

New tripodal iminophosphorane-based ethylene oligomerization catalysts Part II. Catalytic behavior

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Abstract

Seven transition-metal complexes of general formula $RC(CH_2NPR'_3)_3MX_2$ based on new tripodal iminophosphorane ligands were investigated as initiators for the oligomerization of ethylene in the presence of aluminum co-catalysts using high-throughput techniques. In all cases, ethylene consumption peaked at ca. 30 °C and was not drastically affected by varying the nature of the metal ($M = Ni, Fe, Pd, Cu$), the aluminum co-catalyst (MMAO, Et_2AlCl , or $EtAlCl_2$) or the substituents of the tris(iminophosphorane) ligand ($R = Me, Ph$; $R' = cyclopentyl, Ph$). Structural modifications of the organometallic complexes, either at the metal center or within the tripodal ligand, however, had a significant impact on the oligomer distribution obtained. In particular, Pd-based catalyst $(PhC(CH_2NPPH_3)_3)PdCl_2$ displayed an excellent selectivity toward hexene formation. © 2007 Elsevier B.V. All rights reserved.

Keywords: Cu complexes; Fe complexes; Ni complexes; Pd complexes; Tripodal ligand

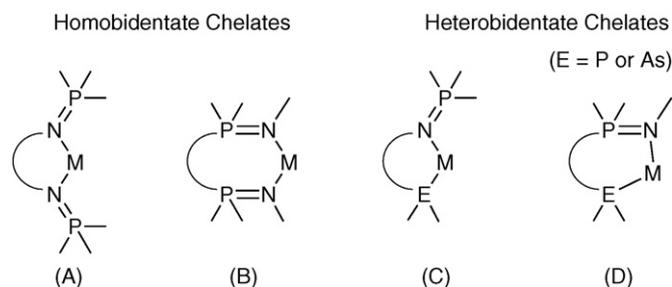
1. Introduction

In recent years, bidentate donor species containing sp^2 -hybridized nitrogen atoms have attracted much attention as ligands for transition metal-catalyzed transformations [1]. An important development in this field was reported by Brookhart and co-workers who showed that α -diimines were efficient ligands for the nickel- or palladium-catalyzed polymerization of ethylene [2,3]. Iminophosphoranes are compounds of general formula $RN=PR'_3$. They possess a highly polarized $N=P$ double bond and coordinate to transition metals via the lone pair of their nitrogen atom to give stable complexes [4,5]. They offer a steric environment relatively similar to that of diimines, but their electronic characteristics (donor strength and π -acceptor capability) are clearly different. So far, homo- and heterobidentate derivatives of types A–D have been the most studied ligands incorporating the iminophosphorane moiety (Scheme 1). Tethering of this group may occur via the nitrogen (structures A and C) or the phosphorus atom (structures B and D).

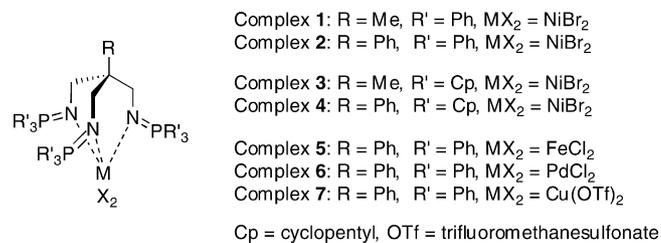
In 1975, Appel and Voltz prepared and characterized the first complexes based on 1,2-*bis*(triphenyl-phosphoranylidene-amino)ethane- $(Ph_3P=N-(CH_2)_2-N=PPh_3)$ and metal halides [6]. This report was later followed by a few publications on the synthesis and catalytic applications of other type A metal complexes for ethylene oligomerization [7,8], allylic alkylation [9,10], or cyclopropanation reactions [11]. Recourse to this kind of transition metal catalysts in polymer chemistry or for organic synthesis remains, however, uncommon. In contrast, ligands possessing two $N=P$ functionalities linked together via the phosphorus atoms (structure B in Scheme 1) have been thoroughly investigated [12–15] with an emphasis on *bis*(iminophosphoranyl)methane derivatives, which proved suitable ligands for ethylene polymerization [16,17].

Another class of well-studied bidentate ligands are difunctional compounds that contain one iminophosphorane functionality and a second donor site, which is in most cases a phosphorus or arsenic atom (structures C and D in Scheme 1). In this case, the weakest bond of the chelate may dissociate reversibly without total detachment of the ligand, thereby opening vacant coordination sites on the metal. Complexes based on such ligands have been extensively studied by Cavell and co-

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Scheme 1. Homo- and heterobidentate chelates incorporating the iminophosphorane moiety.



Scheme 2. Transition-metal complexes bearing triiminophosphorane ligands used in this work.

workers. Rhodium [18–23] and palladium [24,25] served mostly as metal centers, but a range of other early or late transition metals, including rhenium, molybdenum, platinum, and iridium, were also investigated [19,22,26].

The small number of complexes based on type A ligands, in which the tethering motive is formally derived from a diamine, prompted us to undertake the study of this poorly explored area, and more specifically, of the hitherto uncharted field of metal complexes bearing tripodal iminophosphorane ligands (Scheme 2). In a previous article, we disclosed the first part of our work in this direction, i.e., the multi-step synthesis of four new triiminophosphorane ligands and their use for the preparation of some representative transition-metal complexes [27].

In this paper, we report on the oligomerization of ethylene promoted by selected metal complexes of Fe(II), Ni(II), Pd(II), and Cu(II) based on the four tridentate iminophosphorane ligands depicted in Scheme 2. The ligands differ from each other by the nature of their bridgehead R substituents (methyl or phenyl groups) and their phosphoranylidene R' substituents (cyclopentyl or phenyl rings). The reactions were carried out using a high-throughput experimental device called “Endeavor” supplied by Argonaut Technologies (now part of Biotage AB). It is a parallel autoclave bench with eight independent reactors that allows eight parallel experimentations under pressure with different conditions for each experiment.

2. Experimental

2.1. General information

All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk and cannula techniques. Solvents were refluxed over appropriate drying agents and dis-

tilled under argon prior to use. Triiminophosphorane ligands and metal complexes derived thereof were prepared according to literature [27]. Complexes 5 and 7 were isolated in 81% and 96% yield, respectively, both as other solids. Their spectroscopic features were similar to those of (PhC(CH₂NPPH₃)₃)CuBr [27] and they afforded satisfactory elemental analyses. The high-throughput screening experiments were carried out using an Endeavor parallel pressure reactor system (Argonaut Technologies, now part of Biotage AB), which had eight mechanically stirred stainless steel reactors equipped with glass liners.

2.2. Typical oligomerization procedure

2.2.1. Endeavor conditioning

Eight Reaction Vessels (RV) were weighted and inserted in an 8-position stainless steel RV rack. The rack, 8 impellers and 2 needles were heated in an oven at 70 °C for at least 1 h (usually overnight). Each hot RV was then inserted in the Endeavor following the procedure described by Argonaut. Air was removed by applying a nitrogen flow through a Teflon tube down to the bottom of the RV and the RV was covered with a nitrogen flow coming from the Endeavor manifold by opening the appropriate valve. All the impellers were placed on the stirrer assembly and the Endeavor was closed after having stopped the nitrogen flow to avoid a bad positioning of the O-rings. A seal check was achieved by pressurizing all the reactors (21 bar), closing each reactor valves, and venting the manifold. The pressure drop should not exceed 0.14 bar in 15 min. After venting all the reactors, the Endeavor conditioning procedure consisting in 10 nitrogen purges at 80 °C was launched for ca. 30 min.

2.2.2. Catalyst sample preparation

A metal complex (ca. 5 mg) was weighted under air in a 1.5 mL vial stored in a desiccator. In a Schlenk flask conditioned under nitrogen, the appropriate amount of toluene (ca. 23 mL, the exact volume was calculated to reach 25 mL after addition of the co-catalyst) was introduced. The vial containing the catalyst was dropped in the toluene flask to dissolve its content. The appropriate amount of an aluminum co-catalyst solution was added and the resulting mixture was kept for ca. 10 min (precontact time). During that period, the 2 needles were taken out of the oven, connected to a 1 mL and a 5 mL glass syringes, respectively, and flushed with nitrogen.

2.2.3. Oligomerization reaction

Each reaction vessel was loaded with 5 mL of *n*-heptane containing 30 ppm of an aluminum scavenger (prepared by mixing 100 mL of *n*-heptane with 0.2 mL of 10% triisobutylaluminum solution). Next, 0.8 mL of *n*-nonane (internal standard) and 0.2 mL of catalyst solution were added using the same syringe. The system was pressurized with 10 bar of ethylene. The Endeavor took control of all the operations and monitoring until the final venting of the reactor vessels. The reactions mixtures were quenched with methanol (0.5 mL) and analyzed by gas chromatography.

3. Results and discussion

3.1. Oligomerization of ethylene with Ni(II) complexes

Since nickel is the metal most frequently employed for the oligomerization of ethylene at the industrial scale [28,29], we first investigated the catalytic activity of complexes **1–4** that had been prepared by chelating NiBr₂(dme) with our four new tripodal ligands (dme is 1,2-dimethoxyethane). Modified methylaluminoxane (MMAO) was added as a co-catalyst with an aluminum-to-nickel molar ratio of 800 and the reactions were carried out in *n*-heptane under 10 bar of ethylene for 1 h. Under these conditions, the oligomerization activities of the four triiminophosphorane nickel complexes remained modest and roughly unaffected by the exact nature of the R and R' substituents. In all four cases, consumption of ethylene did not exceed 150 g C₂H₄ mmol⁻¹ h⁻¹ at 30 °C (Fig. 1). Although this figure is not exceptional, it is nevertheless superior to the one recorded with the corresponding bis(iminophosphorane) nickel complexes, which afforded – in the best cases – an oligomerization activity of ca. 20 g C₂H₄ mmol⁻¹ h⁻¹ when activated by MMAO at the same temperature (Beaufort et al., unpublished results). Increasing the temperature up to 45 °C resulted in a slight decrease of the oligomerization activity. A much sharper drop of catalyst efficiency occurred between 45 and 50 °C. Activity fell then to around 30 g C₂H₄ mmol⁻¹ h⁻¹ and remained at this level until 80 °C (Fig. 1). Hence, at 50–80 °C the oligomerization activity of triiminophosphorane complexes **1–4** became similar to that of the analogous bidentate species at 30 °C, suggesting a higher thermal stability of the tridentate complexes.

In order to better apprehend the influence of the bridgehead and phosphine substituents on the outcome of the reaction, the catalytic efficiencies of complexes **1–4** at temperatures below 50 °C were examined in detail (Fig. 2). Comparison of the triphenylphosphine-iminophosphorane Ni(II) complexes substituted either by a methyl (**1**) or a phenyl group (**2**) at the bridgehead carbon atom revealed that the latter catalyst presented a slightly higher activity, except at 35 °C. For the two

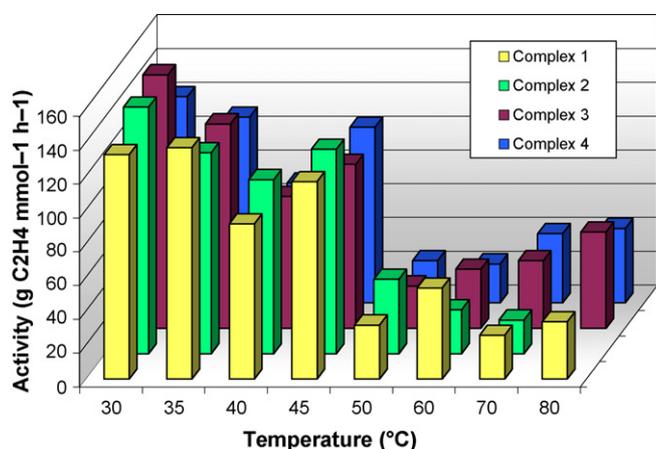


Fig. 1. Oligomerization of ethylene catalyzed by Ni(II) complexes **1–4** at various temperatures.

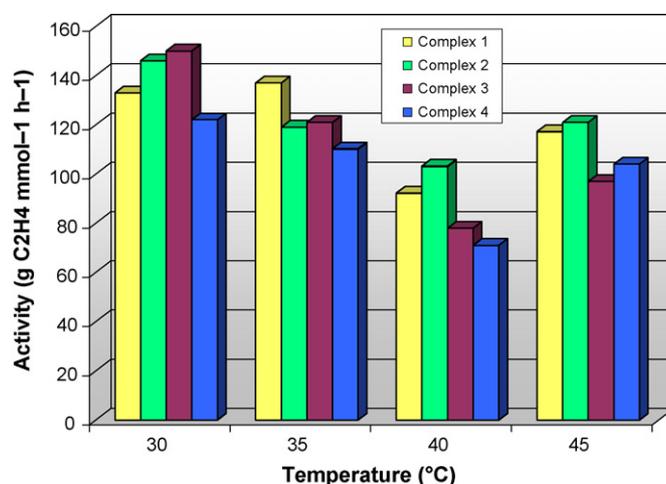


Fig. 2. Influence of the bridgehead and phosphine substituents on the catalytic activity of Ni(II) complexes **1–4** at various temperatures.

tricyclopentylphosphine-based derivatives, the reverse tendency was observed since the complex with a methyl-capped ligand (**3**) was found slightly more active than its phenyl-substituted analogue (**4**), except at 45 °C.

We also put side-by-side species sharing the same bridgehead on their iminophosphorane ligands. The activity of catalyst **1** bearing a methyl bridgehead and a triphenylphosphine moiety was around 130 g C₂H₄ mmol⁻¹ h⁻¹, down from 150 g C₂H₄ mmol⁻¹ h⁻¹ with complex **3** sporting a tricyclopentylphosphine unit (Fig. 2). However, the opposite trend was observed with a phenyl group at the bridgehead position. In this case, the triphenylphosphine-based complex (**2**) always afforded a higher oligomerization activity than its tricyclopentylphosphine counterpart (**4**) (~140 vs. 120 g C₂H₄ mmol⁻¹ h⁻¹).

Altogether, changing the nature of the bridgehead and phosphine substituents had only a limited influence on the ethylene consumption promoted by complexes **1–4**. Yet, and rather intriguingly, the two structural features seemed to be linked and interdependent, since associating the next of kin, either aromatic (phenyl/phenyl) or aliphatic (methyl/cyclopentyl), usually led to the highest catalytic efficiencies.

GC analysis of the reaction mixtures indicated that the oligomers obtained with complexes **1–4** were mainly butenes and hexenes (Table 1). Whatever the reaction temperature and catalyst used, 1-butene and isobutene formed the bulk of the C₄ fraction, while 1-hexene was the most important component of the C₆ fraction. Contrary to the total consumption of ethylene, the relative amounts of butenes and hexenes shifted markedly with the nature of the iminophosphorane ligand employed. Indeed, catalyst precursor (PhC(CH₂NPCp₃)₃)NiBr₂ (**4**) was most selective toward hexene formation, whereas complex **2** favored dimerization into butenes and complex **3** led to a larger proportion of higher oligomers. Increasing the temperature, on the other hand, had a much more limited influence on the oligomer distribution, except with (PhC(CH₂NPPPh₃)₃)NiBr₂ (**2**).

Table 1
Oligomer distributions obtained with Ni(II) complexes **1–4** at various temperatures

Complex	T (°C)	Oligomer distribution (mol%) ^a		
		C4	C6	>C6
(MeC(CH ₂ NPPH ₃) ₃)NiBr ₂ (1)	30	21	64	15
(MeC(CH ₂ NPPH ₃) ₃)NiBr ₂ (1)	60	19	65	15
(PhC(CH ₂ NPPH ₃) ₃)NiBr ₂ (2)	30	49	33	18
(PhC(CH ₂ NPPH ₃) ₃)NiBr ₂ (2)	60	62	28	10
(MeC(CH ₂ NPCp ₃) ₃)NiBr ₂ (3)	30	35	40	25
(MeC(CH ₂ NPCp ₃) ₃)NiBr ₂ (3)	80	29	37	33
(PhC(CH ₂ NPCp ₃) ₃)NiBr ₂ (4)	30	12	85	3
(PhC(CH ₂ NPCp ₃) ₃)NiBr ₂ (4)	70	15	82	3

Reaction conditions: 0.5 mmol of nickel complex in the presence of MMAO (Al/Ni = 800), 10 bar of C₂H₄ (constant pressure), 5 mL of *n*-heptane for 1 h.

^a Determined by GC analysis.

3.2. Influence of the co-catalyst

Using nickel complexes **1** and **2** as catalysts precursors, we have carried out the oligomerization of ethylene at various temperatures in the presence of diethylaluminum chloride (DEAC, Et₂AlCl) instead of MMAO (Fig. 3). On the whole, this change of alkylating agent did not result in any significant enhancement of the catalyst efficiency. Only at 30 °C in the case of complex **1**, did DEAC somewhat outperform MMAO, as the catalytic activity peaked at ca. 160 g C₂H₄ mmol⁻¹ h⁻¹. This effect did not persist at higher temperatures, however. With both co-catalysts, the ethylene oligomerization activity was maximal at 30 °C and dramatically decreased above 45 °C. Similar oligomer distributions were observed with each of the two catalyst precursors (MeC(CH₂NPPH₃)₃)NiBr₂ (**1**) and (PhC(CH₂NPPH₃)₃)NiBr₂ (**2**) when tested with DEAC as activator. Both systems afforded ca. 35–50% of butenes at 30 °C with no remarkable oligomer selectivity.

Catalyst activation by ethylaluminum dichloride (EADC, EtAlCl₂), which is more acidic than DEAC, was also investigated in the case of complex **3**. Recourse to this alkylating agent yielded an oligomerization activity similar to those observed previously with MMAO or DEAC, although it decreased somewhat more slowly as temperature increased (Table 2).

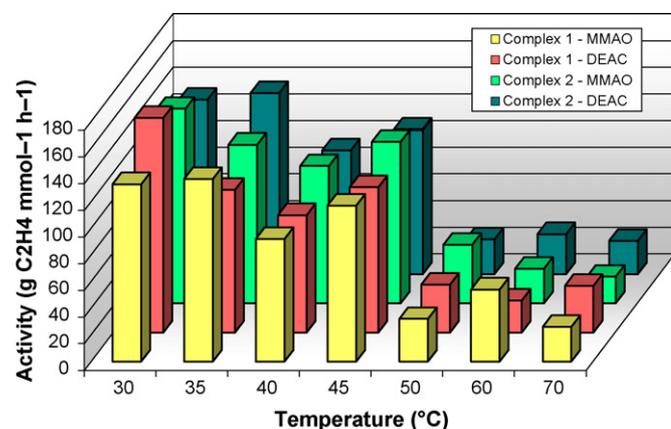


Fig. 3. Influence of the co-catalyst on the oligomerization of ethylene catalyzed by (MeC(CH₂NPPH₃)₃)NiBr₂ (**1**) or (PhC(CH₂NPPH₃)₃)NiBr₂ (**2**) at various temperatures.

3.3. Influence of the metal

Triiminophosphorane complexes of Fe(II), Pd(II), and Cu(II) were prepared by complexing the tripodal ligand PhC(CH₂NPPH₃)₃ with FeCl₂, PdCl₂, and Cu(OTf)₂, respectively. These species were tested as catalyst precursors for ethylene oligomerization in the presence of MMAO at various temperatures (Fig. 4). The screening was carried out with the Endeavor high-throughput system using the experimental procedure set up for nickel complexes. Results showed that the metal had only a limited influence on the outcome of the reaction. This was a rather unexpected observation. For all catalysts under scrutiny (**2**, **5–7**), consumption of ethylene evolved in a similar fashion within the 30–80 °C temperature range. The rate of oligomerization was highest toward the lowest end (ca. 140 g C₂H₄ mmol⁻¹ h⁻¹ at 30 °C) and slowly decreased until 50 °C. Above that threshold, it sharply plunged to about 20 g C₂H₄ mmol⁻¹ h⁻¹. Thus, the temperature–activity profiles recorded by varying the metal center closely paralleled those obtained when the tripodal ligand was changed (cf. Fig. 1). Noteworthy, the Pd-based complex **6** was slightly more active than its counterparts with a maximum consumption of ca. 180 g C₂H₄ mmol⁻¹ h⁻¹ at 35 °C.

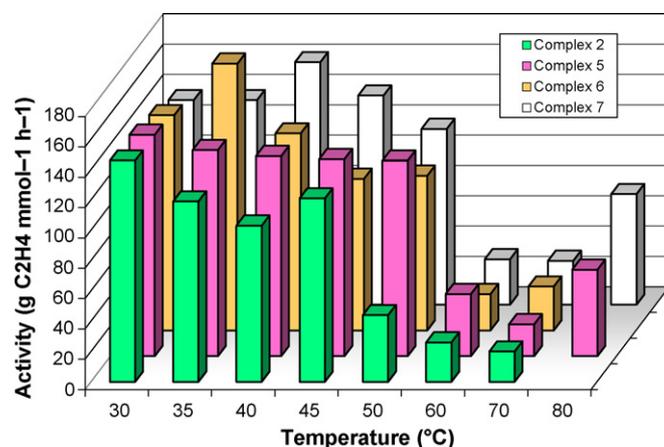


Fig. 4. Oligomerization of ethylene catalyzed by triiminophosphorane complexes of Ni(II) (**2**), Fe(II) (**5**), Pd(II) (**6**), and Cu(II) (**7**) at various temperatures.

Table 2
Influence of the co-catalyst on the oligomerization activity of complex **3** at various temperatures

Co-catalyst	Oligomerization activity (g C ₂ H ₄ mmol ⁻¹ h ⁻¹)			
	30 °C	35 °C	40 °C	45 °C
MMAO	150	121	78	97
DEAC	123	110	79	110
EADC	153	116	103	113

Reaction conditions: 0.5 mmol of (MeC(CH₂NPCp₃)₃)NiBr₂ (**3**) in the presence of an aluminum co-catalyst (Al/Ni = 800), 10 bar of C₂H₄ (constant pressure), 5 mL of *n*-heptane for 1 h.

Table 3
Oligomer distributions obtained with various transition-metal complexes at 30 °C

Complex	Oligomer distribution (mol%) ^a		
	C4	C6	>C6
(PhC(CH ₂ NPPh ₃) ₃)NiBr ₂ (2)	49	33	18
(PhC(CH ₂ NPPh ₃) ₃)FeCl ₂ (5)	50	26	23
(PhC(CH ₂ NPPh ₃) ₃)PdCl ₂ (6)	4	93	3
(PhC(CH ₂ NPPh ₃) ₃)Cu(OTf) ₂ (7)	30	50	20

Reaction conditions: 0.5 mmol of catalyst in the presence of MMAO (Al/M = 800), 10 bar of C₂H₄ (constant pressure), 5 mL of *n*-heptane for 1 h.

^a Determined by GC analysis.

Although the four metal complexes examined in this study reacted with ethylene at about the same rate, they afforded mixtures of oligomers (mainly butenes and hexenes) with significantly different selectivities (Table 3). Nickel and iron catalytic species (**2** and **5**, respectively) favored butene formation (up to 50 mol% of the product distribution) together with a lesser amount of higher oligomers (mostly hexenes), whereas palladium and copper complexes **6** and **7** produced more hexenes than butenes. Palladium complex **6**, in particular, displayed an impressive selectivity, affording almost exclusively hexenes from ethylene.

4. Conclusion

The catalytic activity of seven transition-metal complexes bearing new tripodal iminophosphorane ligands was investigated in the oligomerization of ethylene using high-throughput techniques. In all cases, ethylene consumption peaked at ca. 30 °C and was not drastically affected by varying the nature of the metal (Ni, Fe, Pd, Cu), the aluminum co-catalyst (MMAO, DEAC, or EADC) or the substituents of the tris(iminophosphorane) ligand. Structural modifications of the organometallic complexes, either at the metal center or within the tripodal ligand, however, had a significant impact on the oligomer distribution obtained. In particular, the Pd-based catalyst (PhC(CH₂NPPh₃)₃)PdCl₂ (**6**) displayed an excellent selectivity toward hexene formation.

Acknowledgments

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