

Reactions of a Phosphinoimino-thiazoline-Based Metalloligand with Organic and Inorganic Electrophiles and Metal-Induced Ligand Rearrangements

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The reaction of the neutral Pt(II) bischelated complex cis-[Pt{Ph₂PN....C...NCH₂CH₂S}₂]

([Pt($\mathbf{2}_{-H}$)₂], **1**; **2** = Ph₂PNHC=NCH₂CH₂S, *N*-(diphenylphosphino)-thiazoline-2-amine) with the organic electrophile EtN=C=S yielded complex [Pt($\mathbf{2}_{-H}$)($\mathbf{2}_{-H} \cdot \text{EtNCS}$)] (**3**) as a result of the nucleophilic attack of the coordinated 2-((diphenylphosphino)imino)thiazolidin-3-yl moiety on the heteroallene carbon atom and coordination of the sulfur atom to the metal. The reaction of **1** with [Cu(NCMe)₄]PF₆ also proceeded by nucleophilic attack of the P–N nitrogen atom on Cu(I) and afforded the coordination polymer [**1**·Cu]_∞[PF₆]_∞ (**4**). The reaction of ligand **2** with NiBr₂·xH₂O resulted in a molecular rearrangement and afforded an unexpected pentacoordinated diamagnetic

complex, $[Ni(2){trans-Ph_2PN=C-N(PPh_2)CH_2CH_2S}Br]Br$ (6), which likely arises from a metaltemplated ligand coupling in the presence of water acting as promoter. Complex 6 was evaluated as a precatalyst for ethylene oligomerization, showing good activities with EADC as cocatalyst. All new complexes were structurally characterized by X-ray diffraction.

Introduction

Chelating *P*,*N* ligands and their metal complexes continue to attract much interest owing to their intrinsic properties and numerous applications.¹ We recently found that unusual molecular rearrangements involving P–C and P–N bond formation/breaking can occur during the synthesis of the phosphine ligands (2-oxazoline-2-ylmethyl)diphenylphosphine (L_{tox}) and (2-thiazoline-2-ylmethyl)diphenylphosphine (L_{th}).² These

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ligands readily form a number of transition metal complexes.³ Subtle but sometimes significant differences have been observed between oxazoline- and thiazoline-based systems.²



When the PCH₂ group in a chelate structure of type **A** (Chart 1) is replaced with an isoelectronic PNH unit, as in **B**, deprotonation in α -position to phosphorus is facilitated, and the resulting metal complexes, of type **C** and **D**, respectively, can be used as metalloligands owing to the resulting electronrich character of the carbon or nitrogen centers, respectively, which are the sites of reaction with electrophiles.⁴ Similarly, starting from complexes of the type **E** and **F**, which contain neutral, chelating P,O ligands, metalloligands of type **G** and **H**,⁵ respectively, have been obtained and their reactivity

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investigated.^{1f,6} The enhanced acidity of the NH group in $Ph_2PNHPPh_2$ compared to that of the CH_2 group in $Ph_2PCH_2PPh_2$ has also been recognized.⁷ Neutral Pt(II) bischelated complexes containing moieties of type **D** were recently synthesized from a series of functional phosphines based on amino-thiazole and -thiazoline moieties in the presence of NEt₃ as a base (see Scheme 1 for phosphino-amino thiazoline derivatives).⁴

Complex *cis*-[$Pt{Ph_2PN....C...NCH_2CH_2S}_2$] (1) reacts

faster with metal centers such as $Ag(I)^{4b}$ and $Au(I)^{4a}$ and yields more stable products than its analogues in which the thiazoline moiety is replaced with the heteroaromatic groups benzothiazole, thiadiazole, or thiazole. In contrast to the latter complexes, complex 1 shows fluorescence emission in the solid state at room temperature, which can be tuned by exposing the complex to alcohols.^{4a} Such molecules interact in the solid state with the exocyclic, deprotonated, and electron-rich nitrogen atoms via H-bonds. These N donors are therefore central to the chemical and physical properties of complexes of type 1, whereas the sulfur atoms have remained, so far, spectators. Herein, we explore the reactivity of 1 toward further electrophilic reagents, such as the organic heteroallene EtN=C=S and Cu(I) complexes, to examine the level of selectivity of these reactions. We shall see that in both cases the P-N nitrogen is again selectively involved in the reactions, while no insertion into the Pt(II)-N bond is observed. We have also observed a water-promoted rearrangement of the diphenylphosphino-2-amino-2-thiazoline ligand, which results in an unexpected Ni(II) bromide complex. Its formation further highlights that caution should be exerted

in the absence of an exhaustive structural characterization when attempting to relate the structures of Ni(II) complexes to their catalytic properties. Indeed, numerous P,N-chelated Ni(II) complexes are highly active precatalysts in, for example, ethylene oligomerization,⁸ and **6** was evaluated as a precatalyst for this reaction.

Results and Discussion

Reacti	ons	with an	Organic	Electro	phile.	We p	revio	ous	sly
reacted	the	stable	neutral	Pt(II)	bisch	elate	com	pl	ex
cis-[Pt{P	h ₂ PN	<u>√…</u> C.	$\cdot \cdot NCH_2$	$[H_2S]_2]$	([Pt(2	е _{-н)2}],	1;	2	=

Ph₂PNHCSCH₂CH₂N) (Scheme 1) with Ag(I) and Au(I) salts to form bimetallic complexes in which the d¹⁰ metal center is coordinated to one or both of the electron-rich nitrogen atoms of the 2-((diphenylphosphino)imino)thiazolidin-3-yl moiety.⁴ We have now exploited the nucleophilicity of the latter atoms toward the organic electrophilic heteroallene EtN=C=S to examine the regioselectivity of the reaction and functionalize further the metalloligand. Reaction of EtN=C=S with 1 afforded the complex $[Pt(2_{-H}) (2_{-H} \cdot \text{EtNCS})$] (3, Scheme 2), and its structure was determined by single-crystal X-ray diffraction (Figure 1). The isothiocyanate molecule has reacted selectively on one of the noncoordinated nitrogen atoms through its electrophilic sp-hybridized carbon. The resulting ligand chelates the metal through the phosphorus and the newly formed thioureate function, while the originally chelating thiazoline moiety has been decoordinated. A control of the temperature is essential since below 80 °C the reaction is extremely slow, whereas above 85 °C side products are observed. Clean incorporation of a second EtN=C=S molecule was not observed.

In the molecular structure of **3** in $3 \cdot CH_2Cl_2$, the metal center remains chelated by one of the deprotonated ligands 2_{-H} of precursor 1, through the P2 and N5 atoms. The slightly distorted square-planar coordination is completed by a monoanionic P,S chelating ligand resulting from the addition of EtN=C=S to 2_{-H} and formation of the C4-N1 bond. The P1 and P2 phosphine donor atoms are in mutually *cis* position. The geometrical parameters of the ligand 2_{-H} remain analogous to those found in the parent complex 1,4a with a notably short P2-N4 bond and a delocalization of the thiazoline C-N double bond over the N5-C20-N4 group. The N1–C1 bond in the 2_{-H} · EtNCS moiety is significantly longer than the N4-C20 bond, while the thiazoline N=C double bond is now localized between N2 and C1. The N1, C4,S1,N3 group of atoms can be seen as forming a deprotonated thiourea, with a thiolate character for the C-S group.

Reactions of organic isocyanates and isothiocyanates with the sp² carbon in α -position to the coordinated phosphorus

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Pt(II) complex bearing a P,S chelating Ph₂PN(R)C(=NR)S ligand, sharing similarities with 2_{-H} · EtNCS, resulted from the reaction of RNHC(=S)NHR thioureas with $[Pt(dppm_{-H})_2]$ $(dppm = bis(diphenylphosphino)methane).^{10}$ We did not observe any reaction between 1 and CO₂, another heterocumulene, which is known, however, to be less reactive.¹¹

1



Figure 1. ORTEP of the molecular structure of 3 in $3 \cdot CH_2Cl_2$. Hydrogen atoms and solvent molecules are omitted for clarity. Ellipsoids include 50% of the electron density. Selected distances (Å) and angles (deg): Pt1-P1 2.2256(12), Pt1-P2 2.2754(13), Pt1-N5 2.069(4), Pt1-S1 2.3045(13), P1-N1 1.724(4), P2-N4 1.666(5), N1-C4 1.407(6), N1-C1 1.419(6), N2-C1 1.264(7), C1-S3 1.781(6), C4-S1 1.770(5), N3-C4 1.27(2), N4-C20 1.319(7), N5-C20 1.333(7), C20-S2 1.771(5); P1-Pt1-P2 101.82(5), N5-Pt1-P2 79.66(13), N5-Pt1-S1 90.91(12), P1-Pt1-S1 87.67(5).

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Scheme 3



Figure 2. Solid-state ${}^{31}P{}^{1}H{}$ MAS NMR spectrum of 4. Lowintensity peaks at ca. 150, -20, and -60 ppm are rotation bands.



Figure 3. ORTEP of the structure of the cationic, asymmetric unit in $4 \cdot CH_2Cl_2 \cdot CH_3CN$. Hydrogen atoms and solvent molecules are omitted for clarity. Ellipsoids include 50% of the electron density. Selected distances (Å) and angles (deg): Pt1-P2 2.241(3), Pt1-P1 2.250(3), Pt1-N2 2.102(10), Pt1-N4 2.105(10), Cu1-N1 1.881(10), P1-N1 1.684(11), P2-N3 1.683(10), N1-C1 1.332(17), N2-C1 1.319(15), N3-C16 1.325(17), N4-C16 1.329(15); P2-Pt1-P1 100.24(11), N4-Pt1-P2 80.6(3), N2-Pt1-P1 80.4(3), N2-Pt1-N4 98.8(4), N1-Cu1-N3 179.4(5).

Reactions with an Inorganic Electrophile. Complex 1 reacted with [Cu(NCMe)₄]PF₆ on the same P-bound nitrogen as the isothiocyanate. This selective reaction resulted rapidly in the precipitation of the remarkably stable bimetallic polymer $[1 \cdot Cu]_{\infty}[PF_6]_{\infty}$ (4, Scheme 3), whose insolubility in organic solvents, including DMSO, facilitates its purification. In the solid state, its ³¹P{¹H} MAS NMR spectrum (Figure 2) shows a singlet at 70 ppm, with ¹⁹⁵Pt satellites [¹J(³¹P,¹⁹⁵Pt) = 3220 Hz] and the typical PF₆ septuplet



Figure 4. Orthogonal views of the crystal structure of the Pt(II)–Cu(I) coordination polymer $4 \cdot CH_2Cl_2 \cdot CH_3CN$, displaying a fraction of the infinite $[1 \cdot Cu]_{\infty}$ cationic chain. Views are approximately along axis *c* (up) and *b* (down). Color code: blue: nitrogen, yellow: sulfur, gray: carbon, violet: phosphorus.



at-144 ppm. This spectrum is fully consistent with the results of an X-ray diffraction study performed on single crystals of $4 \cdot CH_2Cl_2 \cdot MeCN$ obtained by slow diffusion of an acetonitrile solution of $[Cu(NCMe)_4]PF_6$ into a dichloromethane solution of 1 (Figures 3 and 4).

In the structure of **4**, the Pt(II) bischelated complex **1** is bonded to Cu(I) cations through the nitrogen atoms in α -position to the phosphorus donors. Units of **1** are thus connected by bare Cu(I) cations to form an infinite cationic chain of formula $[1 \cdot Cu]_{\infty}$. The copper atoms show a slightly distorted linear coordination geometry, with a Cu–N bonding distance of 1.881(10) Å, similar to those reported for such a bond in the literature [mean values from CCDC for Cu–N bonds: 1.882 Å (based on 427 Cu–N distances in twocoordinated Cu complexes) or 1.880 Å (based on 97 structures displaying two sp² N atoms and a two-coordinated Cu center)]. This is reminiscent of the situation found in a heterotrinuclear complex in which a Cu(I) cation bridges

two neutral $[Pd(dmba){Ph_2PN...C(...O)Me}]$ complexes via their P-bound nitrogen atom (Scheme 4).^{5b} The geometrical parameters within 4 are similar to those displayed by the parent complex.

The crystal packing in $4 \cdot CH_2Cl_2 \cdot MeCN$ (Figure 5) deserves some comments. Cationic $[1 \cdot Cu]_{\infty}$ chains are adjacent and form cationic layers, which alternate with anionic layers



Figure 5. Structural diagram of the crystal packing in $4 \cdot CH_2Cl_2 \cdot CH_3CN$: quadruple cell content (up, phenyls omitted) and orthogonal view of one of the anionic $PF_6 \cdot CH_2Cl_2 \cdot MeCN$ layers.



of formula $PF_6 \cdot CH_2Cl_2 \cdot MeCN$. The photophysical properties of this bimetallic coordination polymer will be examined in the near future.

The reactivity of the exocyclic nitrogen atom in chelated phosphino-aminothiazolines was further confirmed when **2** was reacted with NiBr₂·xH₂O, in an attempt to prepare a bischelated Ni(II) complex. Whatever the L/Ni ratio between 1 and 3, the reaction readily gave rise to the formation of the Ni(II) complex [Ni(**2**)(**5**)Br]Br (**6**, Scheme 5, Figure 6), in which **5** is the neutral diphosphine (*E*)-*N*-(3-diphenylphosphino)thiazolidin-2-ylidene)-diphenylphosphinamine *E*-Ph₂PN=

$$C-N(PPh_2)CH_2CH_2S.$$



Figure 6. ORTEP of the molecular structure of the cationic complex in $6 \cdot CH_2Cl_2$. Hydrogen atoms and solvent molecules are omitted for clarity. Ellipsoids include 50% of the electron density. Selected distances (Å) and angles (deg): Ni1–N2 1.942(5), Ni1–P2 2.1742(16), Ni1–P3 2.1898(17), Ni1–P1 2.2880(16), Ni1–Br1 2.4577(9), P1–N1 1.703(5), P2–N3 1.659(5), P3–N4 1.717(5), N1–C1 1.334(8), N2–C1 1.290(8), N2–C2 1.470(8), N3–C16 1.295(8), N4–C16 1.360(8); P3–Ni1–P1 120.30(6), P1–Ni1–Br1 111.91(5), P3–Ni1–Br1 127.34(5), P2–Ni1–P1 98.27(6), N2–Ni1–P2 178.23(16), P2–Ni1–P3 89.23(6), P2–Ni1–Br1 89.88(5), N2–Ni1–P3 90.47(15), N2–Ni1–P1 83.39(15), N2–Ni1–Br1 88.91(15).





In the molecular structure of **6** in $6 \cdot CH_2Cl_2$, the metal center in the cationic complex shows a slightly distorted trigonal-bipyramidal coordination geometry, the nickel atom being chelated by ligand 2 (through P1 and N2), a terminal bromide, and P,P-chelating diphosphine 5. The N2 atom from 1 and P2 from 5 are in mutually *trans* positions, occupying the apexes of the bipyramid. A bromide ligand is in the equatorial plane, while a second bromide acts as a counterion, far from the metal center. Despite a disorder in the N4, C17, C18, S2, C16 ring, which affects the environment of N4 and prevents a detailed discussion of the bond angles, this nitrogen atom shows an almost planar geometry. This is suggestive of interactions of its lone pair with C16 and is consistent with a C16-N4 bond distance intermediate between a single and a double bond. Ligand 5 is the (E)isomer, with respect to the N3=C16 double bond, of the diphosphine prepared earlier by reaction of Ph2PCl with 2-amino-2-thiazoline.^{4b} In this reaction, the (E) isomer was not observed.^{4b} Furthermore, monophosphine 2 was shown to be in equilibrium with (Z)-5 and 2-amino-2-thiazoline (Scheme 6).^{4b}

However, several observations indicate that this equilibrium is unlikely to be the source of (E)-5 in 6: (a) this would imply a $(Z) \rightarrow (E)$ isomerization of the phosphine, which has been observed neither for the free ligand nor in the reactions



of (Z)-5 with Pd(II) salts; (b) the equilibrium between monophosphine 2 and (Z)-5 and 2-amino-2-thiazoline is dramatically shifted to the left in THF (the solvent used for the formation of 6; and (c) the reaction of 2 with anhydrous NiBr₂ did not give 6, suggesting a role for water in the ligand rearrangement, but the products could not be characterized due to their poor solubility in organic solvents. Since hydrolysis products were not observed when NiBr₂· xH_2O was used in place of NiBr₂, water would act as a promoter for the reaction and not as a stoichiometric reagent. To summarize, it is likely that (E)-5 is formed by a metal-templated coupling of two molecules of 2, with concomitant formation of 2amino-2-thiazoline. A tentative reaction pathway is proposed in Scheme 7, featuring hydrolytic P-N bond cleavage and coupling between coordinated diphenyl-phosphinous acid and 2. Pt(II) salts of the type *a* have been indeed observed in the case of diphenylphosphino-2-amino-2thiazoles.12

A pentacoordinated Ni(II) center with P₃,N,Br donors has been observed in a complex resulting from partial hydrolysis of a bis-aminophosphine, one of the three P–N bonds underwent hydrolysis, and the resulting phosphinate was coordinated to the Ni center.¹³

Complex 6 is diamagnetic, and its ${}^{31}P{}^{1}H$ NMR data are fully consistent with its X-ray structure. The spectrum (Figure 7) corresponds to the expected ABC spin system and consists of three doublets of doublets at δ 44.6, 53.8, and 61.3 ppm tentatively assigned to P1–P3, respectively, showing



Figure 7. ${}^{31}P{}^{1}H$ NMR spectrum of **6** in CDCl₃. Tentative assignment. See Figure 6 for the atom labeling.

second-order effects and coupling constants of 290 Hz (P1,P3), 109 Hz (P2,P3), and 49 Hz (P1,P2), respectively.¹⁴

Catalytic Oligomerization of Ethylene. Complex **6** has been tested as a precatalyst in the oligomerization of ethylene with variable amounts of AlEtCl₂ and MAO as cocatalysts (Table 1). Under conditions similar to those previously used with other Ni(II) complexes with P,N ligands, ^{8a,c,e,f,15} we observed only a moderate activity of ca. 5200 mol C₂H₄/(mol Ni · h) with MAO (300 equiv), with formation of mostly butenes and hexenes (of which 43% α -butene and 12.3% α -hexene, respectively); traces of octenes and decenes were also observed.

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Table 1. Catalytic Data for Complex 6 in Ethylene Oligomerization with EADC and MAO as Cocatalyst⁴

MAO (equiv)		S	electivity (mass %	6)	productivity $[g C_2H_4/(g Ni \cdot h)]$	$\begin{array}{c} TOF \; [mol \; C_2 H_4 / \\ (mol \; Ni \cdot h)] \end{array}$	1-butene (mol %)
	EADC (equiv)	C ₄	C ₆	C ₈			
	3	91	8	1	1386	2900	17
	6	85	13	1	15150	31 700	14
	10	73	24	2	18 400	38 500	6
300		77	14	7	2485	5200	43

^{*a*} Conditions: T = 30 °C, 10 bar of C₂H₄, 35 min, 4×10^{-5} mol of complex; solvent: 13.5, 12, and 10 mL of chlorobenzene for 3, 6, 10 equiv of EADC, respectively (1.5, 3, and 5 mL of EADC solution in toluene); 12 mL of chlorobenzene for MAO (8 mL of cocatalyst solution).

However, with as little as 6 or 10 equiv of AlEtCl₂ (EADC), a significant conversion [TOF: 31700 and 38 500 mol C₂H₄/ (mol Ni · h) respectively] was observed and mostly dimers were formed (85% and 73%, respectively). A significant isomerization process occurred, since only a small percentage of 1-butene was observed. The remaining products were hexenes, whereas only traces of higher olefins were detected. With 3 equiv of EADC, the activity dropped significantly [TOF: 2900 [mol C₂H₄/(mol Ni · h)].

Conclusion

The multidentate thiazoline-based aminophosphine ligand 2 has a rich coordination chemistry. When deprotonated, their bischelated platinum(II) complexes show a remarkable stability. However, this does not preclude further reactions of these metalloligands with organic or inorganic electrophiles. The deprotonated exocyclic nitrogen atoms can be selectively involved in the formation of bimetallic coordination polymers, which may display interesting photophysical properties.^{4b} The sulfur atoms do not participate in direct bonding with the electrophiles examined and remain spectators, although, electronically, they may have an important role in improving the donor properties of the exocyclic nitrogens. Complex 6 was tested in the catalytic oligomerization of ethylene and showed good activities when EADC was used as cocatalyst, producing mostly butenes, albeit with a low selectivity for α -olefins, whereas the use of MAO as cocatalyst resulted in low conversion.

Experimental Section

General Considerations. All manipulations were carried out under an inert argon atmosphere, using standard Schlenk-line conditions and dried and freshly distilled solvents. Unless otherwise stated, the ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on a Bruker Avance 300 instrument at 300.13, 75.47, and 121.49 MHz, respectively, using TMS or H₃PO₄ (85% in D₂O) as external standards, with downfield shifts reported as positive. All NMR spectra were measured at 298 K, unless otherwise specified. The assignment of the signals was made by ¹H, ¹H-COSY, ¹H, ¹³C-HMQC, and ¹³C-HSQC experiments. Elemental C, H, and N analyses were performed by the Service de Microanalyses, Université de Strasbourg (France). Complex 1 and ligand 2 (N-(diphenylphosphino)thiazoline-2-amine) were prepared according to literature procedures.⁴ Ph₂PCl and NEt₃ were freshly distilled before use. Anhydrous NiBr₂ was prepared by treatment of the hydrated salt with thionyl chloride. Hydrated NiBr₂ (NiBr₂. xH_2O) was prepared by dissolving a known quantity of anhydrous NiBr2 in water followed by drying under vacuum. Other chemicals were commercially available and were used as received.

Preparation and Spectroscopic Data for 3. Solid complex 1 (0.100 g, 0.13 mmol) was dissolved in a minimum amount of liquid EtNCS. The resulting solution was stirred at 83 °C for

10 h and then cooled to room temperature. The volatiles were removed under reduced pressure, and the residue obtained was washed with pentane (3 × 10 mL). Evaporation of the volatiles gave compound **3** as a colorless powder. Yield: 0.080 g, 72%. The product was recrystallized by layering a CH₂Cl₂ solution of **3** with pentane. ¹H NMR (CDCl₃): δ 1.32 (t, 3H, ³J_{H-H} = 7.3 Hz, CH₃, EtNCS), 2.68 (t, 2H, ³J_{H-H} = 7.8 Hz, SCH₂, P,S), 3.40 (t, 2H, ³J_{H-H} = 7.8 Hz, NCH₂, P,S), 3.52 (t, 2H, ³J_{H-H} = 7.3 Hz, SCH₂, P,N), 3.59 (q, 2H, ³J_{H-H} = 7.3 Hz, CH₂, EtNCS), 4.14 (t, 2H, ³J_{H-H} = 7.3 Hz, NCH₂, P,N), 6.99–7.52 (m, 20H, Ph). ³¹P{¹H} MMR (CDCl₃): δ 67.6 (d, ²J(P,P) = 7.5 Hz, ¹J(³¹P-¹⁹⁵Pt) = 3274 Hz, P,S), 78.9 (d, ²J(P,P) = 7.5 Hz, ¹J(³¹P-¹⁹⁵Pt) = 2893 Hz, P,N). ¹³C{¹H} MMR (CDCl₃): δ 15.4 (s, CH₃, EtNCS), 33.4 (s, SCH₂, P,S), 35.8 (d with ¹⁹⁵Pt satellites, ⁴J(C,P) = 5.3 Hz, ³J(¹³C, ¹⁹⁵Pt) = 39 Hz, SCH₂, P,N), 48.2 (s, CH₂, EtNCS), 55.7 (d, with ¹⁹⁵Pt satellites, ³⁺⁴J (C,P) = 4.1 Hz, ²J(¹³C, ¹⁹⁵Pt) = 40 Hz, NCH₂, P,N), 57.1 (s, NCH₂, P,S), 127.5-133.3 (m, Ph), 156.9 (d, ²J(C,P) = 24.5 Hz, PtSC), 159.6 (d, ²J(C,P) = 4.1 Hz, N=C-S, P,S), 189.0 (s, N=C-S, P,N). Anal. Calcd for C₃₃N₅H₃₃P₂S₃NPt (852.57): C 46.47, H 3.90, N 8.21. Found: C 46.16, H 4.05, N 7.99.

Preparation and Spectroscopic Data for 4. A solution of $[Cu(NCMe)_4]PF_6$ (0.050 g, 0.134 mmol) in MeCN (4 mL) was added to a stirred solution of complex **1** (0.103 g, 0.134 mmol) in CH₂Cl₂ (10 mL). A colorless precipitate formed immediately. The solution was stirred for 1 h, and the solid was collected by filtration and washed with MeCN (10 mL) and CH₂Cl₂ (10 mL), yielding **4** as a colorless microcrystalline powder. Yield: 0.122 g, 94%. Single crystals suitable for X-ray diffraction were obtained within 1 day at room temperature, upon slow diffusion of a MeCN (1 mL) solution of $[Cu(NCMe)_4]PF_6$ (0.005 g, 0.014 mmol) into a CH₂Cl₂ (1 mL) solution of complex **1** (0.010 g, 0.013 mmol). ³¹P{¹H} MAS NMR (solid): δ –144 (sept, ¹*J*(P,F) = 714 Hz, PF₆), 70 (s, with ¹⁹⁵Pt satellites, ¹*J*(P, ¹⁹⁵Pt) = 3239 Hz, polymer). Anal. Calcd for C₃₀H₂₈CuF₆N₄P₃PtS₂ (974.2): C 36.98, H 2.90, N 5.75. Found: C 36.81, H 3.06, N 5.69.

Preparation and Spectroscopic Data for 6. To a solution of N-(diphenylphosphino)-2-amino-2-thiazoline 2 (0.786 g, 2.74 mmol) in CH₂Cl₂ (100 mL) was added NiBr₂·xH₂O (prepared from 0.200 g, 0.91 mmol, NiBr₂) was added. The resulting solution was stirred under N2 for 3 h. The volatiles were removed under reduced pressure, and the violet residue obtained was washed with THF (10 mL). Evaporation of the volatiles gave compound 6 as a violet powder, yield (based on NiBr₂): 0.571 g, 64%. The product was recrystallized by layering a CH_2Cl_2 solution of 6 with diethyl ether. ¹H NMR (CDCl₃): δ multiplets at 1.77 (m, 1H), 2.70 (m, 3H), 3.23 (m, 1H), 3.50 (m, 1H), 3.94 (m, 1H), 4.17 (m, 1H), 6.70–8.20 (m, 30H, Ph), 10.5 (br, 1H, NH). ${}^{31}P{}^{1}H{}$ NMR (CDCl₃) (tentative assignment, see Figure 6 for labeling): δ 44.6 (dd, ²J(P2,P3) = 109 Hz, ${}^{2}J(P1,P3) = 290$ Hz, P3), 53.8 (dd, ${}^{2}J(P2,P3) = 109$ Hz, ${}^{2}J(P1,$ P2)=49 Hz, P2), 61.3 (dd, ${}^{2}J(P1,P3) = 290$ Hz, ${}^{2}J(P1,P2) = 49$ Hz, P1). ESI-MS (positive ions): m/z 894.9 $[M - Br]^+$, [M - Br - $HBr]^+ = 814.0.$ Anal. Calcd for $C_{42}N_4H_{39}Br_2P_3S_2Ni$ (975.34): C 51.72, H 4.03, N 5.74. Found: C 51.43, H 3.99, N 5.71.

Catalytic Oligomerization of Ethylene. The catalytic reactions were performed in a magnetically stirred (900 rpm) 145 mL stainless steel autoclave. A 125 mL glass container was used to

	$3 \cdot CH_2Cl_2$	$4 \cdot CH_2Cl_2 \cdot CH_3CN$	$6 \cdot \mathrm{CH}_2 \mathrm{Cl}_2$
formula	$C_{33}H_{33}N_5P_2PtS_3,CH_2Cl_2$	$C_{30}H_{28}CuN_4P_2PtS_2 \cdot PF_6,$ CH ₃ CN,CH ₂ Cl ₂	$C_{42}H_{39}Br_2N_4NiP_3S_2,CH_2Cl_2$
$M_{\rm r}$	937.78	1100.20	1060.26
cell setting	orthorhombic	monoclinic	monoclinic
space group	$P2_{1}2_{1}2_{1}$	$P2_1/c$	$P2_1/c$
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.2952(2),	12.1087(3),	14.1050(5),
	15.7977(2),	26.9287(8),	20.0528(4),
	24.6944(4)	14.9896(4)	20.2434(5)
α, β, γ (deg)	90.00,	90.00,	90.00,
	90.00,	127.683(2),	128.553(2),
	90.00	90.00	90.00
$V(Å^3)$	3626.19(11)	3868.1(2)	4477.7(2)
Z	4	4	4
$D_{\rm x} ({\rm Mg}{\rm m}^{-3})$	1.718	1.889	1.573
$\mu (\text{mm}^{-1})$	4.31	4.59	2.57
cryst size (mm)	$0.15 \times 0.15 \times 0.12$	0.15 imes 0.07 imes 0.07	$0.24 \times 0.15 \times 0.15$
measd reflns	24 323	21 049	25 849
indep reflns	10494	7568	8809
obsvd reflns	9513	6036	6637
R _{int}	0.047	0.062	0.061
$\theta_{\rm max}$ (deg)	30.1	26.0	26.0
$R[F^2 > 2\sigma(F^2)]$	0.036	0.070	0.060
$wR(F^2)$	0.089	0.191	0.176
S	1.02	1.14	1.11
no. of params	463	482	532
Flack param	-0.001(5)		

Table 2. X-ray Data Collection and Refinement Parameters

avoid corrosion of the autoclave walls. The preparation of the precatalyst solution was prepared by dissolving 39.2 mg of dried crystals of 6 (4 \times 10⁻⁵ mol) in chlorobenzene. When AlEtCl₂ was used as a cocatalyst, 4×10^{-5} mmol of **6** was dissolved in 13.5, 12, or 10 mL of cholorobenzene depending on the amount of the cocatalyst and injected into the reactor under an ethylene flux. Then 1.5, 3, or 5 mL of a cocatalyst toluene solution, (3, 6, or 10 equiv, respectively) was added (total volume: 15 mL). With MAO as a cocatalyst, 4×10^{-5} mol of 6 was dissolved in 12 mL in chlorobenzene and injected into the reactor under an ethylene flux. Then 8 mL of a cocatalyst solution and 300 equiv of MAO were added. All catalytic reactions were started between 25 and 30 °C. No cooling of the reactor was done during the reaction. After injection of the catalyst and cocatalyst solutions under a constant low flow of ethylene, the reactor was pressurized to 10 bar. The temperature increased, due 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 min) 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 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 amount of ethylene not consumed was thus determined. Although this method is of limited accuracy, it was used throughout and gave satisfactory reproducibility. 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, 0.8 mbar) into a second Schlenk flask previously immersed in liquid nitrogen in order to avoid loss of product.

X-ray Data Collection, Structure Solution, and Refinement for All Compounds. Suitable crystals for the X-ray analysis of all compounds were obtained as described above. The intensity data were collected at 173(2) K on a Kappa CCD diffractometer¹⁶ (graphite-monochromated Mo K α radiation, $\lambda = 0.71073$ Å). Crystallographic and experimental details for the structures are summarized in Table 2. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2 , SHELXL-97)¹⁷ with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined *riding* on the corresponding parent atoms. For $4 \cdot CH_2Cl_2 \cdot CH_3CN$, the C-Cl bond lengths of the dichloromethane molecule were restrained to 1.750 Å. In 3. CH₂Cl₂, the isothiocyanate NEt group was found disordered in two positions with equal occupancy factors and refined with restrained anisotropic parameters. The dichloromethane molecule was disordered in two positions, with equal occupancy factors, having a chlorine and the carbon in common. For all compounds, a MULTISCAN absorption correction was applied.¹⁸ CCDC 776723 (3·CH₂Cl₂), CCDC 776724 (4·CH₂Cl₂·MeCN), and CCDC 776725 $(6 \cdot CH_2Cl_2)$ contain the supplementary crystallographic data for this paper, which can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data request/cif.

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Supporting Information Available: CIF files giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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