 84.61 ppm; spectroscopic simulations afforded the coupling constants $^{2+3}J(P_A P_B) = ^{2+3}J(P_A' P_B') = 77.30$ Hz, $^3J(P_A P_B') = 66.34$ Hz, $^4J(P_A P_A') = 76.44$ Hz, $^2J(P_B P_B') = 76.38$ Hz. MS (ESI): m/z 568.07 $[M]^{2+}$.

General Procedure for the Catalytic Ethylene Oligomerization Reaction. All catalytic reactions were carried out in a

magnetically stirred (900 rpm) 145 mL stainless steel autoclave. A 125 mL glass container was used to protect the inner walls of the autoclave from corrosion. All catalytic tests were started at 30 °C, and no cooling of the reactor was done during the reaction. After injection of the catalytic solution and of the cocatalyst under a constant low flow of ethylene, the reactor was pressurized to 10 bar. A temperature increase was observed which resulted solely from the exothermicity of the reaction. The 10 bar working pressure was maintained during the experiments through a continuous feed of ethylene from a reserve bottle placed on a balance to allow continuous monitoring of the ethylene uptake. The oligomerization products and remaining ethylene were only collected from the reactor at the end of the catalytic experiment. At the end of each test (35 min) a dry ice bath, and in the more exothermic cases also liquid N_2 , was used to rapidly cool the reactor, thus stopping the reaction. When the inner temperature reached 0 °C, the ice bath was removed, allowing the temperature to slowly rise to 10 °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 products in the reactor were hydrolyzed 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, 0.3 mmHg) into a second Schlenk flask previously immersed in liquid nitrogen in order to avoid any loss of product. For GC analyses, 1-heptene was used as an internal reference. $AlEtCl_2$ was used as a cocatalyst and, depending on the amount used (3, 10, or 40 equiv), the required quantity of Ni(II) complex was dissolved in 13.5 (3 equiv of EADC) or 10 mL (10 and 40 equiv of EADC) of chlorobenzene, and this solution was injected into the reactor. The cocatalyst solution, 1.5 or 5 mL corresponding to 3 or 10 and 40 equiv, respectively, was then added. Therefore, the total volume of the solution inside the reactor was 15 mL.

■ ASSOCIATED CONTENT

■ Supporting Information

Tables giving X-ray data collection, structure solution, and structure refinement details for compounds **4**, **4**·**S**, **5**· $2CH_2Cl_2$, and **6**· C_3H_6O (Table S1) and for compounds **7**· $4CH_2Cl_2$, **8**· CH_2Cl_2 and **9** (Table S2) and CIF files giving crystallographic data for all seven compounds, and text, tables, and figures giving structural comparisons between ligand **4** and three *p*-phenyl-functionalized DPPA-type ligands, the $^{31}P\{^1H\}$ NMR spectra of complex **7** and their evolution after addition of NEt_3 ·HCl (1 and 2 equiv), and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>. CIF files of these compounds have also 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 873232 and 985336–985341.

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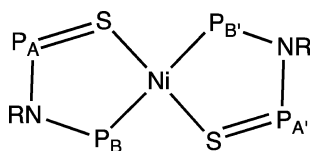
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Notes

The authors declare no competing financial interest.

Scheme 5. Spin System Used for the Assignment of the $^{31}P\{^1H\}$ NMR Resonances of Complex **7**



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REFERENCES

- (1) For selected reviews see e.g.: (a) Hierro, J.-C.; Amardeil, R.; Bentabet, E.; Broussier, R.; Gautheron, B.; Meunier, P.; Kalck, P. *Coord. Chem. Rev.* **2003**, *236*, 143. (b) Appleby, T.; Woollins, J. D. *Coord. Chem. Rev.* **2002**, *235*, 121 and references therein. (c) Bhattacharyya, P.; Woollins, J. D. *Polyhedron* **1995**, *14*, 3367 and references therein. Other specific examples are cited in the manuscript.
- (2) (a) Rosa, V.; Fliedel, C.; Ghisolfi, A.; Pattacini, R.; Avilés, T.; Braunstein, P. *Dalton Trans.* **2013**, *42*, 12109. (b) Fliedel, C.; Pattacini, R.; Braunstein, P. *J. Cluster Sci.* **2010**, *21*, 397. (c) Ganesamoorthy, C.; Balakrishna, M. S.; Mague, J. T. *Inorg. Chem.* **2009**, *48*, 3768. (d) Rodriguez-Zubiri, M.; Gallo, V.; Rosé, J.; Welter, R.; Braunstein, P. *Chem. Commun.* **2008**, 64. (e) Gallo, V.; Mastroiilli, P.; Nobile, C. F.; Braunstein, P.; Englert, U. *Dalton Trans.* **2006**, 2342.
- (3) (a) Posset, T.; Rominger, F.; Blümel, J. *Chem. Mater.* **2005**, *17*, 586. (b) Schwyer-Tihay, F.; Braunstein, P.; Estournès, C.; Guille, J. L.; Lebeau, B.; Paillaud, J.-L.; Richard-Plouet, M.; Rosé, J. *Chem. Mater.* **2003**, *15*, 57. (c) Braunstein, P.; Kormann, H.-P.; Meyer-Zaika, W.; Pugin, R.; Schmid, G. *Chem. Eur. J.* **2000**, *6*, 4637.
- (4) Fliedel, C.; Faramarzi, V.; Rosa, V.; Doudin, B.; Braunstein, P. *Chem. Eur. J.* **2014**, *20*, 1263.
- (5) For recent examples see e.g.: (a) Aydemir, M.; Baysal, A.; Sahin, E.; Gümgüm, B.; Özkaz, S. *Inorg. Chim. Acta* **2011**, *378*, 10. (b) Ganesamoorthy, C.; Balakrishna, M. S.; Mague, J. T. *J. Organomet. Chem.* **2009**, *694*, 3390. (c) Ganesamoorthy, C.; Balakrishna, M. S.; Mague, J. T.; Tuononen, H. M. *Inorg. Chem.* **2008**, *47*, 7035. (d) Paolillo, R.; Gallo, V.; Mastroiilli, P.; Nobile, C. F.; Rosé, J.; Braunstein, P. *Organometallics* **2008**, *27*, 741. (e) Gümgüm, B.; Biricik, N.; Durap, F.; Özdemir, I.; Gürbüz, N.; Ang, W. H.; Dyson, P. J. *Appl. Organomet. Chem.* **2007**, *21*, 711. (f) Mandal, S. K.; Gowda, G. A. N.; Krishnamurthy, S. S.; Zheng, C.; Li, S.; Hosmane, N. S. *J. Organomet. Chem.* **2003**, *676*, 22. More examples are available in refs 21a–d and 23b–e.
- (6) See e.g.: (a) McGuinness, D. S. *Chem. Rev.* **2011**, *111*, 2321 and references therein. (b) Agapie, T. *Coord. Chem. Rev.* **2011**, *255*, 861 and references therein. (c) Reddy Aluri, B.; Peulecke, N.; Peitz, S.; Spannenberg, A.; Müller, B. H.; Schulz, S.; Drexler, H.-J.; Heller, D.; Al-Hazmi, M. H.; Mosa, F. M.; Wöhl, A.; Müller, W.; Rosenthal, U. *Dalton Trans.* **2010**, *39*, 7911 (Cr and Ni complexes). (d) Dixon, J. T.; Green, M. J.; Hess, F. M.; Morgan, D. H. *J. Organomet. Chem.* **2004**, *689*, 3641 and references therein.
- (7) See e.g.: (a) Schultz, M.; Eisenträger, F.; Regius, C.; Rominger, F.; Hanno-Igels, P.; Jakob, P.; Gruber, I.; Hofmann, P. *Organometallics* **2012**, *31*, 207. (b) Song, K.; Gao, H.; Liu, F.; Pan, J.; Guo, L.; Zai, S.; Wu, Q. *Eur. J. Inorg. Chem.* **2009**, 3016. (c) Lavanant, L.; Rodrigues, A.-S.; Kirillov, E.; Carpentier, J.-F.; Jordan, R. F. *Organometallics* **2008**, *27*, 2107. (d) Dennett, J. N. L.; Gillon, A. L.; Heslop, K.; Hyett, D. J.; Fleming, J. S.; Lloyd-Jones, C. E.; Orpen, A. G.; Pringle, P. G.; Wass, D. F.; Scutt, J. N.; Weatherhead, R. H. *Organometallics* **2004**, *23*, 6077. (e) Cooley, N. A.; Green, S. M.; Wass, D. F.; Heslop, K.; Orpen, A. G.; Pringle, P. G. *Organometallics* **2001**, *20*, 4769. (f) Wass, D. F. (BP Chemicals Ltd) WO01/10876, 2001. (g) Hofmann, P.; Perez-Moya, L. A.; Krause, M. E.; Kumberger, O.; Müller, G. *Z. Naturforsch., B* **1990**, *45b*, 897.
- (8) (a) Dagorne, S.; Fliedel, C. *Top. Organomet. Chem.* **2013**, *41*, 125 and references therein. Specific examples of Ni/Al bimetallic complexes: (b) Azoulay, J. D.; Koretz, Z. A.; Wu, G.; Bazan, G. C. *Angew. Chem.* **2010**, *122*, 8062; *Angew. Chem., Int. Ed.* **2010**, *49*, 7890. (c) Weng, Z.; Teo, S.; Koh, L. L.; Hor, T. S. A. *Chem. Commun.* **2006**, 1319.
- (9) Jabri, A.; Crewdson, P.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *Organometallics* **2006**, *25*, 715.
- (10) (a) Keim, W. *Angew. Chem., Int. Ed.* **1990**, *29*, 235 and references therein. (b) Keim, W.; Behr, A.; Gruber, B.; Hoffmann, B.; Kowaldt, F. H.; Kürschner, U.; Limbäcker, B.; Sistig, F. P. *Organometallics* **1986**, *5*, 2356.
- (11) (a) Svejda, S. A.; Brookhart, M. *Organometallics* **1999**, *18*, 65. (b) Killian, C. M.; Johnson, L. K.; Brookhart, M. *Organometallics* **1997**, *16*, 2005. (c) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414.
- (12) Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W. *Organometallics* **1998**, *17*, 3149.
- (13) (a) Chavez, P.; Guerrero Rios, I.; Kermagoret, A.; Pattacini, R.; Meli, A.; Bianchini, C.; Giambastiani, G.; Braunstein, P. *Organometallics* **2009**, *28*, 1776. (b) Kermagoret, A.; Braunstein, P. *Organometallics* **2008**, *27*, 88. (c) Kermagoret, A.; Braunstein, P. *Dalton Trans.* **2008**, 822. (d) Braunstein, P.; Chauvin, Y.; Mercier, S.; Saussine, L. C. R. *Chim.* **2005**, *8*, 31. (e) Speiser, F.; Braunstein, P.; Saussine, L. *Acc. Chem. Res.* **2005**, *38*, 784 and references therein.
- (14) (a) Braunstein, P. *J. Organomet. Chem.* **2004**, *689*, 3953. (b) Braunstein, P.; Naud, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 680. (c) Slone, C. S.; Weinberger, D. A.; Mirkin, C. A. *Prog. Inorg. Chem.* **1999**, *48*, 233. (d) Zhang, W.-H.; Chien, S. W.; Hor, T. S. A. *Coord. Chem. Rev.* **2011**, *255*, 1991.
- (15) Ghisolfi, A.; Fliedel, C.; Rosa, V.; Pattacini, R.; Thibon, A.; Monakhov, K. Yu.; Braunstein, P. *Chem Asian J.* **2013**, *8*, 1795.
- (16) Zhang, S.; Pattacini, R.; Braunstein, P. In *Advances in Organometallic Chemistry and Catalysis: The Silver/Gold Jubilee International Conference on Organometallic Chemistry Celebratory Book*; Pombeiro, A. J. L., Ed.; Wiley: Hoboken, NJ, 2014.
- (17) Kermagoret, A.; Pattacini, R.; Chavez Vasquez, P.; Rogez, G.; Welter, R.; Braunstein, P. *Angew. Chem.* **2007**, *119*, 6558; *Angew. Chem., Int. Ed.* **2007**, *46*, 6438.
- (18) Flapper, J.; Kooijman, H.; Lutz, M.; Spek, A. L.; van Leeuwen, P. W. N. M.; Elsevier, C. J.; Kamer, P. C. J. *Organometallics* **2009**, *28*, 3272.
- (19) O'Reilly, M.; Pattacini, R.; Braunstein, P. *Dalton Trans.* **2009**, 6092.
- (20) See e.g. the synthesis of ligand **1**: Weng, Z.; Teo, S.; Hor, T. S. A. *Dalton Trans.* **2007**, 3493.
- (21) (a) Kayan, C.; Biricik, N.; Aydemir, M.; Scopelliti, R. *Inorg. Chim. Acta* **2012**, *385*, 164. (b) Kayan, C.; Biricik, N.; Aydemir, M. *Transition Met. Chem.* **2011**, *36*, 513. (c) Biricik, N.; Kayan, C.; Gümgüm, B.; Fei, Z.; Scopelliti, R.; Dyson, P. J.; Gürbüz, N.; Özdemir, İ. *Inorg. Chim. Acta* **2010**, *363*, 1039. (d) Durap, F.; Baysal, A.; Akba, O.; Gümgüm, B.; Özkaz, S.; Yıldırım, L. T. *Polyhedron* **2009**, *28*, 2313. (e) Biricik, N.; Durap, F.; Kayan, C.; Gümgüm, B. *Heteroat. Chem.* **2007**, *6*, 613. (f) Biricik, N.; Fei, Z.; Scopelliti, R.; Dyson, P. J. *Helv. Chim. Acta* **2003**, *86*, 3281. (g) Gaw, K. G.; Smith, M. B.; Slawin, A. M. Z. *New J. Chem.* **2000**, *24*, 429. (h) Balakrishna, M. S.; Klein, R.; Uhlenbrock, S.; Pinkerton, A. A.; Cavell, R. G. *Inorg. Chem.* **1993**, *32*, 5676. (i) Seidel, W.; Alexiev, M. Z. *Anorg. Allg. Chem.* **1978**, *438*, 68.
- (22) (a) Venkatakrishnan, T. S.; Krishnamurthy, S. S.; Nethaji, M. J. *Organomet. Chem.* **2005**, *690*, 4001. (b) Raghuraman, K.; Krishnamurthy, S. S.; Nethaji, M. J. *Organomet. Chem.* **2003**, *669*, 79. (c) Faller, J. W.; Lloret-Fillol, J.; Parr, J. *New J. Chem.* **2002**, *26*, 883. (d) Simón-Manso, E.; Valderrama, M.; Gantzel, P.; Kubiak, P. K. *J. Organomet. Chem.* **2002**, *651*, 90. (e) Slawin, A. M. Z.; Woollins, J. D.; Zhang, Q. *Dalton Trans.* **2001**, 621. (f) Balakrishna, M. S.; Panda, R.; Smith, D. C., Jr.; Klamann, A.; Nolan, S. P. *J. Organomet. Chem.*

- 2000, 599, 159. (g) Babu, R. P. K.; Aparna, Z.; Krishnamurthy, S. S.; Nethaji, M. *Phosphorus, Sulfur Silicon Relat. Elem.* **1995**, 103, 39.
- (23) (a) Al-Masri, H. T. *Synth. React. Inorg., Met.-Org., Nano-Met. Chem.* **2013**, 43, 102. (b) Aydemir, M.; Baysal, A.; Özkar, S.; Yıldırım, L. T. *Polyhedron* **2011**, 30, 796. (c) Akba, O.; Durap, F.; Aydemir, M.; Baysal, A.; Gümgüm, B.; Özkar, S. *J. Organomet. Chem.* **2009**, 694, 731. (d) Biricik, N.; Durap, F.; Kayan, C.; Gümgüm, B.; Gürbüz, N.; Özdemir, İ.; Ang, W. H.; Fei, Z.; Scopelliti, R. *J. Organomet. Chem.* **2008**, 693, 2693. (e) Aydemir, M.; Baysal, A.; Gümgüm, B. *J. Organomet. Chem.* **2008**, 693, 3810. (f) Durap, F.; Biricik, N.; Gümgüm, B.; Özkar, S.; Ang, W. H.; Fei, Z.; Scopelliti, R. *Polyhedron* **2008**, 27, 196. (g) Biricik, N.; Durap, F.; Gümgüm, B.; Fei, Z.; Scopelliti, R. *Transition Met. Chem.* **2007**, 32, 877.
- (24) Fei, Z.; Scopelliti, R.; Dyson, P. J. *Dalton Trans.* **2003**, 2772.
- (25) Naik, S.; Mague, J. T.; Balakrishna, M. S. *Inorg. Chim. Acta* **2013**, 407, 139.
- (26) Ajibade, P. A.; Onwudiwe, D. C.; Omondi, B. *Acta Crystallogr.* **2012**, E68, o3491.
- (27) For a discussion about the effective Tolman-based *N*-substituent steric parameter (θ_{N-sub}) for the PNP ligands, see: Cloete, N.; Visser, H. G.; Engelbrecht, I.; Overett, M. J.; Gabrielli, W. F.; Roodt, A. *Inorg. Chem.* **2013**, 52, 2268.
- (28) See e.g.: (a) Li, C.; Pattacini, R.; Braunstein, P. *Inorg. Chim. Acta* **2010**, 363, 4337. (b) Hamada, A.; Braunstein, P. *Inorg. Chem.* **2009**, 48, 1624.
- (29) (a) Stamatopoulos, I.; Placek, M.; Psycharis, V.; Terzis, A.; Svoboda, J.; Kyritsis, P.; Vohlidal, J. *Inorg. Chim. Acta* **2012**, 387, 390. (b) Vougioukalakis, G. C.; Stamatopoulos, I.; Petzetakis, N.; Raptopoulou, C. P.; Psycharis, V.; Terzis, A.; Kyritsis, P.; Pitsikalis, M.; Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, 47, 5241. (c) Sun, Z.; Zhu, F.; Wu, Q.; Lin, S.-a. *Appl. Organomet. Chem.* **2006**, 20, 175. (d) Sushev, V. V.; Kornev, A. N.; Kurskii, Y. A.; Kuznetsova, O. V.; Fukin, G. K.; Budnikova, Y. H.; Abakumov, G. A. *J. Organomet. Chem.* **2005**, 690, 1814. (e) Browning, C. S.; Burrow, R. A.; Farrar, D. H.; Mirza, H. A. *Inorg. Chim. Acta* **1998**, 271, 112.
- (30) (a) Yin, B.-S.; Li, T.-B.; Yang, M.-S. *Acta Crystallogr., Sect. E* **2011**, 67, m1571. (b) Yin, B.-S.; Li, T.-B.; Yang, M.-S. *Acta Crystallogr., Sect. E* **2011**, 67, m1572.
- (31) Levesanos, N.; Stamatopoulos, I.; Raptopoulou, C. P.; Psycharis, V.; Kyritsis, P. *Polyhedron* **2009**, 28, 3305.
- (32) (a) Yang, Q.-Z.; Kermagoret, A.; Agostinho, M.; Siri, O.; Braunstein, P. *Organometallics* **2006**, 25, 5518. (b) Heinicke, J.; Köhler, M.; Peulecke, N.; Kindermann, M. K.; Keim, W.; Köckerling, M. *Organometallics* **2005**, 24, 344. (c) Rieger, B.; Baugh, L. S.; Kacker, S.; Striegler, S. *Late Transition Metal Polymerization Catalysis*; Wiley-VCH: Weinheim, Germany, 2003; p 331.
- (33) Errington, R. J. *Advanced Practical Inorganic and Metalorganic Chemistry*; CRC Press: Boca Raton, FL, 1997; p 246.
- (34) Coucouvanis, D. Useful Reagents and Ligands. In *Inorganic Syntheses*; Wiley: New York, 2002; Vol. 33, Chapter 2, p 78.
- (35) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1972**, 13, 47.
- (36) Hägele, G. WIN-DAISY 3.0; Heinrich-Heine-University Düsseldorf, Dusseldorf, Germany, 1993–1995.