

Catalytic Ethylene Dimerization and Oligomerization: Recent Developments with Nickel Complexes Containing P,N-Chelating Ligands

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ABSTRACT

Catalytic ethylene oligomerization represents a topic of considerable current academic and industrial interest, in particular for the production of linear α -olefins in the C_4 – C_{10} range, whose demand is growing fast. Identifying and fine-tuning the parameters that influence the activity and selectivity of metal catalysts constitute major challenges at the interface between ligand design, coordination/organometallic chemistry, and homogeneous catalysis. In this Account, we show how comparative studies aiming at modulating the coordinating properties of functional ligands for a metal, such as nickel, which is used in industrial processes, lead to beneficial effects in catalytic ethylene oligomerization.

1. Introduction

One of the most important breakthroughs in organometallic chemistry resulted from the discovery by Ziegler et al.¹ that, in the AlR_3 -catalyzed “growth reaction” (Aufbau-

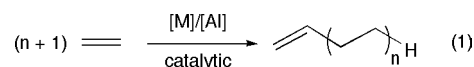
Freddy Speiser was born in 1971 and received his “Diplom” at the Rheinisch Westfälische Technische Hochschule (RWTH) Aachen (Germany) in 1999. He prepared his Ph.D. at the Université Louis Pasteur in Strasbourg and the Institut Français du Pétrole, Rueil Malmaison, under the supervision of Drs. P. Braunstein and L. Saussine on the oligomerization of ethylene catalyzed by new nickel complexes containing P,N ligands. He then joined the Beiersdorf AG in Hamburg in 2002 and is currently a Postdoctoral Research Associate in the group of R. Köhn, University of Bath, England.

Pierre Braunstein was born in 1947 and graduated from the Ecole Supérieure de Chimie de Mulhouse (1969) and obtained his Dr. Ing. (1971) and Doctorat d'Etat (1974) from the Université Louis Pasteur (ULP) in Strasbourg. He is Director of Research with the CNRS and the Director of the Coordination Chemistry Laboratory (UMR 7513 CNRS) of the ULP. His main research interests concern the inorganic and organometallic chemistry of the transition- and main-group elements, where he has (co)authored over 350 scientific publications and review articles. He is a member of various academies, and his most recent awards include the Chini Memorial Lecture (Italian Chemical Society, 2003), the Nyholm Medal (Royal Society of Chemistry, 2003), and the Grand Prix de l'Institut Français du Pétrole (French Académie des Sciences, 2004).

Lucien Saussine was born in Nîmes (France) in 1948. He graduated from the Ecole Nationale Supérieure de Chimie in Paris and worked with Professor M. Julia on the use of organopalladium complexes in organic synthesis. He received his Ph.D. in 1974 from the University Paris VI and, shortly after, joined the homogeneous catalysis group at IFP (Institut Français du Pétrole) where he developed several aspects of the chemistry of transition-metal peroxidic complexes. Since 1986, his research interests deal with the synthesis of new organometallic compounds and their catalytic application for olefin transformation.

reaktion)² of ethylene, nickel salts could modify the nature of the products from α -olefins to 1-butene. This phenomenon became known in the literature as “the nickel effect”^{1,3} and led to the discovery of the “Ziegler catalysis”⁴ and to the remarkable chemistry developed by Wilke and others over decades.⁵ The selective synthesis of C_4 – C_{20} linear α -olefins has become a topic of considerable interest in both academia and industry owing to their growing demand most notably as comonomers with ethylene [C_4 – C_8 to yield branched linear low-density polyethylene (LLDPE) with impressive rheological and mechanical properties⁶], for the synthesis of poly- α -olefins and synthetic lubricants (C_{10}), as additives for high-density polyethylene production and for the production of plasticizers (C_6 – C_{10}) and surfactants (C_{12} – C_{20}).^{7–9} The annual worldwide consumption of polyolefins is close to 10^8 tons. Because the demand for linear α -olefins is growing faster in the C_4 – C_{10} range (a ca. 2.5×10^6 tons/year market) than in the C_{12+} range, the selective formation from ethylene of specific shorter chain α -olefins, which could circumvent the typical, broad Schulz–Flory distributions observed in ethylene oligomerization, is therefore a topic of major fundamental and applied importance.

α -Olefins can be produced by four main processes that operate either by elimination reactions (i–iii) or by chain-growth reactions (iv):¹⁰ (i) the cracking of paraffins, (ii) the dehydrogenation of paraffins, (iii) the dehydration of alcohols, and (iv) the oligomerization of ethylene. The cracking of paraffins still finds widespread application for the synthesis of ethylene, but generally the first three processes no longer play a central role for the preparation of α -olefins. Ethylene is a readily available feedstock, and its oligomerization represents the main source for α -olefins in industry.¹¹ In contrast to the products from processes i–iii, ethylene oligomerization products possess exclusively an even number of carbon atoms and represent commercially most valuable products.^{12–14} The production of α -olefins was initially realized by the “stoichiometric” Alfen process,^{2,8} whereby the chain-growth reaction on aluminum was followed by the liberation of the product in a separate reactor at higher temperatures. A one step catalytic process was developed by Gulf (now Chevron Phillips), where both reactions occur simultaneously in the same reactor. The Ethyl process (now BP Amoco) is a combination of stoichiometric and catalytic chain-growth reactions.^{8,9} In contrast to the SHOP process developed by Shell, which is based on organometallic nickel complexes (see below),^{8,9,15} other systems for ethylene oligomerization or polymerization require transition metals associated with aluminum cocatalysts (eq 1).^{12–14,16–18}

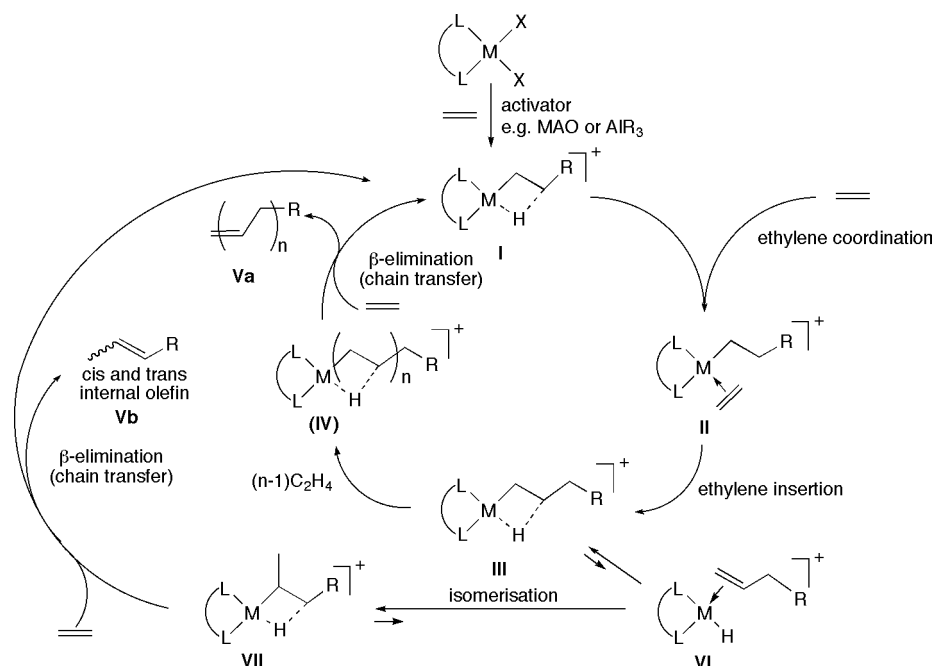


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Scheme 1. Catalytic Ethylene Oligomerization Polymerization



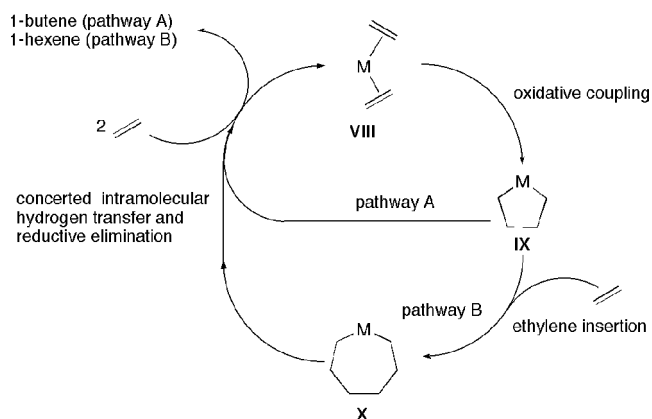
Both oligomerization and polymerization reactions can be represented by a general mechanism that involves common organometallic elementary steps (Scheme 1).

First, a coordinatively unsaturated species is generated, which is stabilized after ethylene insertion by a β -agostic interaction **I**.¹⁹ The coordinated ethylene in complex **II** inserts into the M-alkyl bond to give **III**. Finally, after $(n - 1)$ further insertions leading to **IV**, the product molecule **Va** is eliminated. The exact mechanism that leads to the liberation of the olefin, chain transfer/ β -H elimination, still deserves detailed studies.^{20–23} For values of n ranging from 1 to 40, oligomers are formed, and for larger values of n , polymers are eliminated (Scheme 1). Isomerization leading to internal olefins **Vb** is accounted for by species **VI** and **VII**. The reaction sequence **II–IV** depends strongly on the ethylene concentration (pressure) because the rate of chain transfer relative to chain isomerization increases with the ethylene concentration.^{14,24} Brookhart and co-workers have noted that an increase in ethylene pressure led to an increased selectivity for α -olefins and in the Schulz–Flory constant α . Therefore, any change in the ethylene concentration, e.g., pressure, reaction temperature, and ethylene solubility, will have a decisive influence on the branching ratio in polymerization or on the α -olefin content in oligomerization reactions.¹⁴

Another reaction mechanism, shown in Scheme 2, can apply to systems producing exclusively a single group of olefins such as, e.g., 1-butene or 1-hexene.^{25–28}

Here, two molecules of coordinated ethylene in **VIII** react by oxidative coupling to form a metallacyclopentane **IX**. In the titanium-based Alkylbutol process, an intramolecular hydrogen transfer and a reductive elimination are observed at this stage, liberating 1-butene (pathway A in Scheme 2).²⁵ Insertion of a third molecule of ethylene leads to a metallacycloheptane **X**, which then liberates 1-hexene by reductive elimination. This mechanism is

Scheme 2. Ethylene Oligomerization Involving Metallacyclic Intermediates

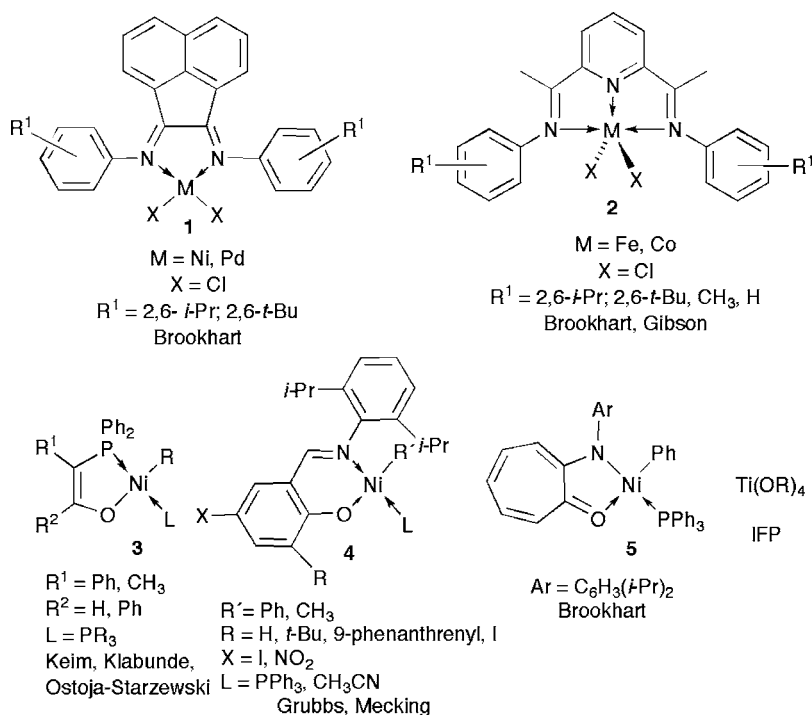


operative with chromium as a metal, in the Phillips process (pyrrolide ligand), the SASOL mixed heteroatomic systems (S,N,S ligands), and the BP system (P,N,P ligands) (pathway B in Scheme 2).²⁹ Although expansion of a seven- to nine-membered metallacycle intermediate was considered unlikely, a new MAO-activated chromium/diphosphinoamine system was recently reported, which allows ethylene tetramerization with selectivities up to 70% for 1-octene.³⁰ Reaction mechanisms, which resemble the concerted coupling, are observed for transition metals such as titanium,^{25,28,31} tantalum,³² nickel,³³ or chromium.^{26,27,34–37}

A significant difference between degenerate polymerization and concerted coupling is that only the former may also yield internal olefins (or branched polymers), whereas the concerted coupling only gives terminal olefins.

Numerous Ni^{II} catalysts tend to favor chain termination over propagation, hence their use in various processes for the dimerization of α -olefins.^{1,3,38} Another characteristic of nickel catalysts in α -olefin oligomerization reactions is

Scheme 3. Complexes for the Catalytic Oligomerization or Polymerization of Ethylene



their tendency to yield internal olefins.^{3,12} However, the catalytic properties of Ni^{II} complexes can be readily modified and fine-tuned by the use of suitable ligands, which underlines the importance of coordination chemistry in homogeneous catalysis.^{3,13–15,17,39}

2. Catalytic Olefin Oligomerization in Recent Years

Because the β -elimination step is relatively facile for late transition metals such as Co, Rh, Ni, and Pd, these metals preferentially lead to oligomerization products such as butenes or hexenes. In contrast, chain propagation dominates for early transition metals (Ti–Cr), which therefore usually constitute polymerization catalysts. However, this simple picture about the transition-metal-catalyzed conversions of ethylene and other α -olefins has required modification in recent years.

Among the most prominent examples of catalyst versatility are the DAD (diazadiene) systems **1** developed by Brookhart and co-workers,^{13,14,40–42} which are based on earlier studies by Balch and Holm,⁴³ tom Dieck,^{44–47} van Koten and Vrieze,⁴⁸ and Walther.⁴⁹ These complexes serve as oligomerization or polymerization catalysts depending on the steric properties of the ligand (Versipol system) (Scheme 3).^{13,14}

The groups of Gibson^{13,17} and Brookhart^{13,14} have successfully used the Fe^{II} and Co^{II} pyridinediimine complexes **2** for the polymerization and the oligomerization of ethylene. Fe^{II} pyridinediimine systems were first reported by Goodyear for the codimerization of butadiene and ethylene (Scheme 3).⁵⁰

A remarkable catalytic system for the oligomerization of ethylene with selective formation of linear α -olefins is the Shell Higher Olefin Process (SHOP). Keim and co-

workers used the Ni(P,O)(PR₃)R' system **3** for ethylene oligomerization¹⁵ and polymerization.^{51,52} Klabunde et al. showed that scavenging of the PR₃ ligand leads to a polymerization catalyst,^{53,54} and also working with Ni(P,O) systems, Ostoja-Starzewski obtained high molecular weight polyethylene.⁵⁵ Continued interest in SHOP-type catalysts led recently to interesting modifications of the R¹ and R² groups.^{56–61} An extension of these P,O-type catalysts **3** resulted in the neutral N,O systems **4**^{62,63} and **5**⁶⁴ for polymerization. Mecking and co-workers applied Grubbs-type catalysts **4** to the ethylene emulsion polymerization in water.^{65,66}

Another prime example is the Alphabutol process developed by the IFP in which a Ti(OR)₄/AlEt₃ system is used for the dimerization of ethylene.³⁸ In contrast, TiCl₄ with the same activator yields polyethylene.

The typical reactivity of chromium catalysts in ethylene polymerization may be turned into a very selective trimerization reaction by changing the nature of the ligands.^{67,68} In both Ti-^{25,28,38} and Cr-^{30,67,68} based catalysis, the role of the ligands is essential because they can completely modify the reactivity of the metal center.

Despite these important developments, the systems described generally provide either ethylene oligomers with broad Schultz–Flory distributions or polymers. Therefore, transition-metal catalysts yielding very narrow product distributions constitute a main target because only very few such examples are known in the literature.^{26–28,30,67,68}

Because the applications of N,N, N,O, and P,O ligands in the α -olefin oligomerization and polymerization and of ethylene in particular have been recently reviewed in detail,^{13–15,17,69} we shall focus in this Account on ethylene oligomerization systems recently developed with difunctional P,N ligands. Their attractivity results from the hope

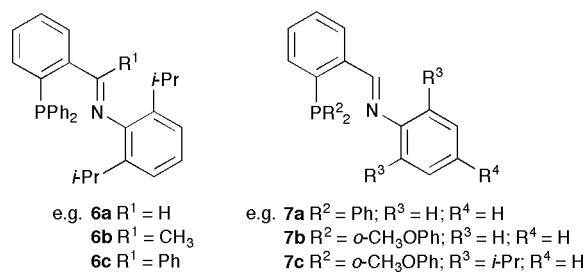
of combining the known stability of Ni^{II} and Pd^{II} phosphine complexes with the interesting catalytic properties of complexes containing even a single arylimine arm.

3. Complexes with P,N Chelates

Unsymmetrical bidentate ligands with a nitrogen and a phosphorus donor atom, often called mixed or hybrid ligands³⁹ and referred to as P,N ligands in the following, can chelate a metal center or bridge two identical or different metal centers. Owing to their bonding versatility, P,N ligands play an important role in the coordination chemistry of transition metals and in homogeneous catalysis.^{39,70–74} These heterofunctional systems often display unique dynamic features, such as hemilability, which provides an efficient molecular activation procedure under mild conditions.³⁹

Modifications of the steric and electronic properties of either the phosphine or the nitrogen donor function is expected to influence the coordination chemistry and catalysis with these systems, as will be shown in the following. Table 1 provides a comparative overview of the catalytic results obtained with various Ni^{II} complexes under comparable conditions (specified in the footnotes).

3.1. Phosphinoimine Ligands in the Oligomerization or Polymerization of Ethylene. Phosphinoimine ligands have only recently attracted attention for the late transition-metal-catalyzed oligomerization, polymerization, and copolymerization of ethylene.^{13,14,17,69,75,76} This includes the phosphinoimine ligands developed by the Eastman Chemical Corporation (**6**),⁷⁷ Shell,⁷⁸ and Rush and co-workers (**7**)⁷⁹ with varying R groups on either the phosphorus- or nitrogen-bound phenyl substituent. Asahi Industries reported a system with only one bulky substituent in the ortho position of the imine aryl ring.⁸⁰

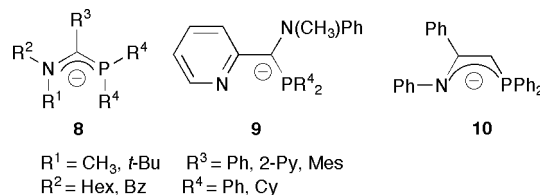


The Ni complexes with **6** only led to the formation of polymers. The influence of the basicity of the phosphine and nitrogen donors was studied and also that of the R¹ substituent in the α position to the nitrogen donor.⁷⁷ When going from R¹ = H to CH₃, and Ph, an increase in activity was observed.

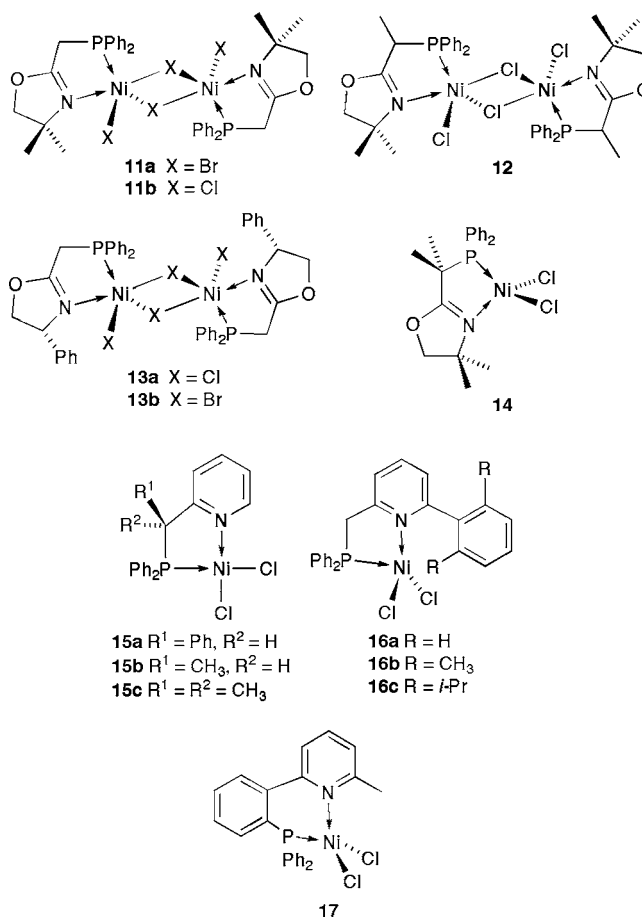
The Pd^{II} triflate and *p*-toluenesulfonate complexes of **7** catalyze the oligomerization of ethylene. When the steric bulk of either the R² or R³ substituents was increased, the product distribution shifted from short to medium chain oligomers. The use of electron-releasing groups for R⁴ considerably increased the reaction rate.⁷⁸

Other P,N systems used in the oligomerization or polymerization of α -olefins include the anionic ligands **8**

and **9** developed by Symyx Technologies⁸¹ and **10**.^{82,83} The influence of the nitrogen substituents on ethylene polymerization was studied with cationic palladium complexes of **8** and **9**.⁸¹ Nickel catalysts based on the anionic phosphinoimine **10** led to medium chain oligomers.⁸²



Considering that the use of nonenolizable imine donors should be beneficial to catalyst thermal and chemical stability, we examined the synthesis, structure, and catalytic properties of various Ni^{II} complexes with phosphino-oxazoline (**11–14**)⁸⁴ and phosphino-pyridine ligands (**15–17**).^{85,86} Increasing alkyl substitution in the α position to phosphorus leads to increasing basicity of the P donor, according to the ³¹P NMR chemical shifts, with consequences on the geometry of the coordination sphere around the metal: distorted trigonal bipyramidal in **11–13**, tetrahedral in **14**, **16**, and **17**, and almost square planar in **15**.^{84–86} The Ni–N and Ni–P distances are significantly shorter in **15c** than in **14**.



The consequences on the catalytic properties were very noticeable (entries **11–17** in Table 1). In all cases, one of our goals was to use as little cocatalyst as possible, not

Table 1. Comparison of the Catalytic Performances of Ni^{II} Complexes with Different P,N-Chelating Ligands^a

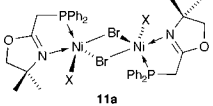
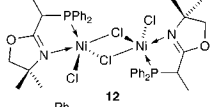

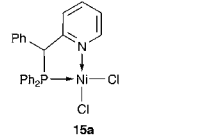
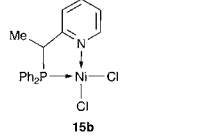
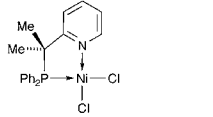
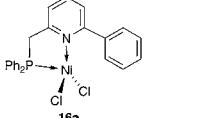
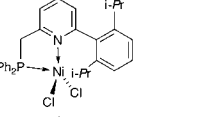
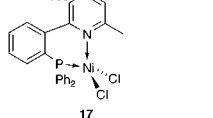
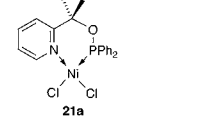
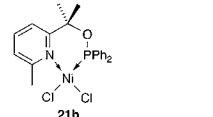
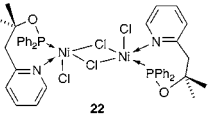
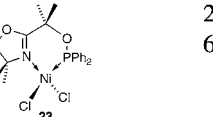
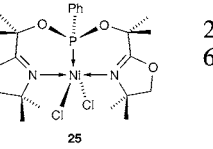
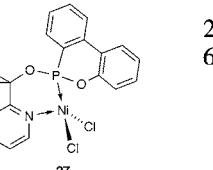
catalyst precursor	cocatalyst (equiv)		productivity ^b	TOF ^c	selectivity (%)				k_{α}^d	comments
	AlEtCl ₂	MAO			C ₄	C ₆	C ₈	α -olefin (C ₄)		
NiCl ₂ (PCy ₃) ₂	2		800	1600	88	12	12	0.09	used for comparison.	
	6		13000	27200	86	14	0.5	9	0.11	Inactive with 400 equiv MAO.
 11a	6		traces	traces	100			nd	Inactive with 400 equiv MAO.	
	12		16300	33800	62	36	2	3	0.39	
	14		17500	36300	56	41	2	3	0.49	
 12	6		18400	38100	64	33	3	13	0.34	inactive with 400 equiv MAO. A comparison between 11a, 12 and 14
 14	2		12300	25400	67	28	3	25	0.28	shows that increasing the degree of substitution α -to P favors activity and selectivity for 1-butene
	6		22000	45900	54	40	1	20	0.50	
		800	3800	7900	72	23	5	38	0.21	
 15a	2		14400	30100	81	18	1	14	0.15	for 15a-c, MAO leads to lower activities but higher selectivities for 1-butene than AlEtCl ₂ .
	6		23600	49400	72	26	2	11	0.24	
		400	4850	10200	81	16	2	34	0.14	
		800	6500	13600	77	18	3	33	0.16	
 15b	2		22100	46100	75	23	2	14	0.20	a comparison between 15a-c shows again that an increase in the degree of substitution α -to P favors activity and selectivity for 1-butene
	6		26400	55200	66	30	3.5	11	0.31	
		400	4800	10000	85	14	2	38	0.11	
		800	5850	12200	83	15	3	35	0.12	
 15c	6		27800	58100	65	32	2.5	11	0.33	inactive with only 2 equiv AlEtCl ₂
		400	3300	7000	73	22	4	34	0.20	
		800	10900	22800	69	22	8	38	0.22	
 16a	2		22600	47300	82	18	1	9	0.14	16a-c and 17 are inactive with 400 equiv MAO
	6		27200	57000	71	29	1	9	0.27	
 16c	2		21200	44400	73	26	1.5	9	0.23	
	6		29100	61000	77	22	1	10	0.19	
 16c	2		10500	22100	92	8		13	0.06	mostly dimerization
	6		26800	56100	70	28	2	9	0.27	
 17	2		7800	16300	87	13	0.1	18	nd	decomposition of 21-23 in the presence of MAO
	6		20900	43700	64	33	3	5	nd	
 21a	2		21200	44400	80	20		10	nd	beneficial effect of Me ortho to N on activity and C ₄ selectivity (see 21a)
	6		23800	49900	71	29		9	nd	

Table 1. (Continued)

catalyst precursor	cocatalyst (equiv)		productivity ^b	TOF ^c	selectivity (%)				k_{α}^d	comments	
	AlEtCl ₂	MAO			C ₄	C ₆	C ₈	α -olefin (C ₄)			
 22	2		19500	40800	61	35	8	0.31	active species probably mononuclear		
	6		23800	49400	59	35	5	6		0.33	
 23	2		14000	30100	81	18	1	14	nd	better activity and C ₄ selectivity than with the analogous phosphine system 14 . Activities 21a < 23 < 21b .	
	6		23600	49500	64	33	3	8	nd		
 25	2		12700	26500	76	22	2	9	0.21	the influence of the tridentate ligand can be appreciated by comparison with 23 and 27 . Decomposition in the presence of MAO.	
	6		15000	31400	70	27	2.5	9	0.26		
 27	2		21100	44200	82	17	1.5	22	0.16	the pyridine and the phosphonite donors lead to better performances than the oxazoline and the phosphinite donors (see 21a and 25)	
	6		27400	57300	75	23	2.5	12	0.21		
		400		3500	7400	94	7	0.5	19		<0.1
		800		6300	13200	90	5	2	17		<0.1

^a Conditions: $T_{\text{initial}} = 30\text{ }^{\circ}\text{C}$ (no cooling of the reactor was done during the reaction and the exothermicity of the reaction, in particular with AlEtCl₂, resulted in a rapid increase of the temperature, however, not above 100 °C), 10 bar C₂H₄, 35 min, 4×10^{-2} mmol of the Ni complex; solvent, 15 mL of toluene (in cases where the reaction was very exothermic, 50 mL of toluene was used, see refs 89 and 91).^b In [g of C₂H₄/(g of Ni) h].^c In [mol of C₂H₄/(mol of Ni) h].^d k_{α} = hexenes (mol)/butenes (mol). These values, sometimes not determined (see the original references), are not the Schultz–Flory constants because our catalysts are mainly dimerization and trimerization catalysts. The fact that the k_{α} value varies for a given catalyst as a function of the nature or quantity of the cocatalyst suggests some incorporation of the butene formed during chain growth.

only for economical reasons but also for a better understanding of the ligand influence on the catalytic properties of the metal complexes. To facilitate comparisons between catalyst precursors, only the results obtained with 2 or 6 equiv of AlEtCl₂ or with 400 or 800 equiv of methylalumoxane (MAO) are reported in Table 1. More details are provided in the original publications. Mostly dimers and trimers were obtained, which corresponds to our objectives. With only 6 equiv of AlEtCl₂, complexes **12** and **14** afforded TOF values of 38 100 and 45 900, respectively, higher than that of 27 200 mol of C₂H₄/(mol of Ni) h obtained with NiCl₂(PCy₃)₂ under similar conditions. In the presence of 800 equiv of MAO, complexes **11–13** and NiCl₂(PCy₃)₂ were inactive, whereas a TOF of 7900 mol of C₂H₄/(mol of Ni) h and a selectivity for 1-butene within the C₄ fraction of 38% were obtained with **14**. Some incorporation of the butene formed probably occurs during chain growth (consecutive reaction).⁸⁴

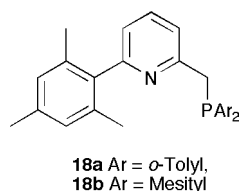
The Ni complexes **15–17** provided high activities in the presence of only 6 equiv of AlEtCl₂. Similar activities were obtained by other groups in the dimerization of ethylene and propene but only when using between 200 and 400 equiv of the cocatalyst.²⁴ The selectivity for C₄ olefins reached 81% for **15a** and 92% for **17** in the presence of 2

equiv of AlEtCl₂. In the presence of 400 or 800 equiv of MAO, complexes **15** yielded lower activities than with AlEtCl₂ as the cocatalyst but higher selectivities for 1-butene (33–38%).⁸⁵

The nature of the N-heterocycle influences the catalytic activity: replacing the oxazoline heterocycle (of **14**) with a pyridine (in **15c**) led to increased activities, 45 900 and 58 100 mol of C₂H₄/(mol of Ni) h, respectively, in the presence of 6 equiv of AlEtCl₂ but to a lower selectivity for α -olefins. For both the phosphino-oxazoline- and phosphino-pyridine-based catalysts, an increased degree of alkyl substitution in the α position to the phosphine donor leads to higher activities for ethylene oligomerization with AlEtCl₂ or MAO as the cocatalyst. This is accompanied in the oxazoline series by an increased selectivity for 1-butene, whereas this parameter has less influence in the pyridine systems.⁸⁵

Complexes with the phosphino-pyridines of type **18**, similar to **16**, have been recently studied by Liu and co-workers⁸⁷ who also found that the bulky aryl ring did not influence the product distribution much in the oligomerization or polymerization of ethylene.

The coordination sphere of the metal atom has tetrahedral geometry in **16a–c** and **19**,^{86,87} in contrast to the

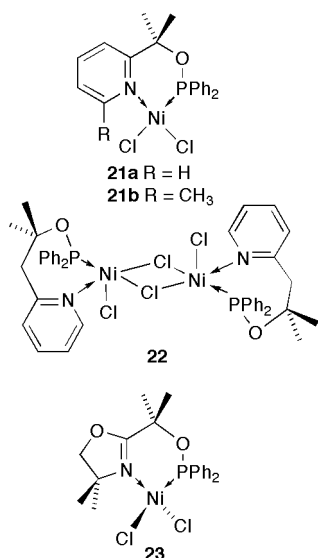


diimine system **20** (Scheme 4). In the latter case, introduction of sterically demanding groups around the metal center strongly influences the product distribution.^{13,14,40–42} The chain length of the products can apparently only be controlled when the sterically demanding groups and the potentially active reaction sites are orthogonal to each other as, e.g., in **20**.

The considerable difference in reactivity between **16** and **19** may be explained by the presence of sterically demanding groups on the aryl rings of the phosphine group in the latter. The influence of substituents on the P-bound phenyl rings has already been pointed out for the phosphinoimines **7**.⁷⁸ A methoxy group in the ortho position on the P-phenyl ring leads to a more active catalyst than with an unsubstituted phenyl. It was observed that an increase in steric hindrance led to a decrease in isomerization.

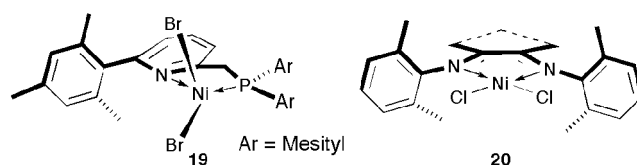
3.2. Modification of the Phosphorus Moiety. Whereas the imine moiety of phosphino-imine ligands may be used to introduce steric hindrance to control the product distribution in the conversion of ethylene^{77,78,88} or to transfer chiral information,^{72,74} the basicity of the phosphorus donor can be easily modified by replacing its alkyl or aryl substituents by alkoxide groups, thus yielding phosphinites, phosphonites, or phosphonates.

3.2.1. Phosphinito-imine Chelates in the Oligomerization of Ethylene. Phosphinito-imines have rarely been used in the oligomerization of ethylene. The new phosphinito-pyridine Ni^{II} complexes **21** and **22** and phosphinito-oxazoline complex **23** were prepared, but in the presence of MAO and AlEt₃, only decomposition of the complexes was observed.



However, in the presence of only 6 equiv of AlEtCl₂, **21–23** provided activities around 49 500 mol of C₂H₄/(mol

Scheme 4. Compared Coordination Geometries in Phosphino-pyridine and Diimine Ni^{II} Complexes



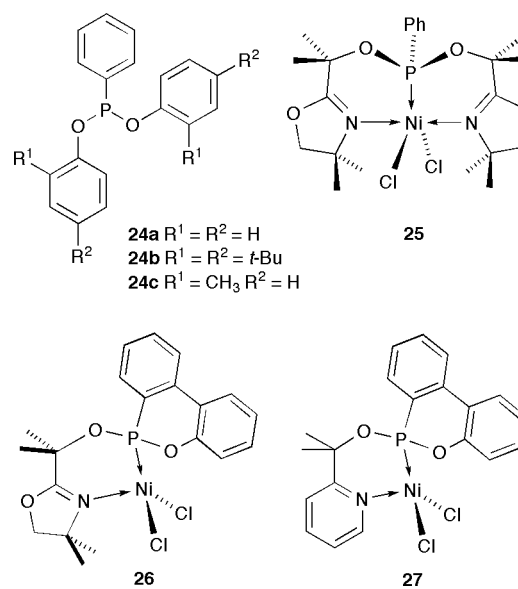
of Ni) h (**21b**, **22**, and **23**), superior to that of NiCl₂(PCy₃)₂. The selectivities for ethylene dimers were as high as 92% with only 1.3 equiv of AlEtCl₂ (**21a** and **23**) (Table 1).⁸⁹

As observed with the phosphine donors (see section 3.1), replacement of the oxazoline heterocycle with an *o*-substituted pyridine led to formation of more active species when 2 equiv of AlEtCl₂ was used because the TOF increased from ca. 30 100 for **23** to 44 400 mol of C₂H₄/(mol of Ni) h for **21b**. However, a less significant difference was observed in the presence of 6 equiv of the cocatalyst.

A comparison between **21a** and **22** showed that an increase of the chelate ring size from six- to seven-membered also resulted in higher catalytic activities when 2 equiv of AlEtCl₂ was used, with TOF values of 16 300 and 40 800 mol of C₂H₄/(mol of Ni) h, respectively.

The consequence of the replacement of a phosphine by a phosphinite donor, which also resulted in an increase of the chelate ring size from 5 to 6, was noted when comparing the TOF values observed in the presence of 6 equiv of AlEtCl₂ for complexes **15c** and **21a** in the pyridine series [58 100 and 43 700 mol of C₂H₄/(mol of Ni) h, respectively] and **14** and **23** in the dimethyl-substituted oxazoline series [45 900 and 49 500 mol of C₂H₄/(mol of Ni) h, respectively].^{84,89}

3.2.2 Phosphonito-imine Chelates in the Oligomerization of Ethylene. Phosphonite complexes have rarely been reported for the catalytic oligomerization or polymerization of α -olefins, although the monodentate phosphonites **24** were used by the Mitsubishi Chemical Corporation in the Ni-catalyzed dimerization of *trans*-2-butene.⁹⁰



In complex **25** with a tridentate phosphonito-oxazoline ligand, the metal coordination is trigonal bipyramidal, whereas in **26** and **27** with a racemic oxaphosphorin moiety associated with an oxazoline or pyridine donor, respectively, it is tetrahedral.⁹¹ In the presence of as little as 1.3 equiv of AlEtCl₂, complex **25** showed an activity of 17 000 mol of C₂H₄/(mol of Ni) h, whereas **27** was inactive. With 2 or 6 equiv of AlEtCl₂, **27** became more active than **25**. High selectivities for ethylene dimers were obtained in the presence of only 2 equiv of AlEtCl₂, up to 76% (**25**) and 82% (**27**). Selectivities for the ethylene dimers of 94 or 90% and for 1-butene within the C₄ fraction of 19 or 17% were observed with complex **27** when 400 or 800 equiv of MAO was used as the cocatalyst, respectively.

Thus, going from the tridentate to bidentate phosphonito-imine (see **25** and **27** or **25** and **23**) led to higher activities but similar selectivities for α -olefins. These differences suggest that the N,P,N ligand in **25** remains tridentate during catalysis. Complex **27** is more stable toward heat and the cocatalyst than **25**.

When comparing the related pyridine-phosphinite and -phosphonite systems **21a** and **27**, it appears that the latter is more active in the presence of 2 or 6 equiv of AlEtCl₂, respectively (Table 1).^{89,91}

4. Conclusion

The catalytic oligomerization of ethylene is a topic of considerable current interest in academic and industrial groups. The demand for linear α -olefins in the C₄–C₁₀ range is growing fast, and the selective formation from ethylene of specific shorter chain α -olefins triggers much research effort. Identifying and fine-tuning the parameters that influence the activity and selectivity of suitable catalysts continue to represent challenges at the interface between ligand design, coordination/organometallic chemistry, and homogeneous catalysis. We have attempted in this Account to show how comparative studies help to improve our understanding of the beneficial effects that can result from changing the coordinating properties of the ligands for a given metal, such as nickel, which is used in industrial processes. A limited selectivity for α -olefins may be explained by (i) reversible β -H elimination after ethylene insertion, followed by reinsertion with the opposite regiochemistry and chain transfer to give 2-butene or (ii) a re-uptake mechanism leading to isomerization of 1-butene. Within the large family of P,N ligands, variables include the basicity of the N-donor moiety, from pyridines to less basic oxazolines, and the stereoelectronic properties of the phosphorus donor, from a phosphine, phosphinite, or phosphonite type. Extending such studies to tridentate N,P,N systems was also possible, as shown with complex **25**. Relatively small variations in the ligand steric and/or electronic properties may favor di- over mono-nuclear structures for their metal complexes, and a comparison between mono- and dinuclear catalyst precursors thus becomes available. This is of course of interest because this may represent a way to generate precursors and perhaps active species with different metal

coordination geometries and coordinative unsaturations, although the nuclearity of the active species cannot be determined at this stage. We have always attempted to use as little cocatalyst as possible, and it was even possible to use only 1.3 equiv of AlEtCl₂ with complexes **21a**, **21b**,⁸⁹ and **25**.⁹¹

Obviously, the synthesis of new functional ligands, their coordination chemistry, and the systematic study of the catalytic properties of their metal complexes will remain essential for improving the production of specific short-chain α -olefins through more active, selective, and stable catalysts.

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