3-Aminoiminoacrylate, 3-Aminoacrylate, and 3-Amidoiminomalonate Complexes as Catalysts for the Dimerization of Olefins

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Nickel(II)−aminoacrylate, −aminoiminoacrylate, and −amidoiminomalonate complexes **1**−**4** are suitable precursors together with appropriate cocatalysts for the catalytic dimerization of ethylene, propylene, and α-olefins with short chain lengths such as 1-hexene. Suitable ligands **IV**−**VI**, **VIII**, **X,** and **XII** generate nickel(II) compounds **1**−**4** active for these catalytic dimerizations. The influence of different substituents attached to the coordinating ligand backbone is tested in the catalytic reactions. Several novel monodentate and chelate nickel(II) precursor complexes **1** and **3** were isolated and also characterized by X-ray structure analysis.

1. Introduction

Olefins with short chain lengths are used as comonomers in the polymerization of ethylene to give linear low-density polyethylene (LLDPE) or for the preparation of detergents and synthetic lubricants. Especially the dimerization of ethylene to butenes is used industrially for generating powering components in fuel with homogeneous titanium catalysts and special cocatalysts in the alphabutol process (IFP).[1] 2-Butene is also produced with the Phillips Petroleum process by dimerization of ethylene.[2] Few technical processes are used in industry for the dimerization of propylene. The nonregioselective olefin dimerization[3] (Dimersol, Institut Français du Pétrole), performed in the absence of any phosphine ligand, affords propene dimers with a composition of 22% *n*-hexenes, 72% 2-methylpentenes, and 6% 2,3-dimethylbutenes. Dimers form 80% of the oligomer mixture, a small amount of trimers (18%) and tetramers (2%) being produced as well. The process works at 50 °C under a pressure sufficient to maintain the reactants in the liquid phase. The catalyst results from the interaction of a nickel salt, soluble in a paraffinic hydrocarbon solvent and an ethylaluminum chloro compound; the active species is formed in situ inside the dimerization reactor.

Regioselective dimerization of propylene to 2,3-dimethylbutenes is currently operated by Sumitomo[4] and BP Chemicals[5] with tricyclohexylphosphine and Ziegler-type catalysts. In the Sumitomo process very high selectivities of 2,3-dimethylbutenes (up to 85%) are obtained at 20−50 °C using toluene as a solvent. On the other hand, the BP Chemical process operates without any solvent at lower temperature and with a simpler catalyst composition, giving a lower selectivity for 2,3-dimethylbutenes.

In the last years, discrete late-metal catalysts have come into focus for ethylene poly- and oligomerization.[6] Dimerization of ethylene has been carried out mainly with complexes of iron,[7] cobalt,[8] palladium,[9] and nickel, while chromium complexes showed excellent activities and selectivities in ethylene trimerization[10] and tetramerization.[11] Most nickel-based oligomerization catalysts contain bidentate P,N-,[12] P,O-,[13] N,N-,[14] or N,O-ligands.[15]

β-Diketiminates have an important role as spectator ligands by virtue of their strong binding to the metal,

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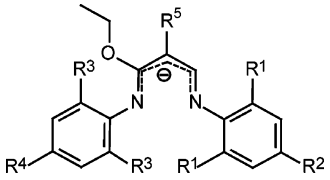


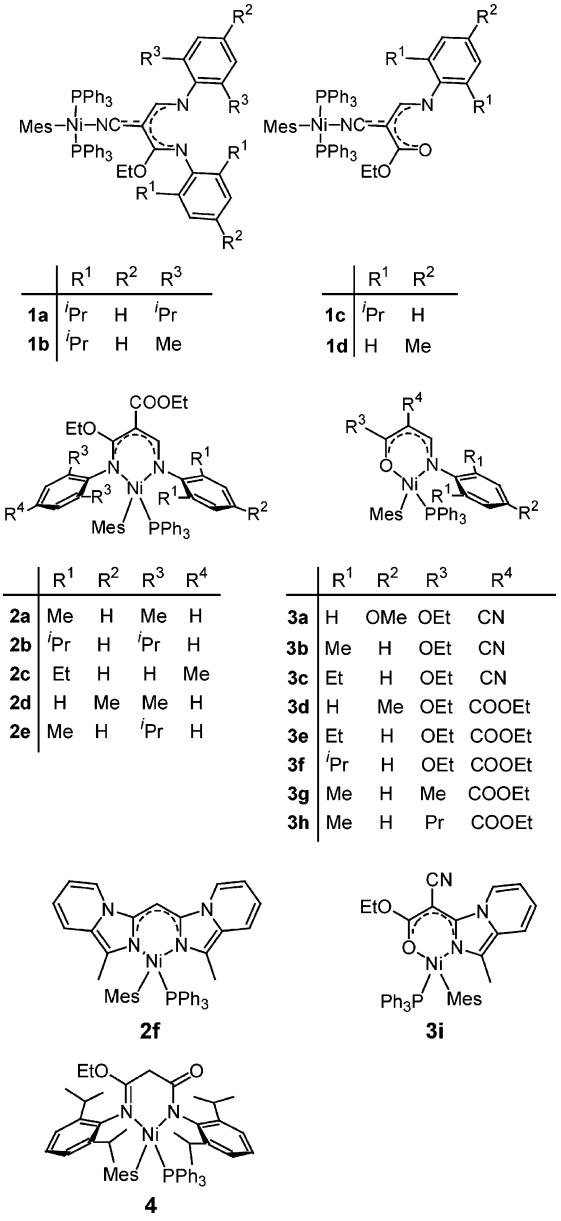
Figure 1. Formula of 3-aminoiminoacrylates.

their tunable and extensive steric demands, and their diversity of bonding modes.[16] Complexes with β-diketiminates are coordinately unsaturated, and this feature is a key factor in their ability to function as catalysts for several processes such as copolymerization of epoxides and CO_2,[17] polymerization of lactide,[18] polymerization of methyl methacrylate,[19] and oligo- and polymerization of olefins.[20] *N*,*N*-β-Diketiminato complexes of nickel, as well as *N*,*O*-ketiminato and Schiff base derivatives, were active in the polymerization of norbornene.[21]

Herein we report a new group of ligands: 3-aminoiminoacrylate, 3-aminoacrylate, and 3-amidoiminomalonate ligands coordinate nickel(II) ions to give the active precatalysts **1**−**4** (Figure 2). Together with the cocatalysts methylaluminoxane (MAO) and ethylaluminum sesquichloride (EASC) **1**−**4** are suitable to dimerize either ethylene or propylene with a high activity to give butenes or hexenes. The nickel(II) aminoacrylate compounds **3b**,**i** are also able to oligomerize 1-hexene. The results of the catalytic reactions with the precatalysts **1**−**4** and suitable cocatalysts will be presented.

2. Results and Discussion

Synthesis of Ligands and Nickel(II) Complexes. As an extension of the class of well-known β-diketiminates, we have synthesized novel 3-aminoiminoacrylates that yield by deprotonation the corresponding monoanionic ligands. An alkoxyl and a second functional group R^5 (i.e. nitrile or ester) are bound to the ligand backbone, noticeably modifying the electronic distribution in the metallacycle of the resulting transition-metal complex compared to the classical β-diketiminates (Figure 1).



	R^1	R^2	R^3
1a	^{i}Pr	H	^{i}Pr
1b	^{i}Pr	H	Me

	R^1	R^2
1c	^{i}Pr	H
1d	H	Me

	R^1	R^2	R^3	R^4
2a	Me	H	Me	H
2b	^{i}Pr	H	^{i}Pr	H
2c	Et	H	H	Me
2d	H	Me	Me	H
2e	Me	H	^{i}Pr	H

	R^1	R^2	R^3	R^4
3a	H	OMe	OEt	CN
3b	Me	H	OEt	CN
3c	Et	H	OEt	CN
3d	H	Me	OEt	COOEt
3e	Et	H	OEt	COOEt
3f	^{i}Pr	H	OEt	COOEt
3g	Me	H	Me	COOEt
3h	Me	H	Pr	COOEt

Figure 2. Molecular formulas of the precatalysts **1**−**4**.

The cyano-substituted aminoiminoacrylates **IVa**,**b** were obtained in a four-step reaction. The first step[22] consists of a chlorination of cyanoacetic acid, followed by condensation with 2,6-diisopropylaniline (Scheme 1). The obtained amide **I** was then converted with an oxonium salt to the related imino ester[23] **II**, which was refluxed with triethyl orthoformate in the presence of acetic anhydride as solvent, in a Claisen reaction.[24] The

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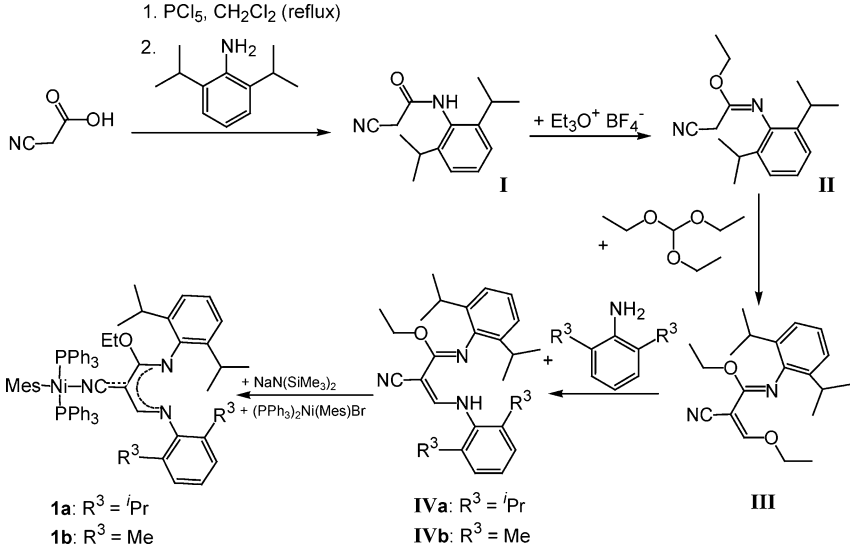
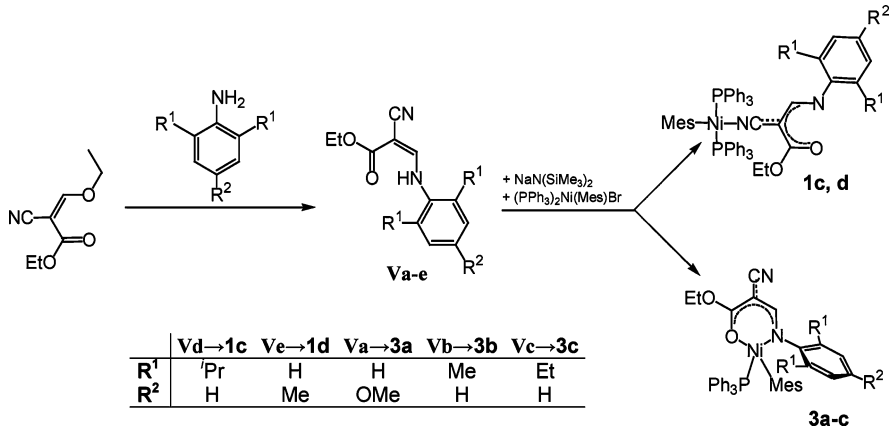
Scheme 1. Synthesis of Cyano-Substituted 3-Aminoiminoacrylates IVa,b



Scheme 2. Synthesis of Cyano-Substituted Aminoacrylates Va−e



	Vd→1c	Ve→1d	Va→3a	Vb→3b	Vc→3c
R^1	*i*Pr	H	H	Me	Et
R^2	H	Me	OMe	H	H

ethoxymethylene group in compound **III** finally reacted with substituted anilines in refluxing methanol to give the products **IVa**,**b** in good yields. The above-described method was not successful with an ester in place of a cyano group at the backbone; in fact, decomposition occurred in the third step, because the imino ester was not stable under these conditions.

A set of differently substituted 3-aminoacrylates **Va**−**e**, **VIa**−**c**, and **VIIIa**,**b** was synthesized by aminolysis of the Claisen adducts.[25] The cyano-substituted aminoacrylates **Va**−**e** were easily prepared by condensation of ethyl (ethoxymethylene)cyanoacetate with diverse anilines in refluxing methanol, using an adapted version of similar reactions already described in the literature (Scheme 2).[25]

This procedure was not effective for obtaining analogous substances bearing an ester group instead of a nitrile; for the synthesis of compounds **VIa**−**c** the reagents had to be heated under stronger conditions and ethanol produced during the reaction had to be distilled away (Scheme 3).

Finally, a third modification of the backbone was attained: the acyl-substituted aminoacrylates **VIIIa**,**b** were synthesized in a two-step reaction from the β-keto esters, using an adapted version of a procedure described in the literature[26] for similar compounds (Scheme 4).

An oxidative heterocyclization of **VIIc** with $CuCl_2$ gave the imidazo[1,5-*a*]pyridyl derivative **VIIIc** in low yields (Scheme 5). **VIIIc** was then reacted with sodium bis(trimethylsilyl)amide and $[(PPh_3)_2Ni(Mes)Br]$,[27] as in the previous cases, to give the nickel(II) complex **3i**.

Another synthetic method was successful with compounds **Xa**,**b** bearing two identically substituted aryl rings. The route consists of a twofold condensation[28a]

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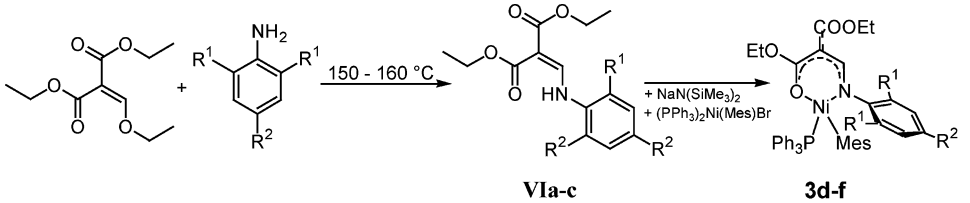
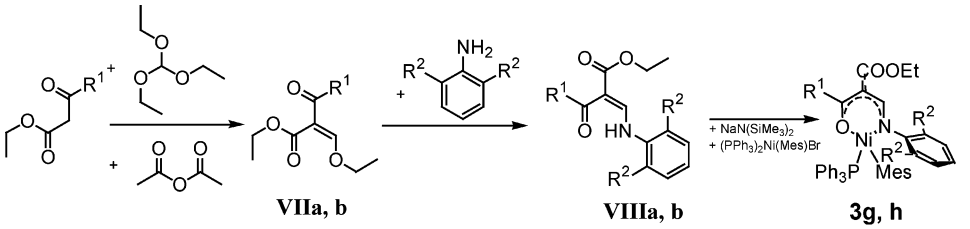
Scheme 3. Synthesis of Ester-Substituted Aminoacrylates VIa−c and the Nickel(II) Complexes 3d−f



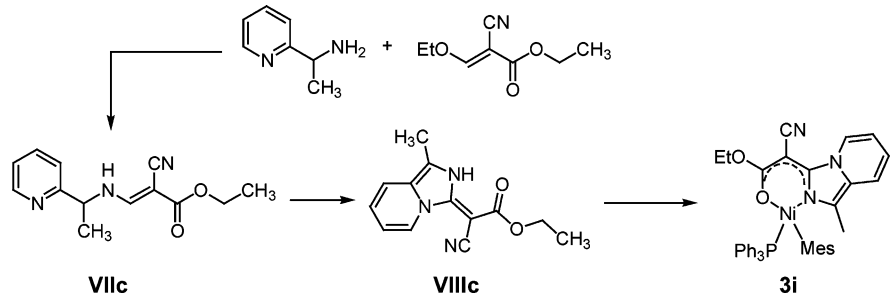
	3d	3e	3f
R^1	H	Et	^{i}Pr
R^2	Me	H	H

Scheme 4. Synthesis of Acyl-Substituted Aminoacrylates VIIIa,b and the Nickel Complexes 3g,h

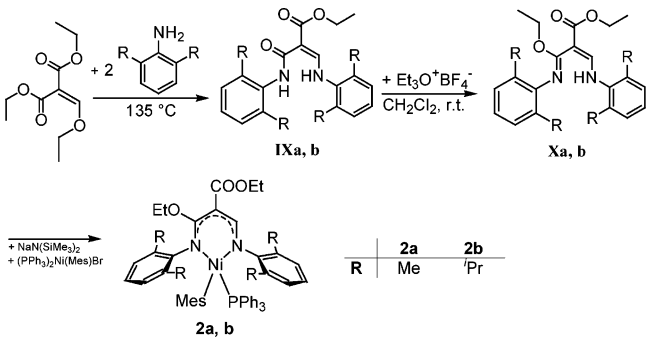


	3g	3h
R^1	Me	*n*-Pr
R^2	Me	Me

Scheme 5. Synthesis of Ethyl (2*E*)-Cyano(1-methylimidazo[1,5-*a*]pyridine-3(2*H*)-ylidene)acetate (VIIIc)



Scheme 6. Synthesis of Ester-Substituted 3-Aminoiminoacrylates Xa,b with Identically Substituted Aryl Rings and Nickel(II) Complexes 2a,b



	2a	2b
R	Me	^{i}Pr

in the absence of any solvent at high temperature with simultaneous distillation of the produced ethanol. The formed 3-aminoiminoacrylamides **IXa**,**b** reacted subsequently with an oxonium salt[23] to the 3-aminoiminoacrylates **Xa**,**b** (Scheme 6).[28b,c]

Several attempts have been made to prepare compound **IVa** using this method and starting from ethyl (ethoxymethylene)cyanoacetate, but it was impossible to obtain the intermediate 3-aminoacrylamide: the condensation always took place only at the ethoxymethylene group and 2-cyano-3-aminoacrylates were obtained. Ester-substituted 3-aminoiminoacrylates **Xc−e** bearing differently substituted aryl rings were synthesized as well. In method A (Scheme 7) diethyl (ethoxymethylene)malonate was condensed[24] with two differently substituted anilines to the 3-aminoiminoacrylamides **Xc−e**, where the intermediates **VI** were formed. The second condensation (amide formation, i.e., from **VI** to **IX**) required stronger reaction conditions than the first one. Method B, on the other hand, employed diethyl malonate which was first condensed with 1 equiv of one substituted aniline.[29] The amide obtained subsequently reacted with triethyl orthoformate and the other aniline derivative.[28,30]

Method A has proven to be more efficient than method B: the overall yields are higher and the first step in method B requires a large excess of diethyl malonate to prevent the immediate formation of the bisamide, while the other reactions can be performed in equimolar amounts.

Finally, the amidoiminomalonate **XII** was synthesized from diethyl malonate by 2-fold condensation with

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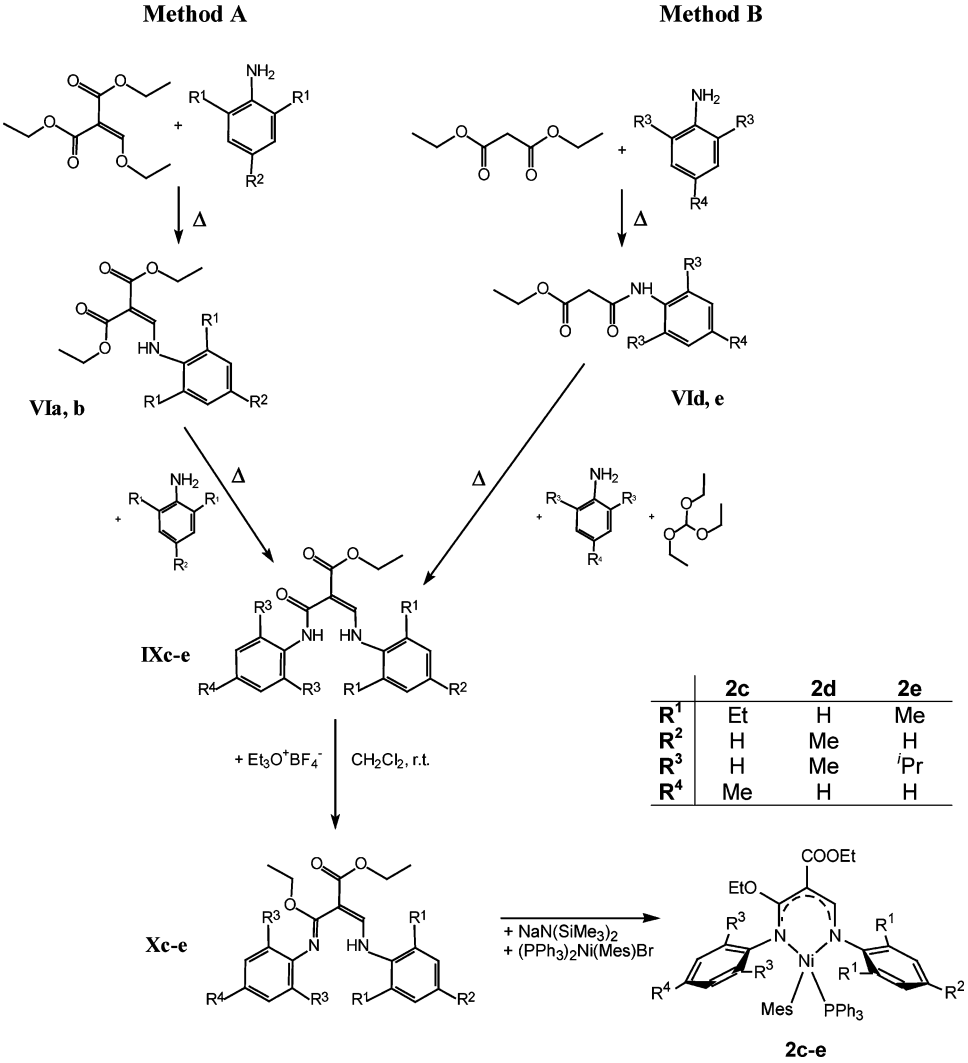
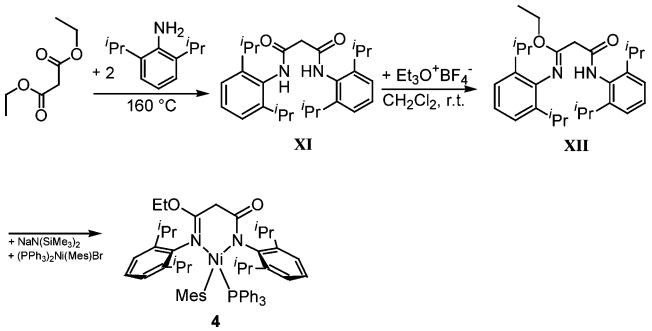
Scheme 7. Syntheses of Ester-Substituted 3-Aminoiminoacrylates Xc−e with Differently Substituted Aryl Rings and the Nickel(II) Complexes 2c−e



	2c	2d	2e
R^1	Et	H	Me
R^2	H	Me	H
R^3	H	Me	^{i}Pr
R^4	Me	H	H

Scheme 8. Synthesis of the Amidoiminomalonate XII and the Nickel(II) Complex 4



diisopropylaniline, followed by reaction with an oxonium salt[23] (Scheme 8).

The ligands **IV**−**VI**, **VIII**, **X**, and **XII** were used to prepare nickel(II) complexes: all of them were employed in their monoanionic form. Both the steric bulk at the aryl rings and electronic effects of the ligand backbone will affect the activity and selectivity of the corresponding nickel catalyst precursors for catalytic oligomerization reactions.

The monoanionic ligands were generated by deprotonation of the corresponding compounds **IV**−**VI**, **VIII**, **X**, and **XII** with sodium bis(trimethylsilyl)amide. The monoanions reacted subsequently with *trans*-(bromomesityl)bis(triphenylphosphino)nickel(II) ((PPh$_3$)$_2$Ni(Mes)-Br)[27] to yield the metal complexes (Schemes 1 and 2). Those compounds were all expected to act as bidentate chelating ligands but, surprisingly, X-ray diffractometry revealed a coordination of the monoanionic ligands **IVa**,**b** to nickel(II) through the cyano group, the ligands not acting as chelating units. The NMR spectra agree with the structural data of **1a**,**b**. The X-ray structure of the complex **1a** shows a tetracoordinated nickel atom with a distorted-square-planar conformation (Figure 3): the angles N(1)−Ni−C(31) and P(1)−Ni−P(2) are 172.5(1) and 173.4(4)°, respectively. The Ni1−N1 bond length is 1.888(3) Å; the nickel−phosphorus distances are 2.243(1) and 2.252(1) Å, while the Ni1−C31 distance is 1.919(3) Å. The observed C1−N2 (1.280(4) Å) and C3−N3 (1.264(4) Å) bond lengths reveal bonds with a high sp^2 imine character. This is also confirmed by the lengths observed for the C1−C2 (1.432(4) Å) and C2−C3 (1.448(4) Å) bonds.

To our knowledge, no examples of any similar complex have been described before. Several potential N,N- and N,O-chelating compounds are published, bearing a nitrile function at their backbone, but they are always

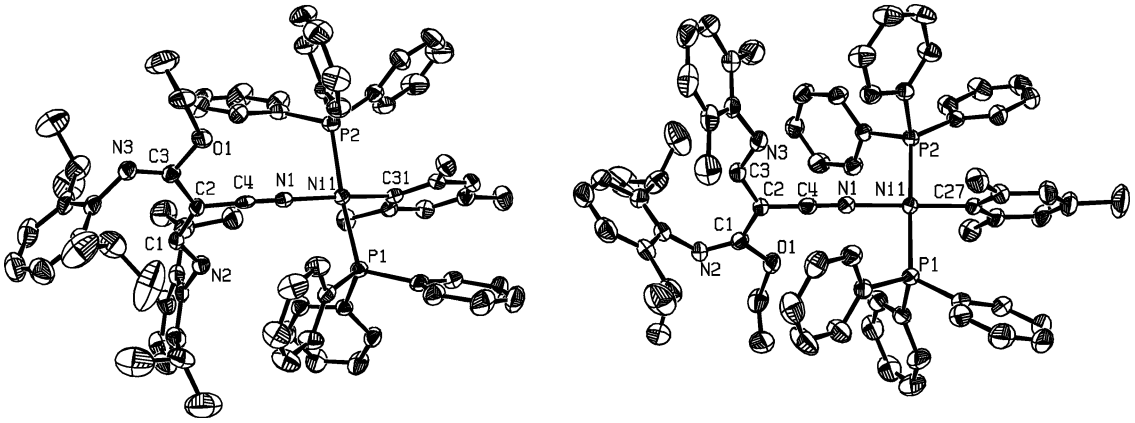


Figure 3. Molecular structures of **1a** (left) and **1b** (right). For **1a**, red crystals suitable for X-ray diffractometry were obtained in hexane/pentane/toluene (10/3/1). Selected bond distances (Å) and angles (deg): C3−N3 = 1.264(4), C2−C3 = 1.448(4), C4−C2 = 1.409(4), N1−C4 = 1.152(4), C1−C2 = 1.432(4), N2−C1 = 1.280(4), Ni1−N1 = 1.888(3), P2−Ni1 = 2.243(1), C31−Ni1 = 1.919(3), P1−Ni1 = 2.252(1); N1−Ni1−P2 = 89.73(8), P2−Ni1−C31 = 90.55(9), C31−Ni1−P1 = 87.82(9), P1−Ni1−N1 = 92.72(8), N1−Ni1−C31 = 172.5(1), P2−Ni1−P1 = 173.4(4). For **1b**, red crystals suitable for X-ray diffractometry were obtained in pentane/toluene (15/1). Selected bond distances (Å) and angles (deg): C4−N1 = 1.157(2), C2−C4 = 1.401(3), C3−C2 = 1.427(3), N3−C3 = 1.289(3), C1−C2 = 1.445(3), O1−C1 = 1.386(2), N2−C1 = 1.278(3), Ni1−N1 = 1.894(2), Ni1−P2 = 2.239(1), Ni1−C27 = 1.899(2), Ni1−P1 = 2.233(1); N3−C3−C2 = 123.1(2), C3−C2−C1 = 125.8(2), C2−C1−N2 = 132.8(2), C2−C4−N1 = 178.8(2), N1−Ni1−P2 = 91.00(5), P2−Ni1−C27 = 89.18(6), C27−Ni1−P1 = 89.73(6), P1−Ni1−N1 = 90.13(5), N1−Ni1−C27 = 179.1(1), P2−Ni1−P1 = 177.4(2).

reported to coordinate to the metal center as bidentate[31] and not monodentate.

The 3-aminoacrylates **Vd**,**e** behaved analogously to the corresponding imino-ligands **IVa**,**b** when reacting with nickel(II), and gave similar complexes **1c**,**d** (Scheme 3). On the other hand, under similar reaction conditions, the 3-aminoacrylates **Va**−**c** yielded the expected N,O-chelating complexes **3a**−**c** by releasing one phosphine ligand. On comparison of **1c** to **3b**,**c**, the increased steric bulk on the aniline (*i*-Pr vs Et and Me) seems to make binding via the cyano group more favorable. This tendency is supported by the fact that the even bulkier N,N ligands lead to similiar structures **1a**,**b**. On the other hand, the ligand on **1d** is not sterically demanding, especially compared to **3a**,**b** (H vs Et and Me). Hence, electronic effects must play an important role as well. Overall, minor changes on the ligand have drastic and difficult to predict effects on the complex structure.

Crystals of the complexes **3a**−**c** were obtained, and their structure was revealed by X-ray structure analysis (Figure 4). The triphenylphosphine ligand occupies the position trans to the coordinated nitrogen atom, while the mesityl group attached to the nickel center is bound in a position trans to the oxygen. The Ni−O, Ni−N, Ni−C, and Ni−P distances in **3a** are similar to those of previously described N,O chelate nickel(II) complexes.[21,31,32] In **3a**, the Ni1−N1 and Ni1−O1 bond lengths are 1.947(3) and 1.940(3) Å and, therefore, are almost identical with published data.[33] The same is observed for the carbon−carbon distances in the metallacycle: C1−C2 (1.339(5) Å) and C2−C3 (1.410(5) Å), respectively. The Ni1−P1 distance is 2.188(1) Å, while the Ni1−C14 bond distance measures 1.892(4) Å. Both distances are markedly shorter compared to **1a**−**d**. In **3a**, the bite angle O1−Ni1−N1 is 92.0(1)°. The metallacycle is planar, and the metal center has a distorted-square-planar coordination sphere. The plane of the mesityl substituent is oriented almost perpendicularly to the plane of the metallacycle, the dihedral angle being 80.4°.

Attempts to crystallize **1c**,**d** were not successful, but it was possible to nonetheless attribute their structure. In fact, the ESI mass spectra of **1a**,**b** and **1c**,**d** clearly showed the molecular peak corresponding to the complex bearing two triphenylphosphines ($(PPh_3)_2Ni(Mes)L$), while such a signal was always absent in the case of the compounds **3a**−**c** ($(PPh_3)Ni(Mes)L$), where the molecular peak indicated the presence of only one triphenylphosphine. In the region 2198−2207 cm^{-1}, IR spectra of the complexes **1a**,**b** and **1c**,**d** showed a weaker absorption band for the C≡N bond, in comparison to the complexes **3a**−**c**,**i** which exhibited strong absorptions in the range of 2173−2204 cm^{-1}.

Even though compounds **Va**−**e** are very similar to each other, they give different complexes under the same reaction conditions. A factor which may explain this behavior lies in the stability of the complexes binding one or two triphenylphosphines, which is significantly influenced by small changes in the ligands. In case of the anionic ligands derived from **IVa**,**b** and **Vd**,**e**, the complex $[(PPh_3)_2Ni(Mes)L]$ is more stable, whereas in the case of **Va**−**c**, $[(PPh_3)Ni(Mes)L]$ is favored. Neither transformations of the complexes $[(PPh_3)_2Ni(Mes)L]$ in $[(PPh_3)Ni(Mes)L]$ through release of triphenylphosphine were observed under the investigated conditions, nor the reverse reaction in the presence of an excess of phosphine. In the case of the ligands derived from **VIa**−**c**, **VIIIa**,**b**, and **Xa**−**e**, the anions have no other good coordinating groups, which would be able to bind to the nickel ion like the cyano group does: for this reason, only chelate complexes **3d**−**h** (Schemes 3 and 4) and **2a**−**e** were obtained. In the case of the nickel(II) complexes **3g**,**h**, the anionic

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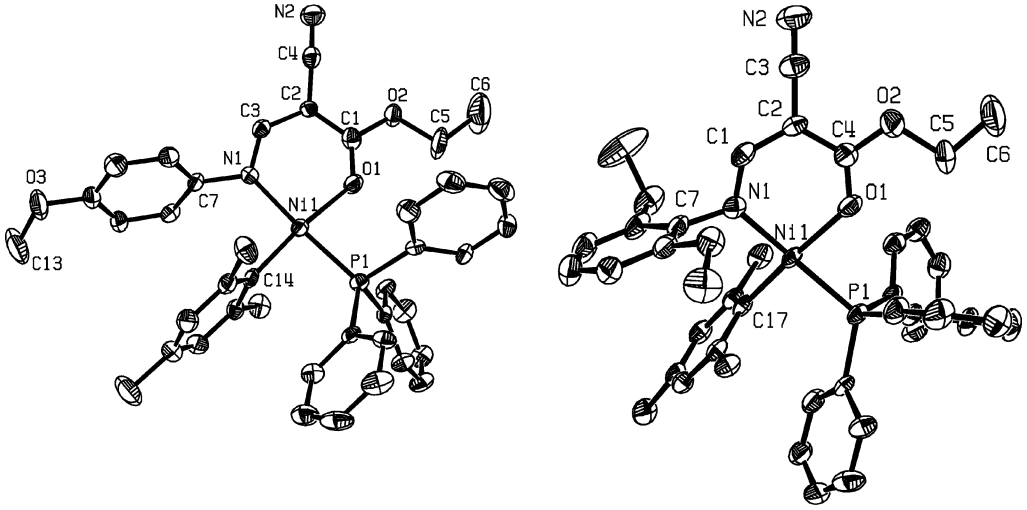

Figure 4. Molecular structures of **3a** (left) and **3c** (right). For **3a**, red crystals suitable for X-ray diffractometry were obtained in hexane/pentane/toluene (3/1/1). Selected bond distances (Å) and angles (deg): C1−O1 = 1.254(5), C1−C2 = 1.399(5), C2−C3 = 1.410(5), C3−N1 = 1.313(4), Ni1−O1 = 1.940(3), Ni1−N1 = 1.947(3), Ni1−C14 = 1.892(4), Ni1−P1 = 2.188(1); O1−C1−C2 = 125.1(4), C1−C2−C3 = 121.8(4), C2−C3−N1 = 128.2(4), O1−Ni1−N1 = 92.0(1), N1−Ni1−C14 = 93.8(1), C14−Ni1−P1 = 88.0(1), P1−Ni1−O1 = 87.0(1), O1−Ni1−C14 = 171.7(2), P1−Ni1−N1 = 171.7(1). For **3c**, red crystals suitable for X-ray diffractometry were obtained in pentane/toluene (8/1). Selected bond distances (Å) and angles (deg): C4−O1 = 1.244(5), C2−C4 = 1.404(6), C1−C2 = 1.406(6), N1−C1 = 1.309(5), Ni1−O1 = 1.941(3), Ni1−N1 = 1.936(4), Ni1−C17 = 1.904(4), Ni1−P1 = 2.185(2); O1−C4−C2 = 124.9(4), C4−C2−C1 = 121.0(4), C2−C1−N1 = 127.8(4), N1−Ni1−O1 = 91.3(1), O1−Ni1−P1 = 86.4(1), P1−Ni1−C17 = 88.4(1), C17−Ni1−N1 = 94.7(2), N1−Ni1−P1 = 173.2(1), O1−Ni1−C17 = 169.9(2).

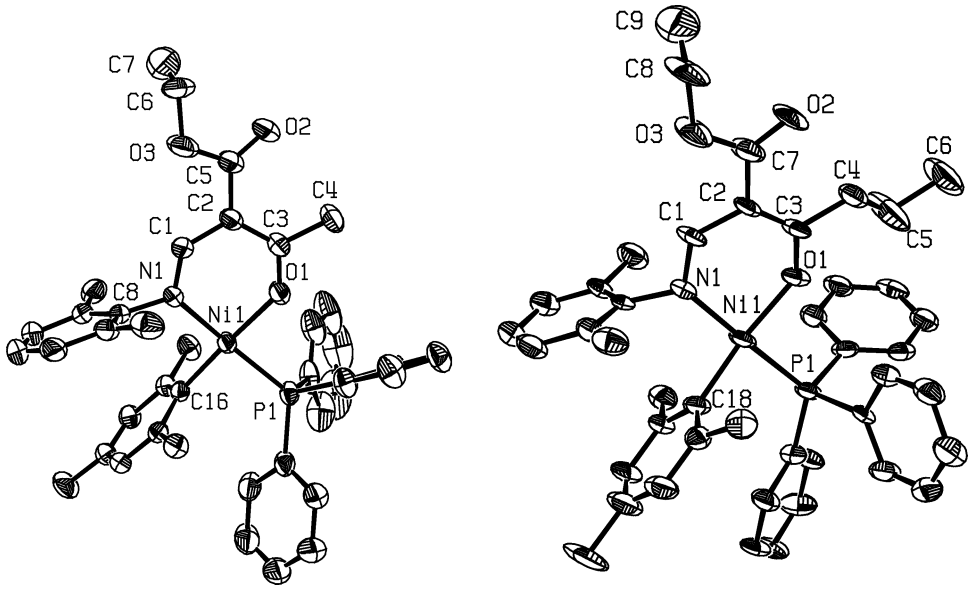

Figure 5. Molecular structures of **3g** (left), **3h** (right). For **3g**, red crystals suitable for X-ray diffractometry were obtained in pentane/hexane/toluene (10/2/1). Selected bond distances (Å) and angles (deg): C1−N1 = 1.309(2), C2−C1 = 1.420(2), C3−C2 = 1.395(3), O1−C3 = 1.271(2), C4−C3 = 1.504(2), Ni1−N1 = 1.937(2), O1−Ni1 = 1.901(1), P1−Ni1 = 2.190(1), C16−Ni1 = 1.903(2); N1−C1−C2 = 128.8(2), C1−C2−C3 = 121.4(2), C2−C3−O1 = 121.5(2), O1−C3−C4 = 114.0(2), N1−Ni1−O1 = 90.55(6), O1−Ni1−P1 = 86.41(4), P1−Ni1−C16 = 88.24(5), C16−Ni1−N1 = 95.48(6), N1−Ni1−P1 = 174.0(1), C16−Ni1−O1 = 170.3(1). For **3h**, red crystals suitable for X-ray diffractometry were obtained in pentane/toluene (7/1). Selected bond distances (Å) and angles (deg): C1−N1 = 1.327(9), C2−C1 = 1.4461(0), C3−C2 = 1.3911(1), O1−C3 = 1.270(9), C4−C3 = 1.519(10), Ni1−N1 = 1.909(6), Ni1−O1 = 1.915(5), Ni1−P1 = 2.184(3), Ni1−C18 = 1.882(7); N1−C1−C2 = 125.8(7), C1−C2−C3 = 121.5(7), C2−C3−O1 = 122.3(7), N1−Ni1−O1 = 90.4(2), O1−Ni1−P1 = 88.1(2), P1−Ni1−C18 = 89.0(2), C18−Ni1−N1 = 93.0(3), N1−Ni1−P1 = 176.6(2), C18−Ni1−O1 = 171.0(3).

ligand coordinates with its keto function, because that oxygen atom has a stronger nucleophilic character than the ester function in the same molecule.[25c]

In **3h**, the triphenylphosphine occupies the trans position of the coordinating nitrogen atom, while the mesityl group attached to Ni is bound in a position trans to the oxygen atom of the keto group (Figure 5). The Ni−O, Ni−N, Ni−C, and Ni−P distances in complex **3h** are slightly shorter compared to the nickel complex **3a**. The Ni1−N1 and Ni1−O1 bond distances are almost identical within the standard deviation range (1.909(6) and 1.915(5) Å).[18] The C1−C2 and C2−C3 distances in the metallacycle are 1.446(10) and 1.391(11) Å, respectively. The Ni1−P1 distance is 2.184(3) Å, while the

Table 1. Dimerization of Ethylene with Nickel(II) Catalysts

no.	cat.[a]	amt (μmol)	cocat.	time (h)	*T* (°C)	yield (g)[b]	TON (×10³)	TOF (×10³/h)	α[c]	*n*-olefins[b] (%)	*iso*-olefins[b] (%)
1	**1a**	10		1	25	0.08	0.29	0.29		43	57
2	**1a**	10	MAO	1	25−45	6.46	23.06	23.06	0.04	27	73
3	**1a**	10	EASC	1	25−74						
4	**1b**	10	MAO	1	25−33	0.65	2.33	2.33		71	29
5	**1c**	10	MAO	1	22−25	31.80	113.49	113.49	0.11	22	78
6	**1d**	10	MAO	0.5	23−35	1.88	6.71	13.41	0.04	27	73
7	**2a**	10	MAO	1	23						
8	**2b**	10	EASC	1	25−70						
9	**2c**	10	EASC	1	25−70						
10	**2d**	10	EASC	1	25−71						
11	**2e**	10	EASC	1	25−72						
12	**2f**	10	EASC	1	25−64						
13	**3a**	14	MAO	1	23−28						
14	**3a**	10	EASC	1	25−70						
15	**3b**	10	MAO	1	25−31						
16	**3b**	10	EASC	1	25						
17	**3c**	10	EASC	1	25−70						
18	**3d**	10	MAO	1	23−42	7.51	26.79	26.79		24	76
19	**3e**	10	MAO	1	23	4.43	15.80	15.80		58	42
20	**3f**	10		1	23−30	13.06	46.60	46.60		30	70
21	**3f**	10	MAO	1	23−70	25.95	92.59	92.59		28	72
22	**3f**	10	EASC	1	25−72						
23	**3g**	10	MAO	1	25−43	6.78	24.19	24.19	0.08	20	80
24	**3g**	10	EASC	1	25−70						
25	**3h**	10	MAO	1	25−34	14.30	50.93	50.93	0.09	24	76
26	**3h**	10	EASC	1	25−70						
27	**3i**	10	MAO	1	25−31						
28	**3i**	10	EASC	1	25−62						
29	**4**	10	MAO	1	25−47	5.8	20.53	20.53	0.11	54	46
30	**4**	10	EASC	1	27−70						

[a] All precatalysts were dissolved in 30 mL of toluene and then activated either with 100 equiv of MAO (0.6 mL of a 10 wt % MAO solution in toluene) or with 300 equiv of $Et_2AlCl{\cdot}EtAlCl_2$ (EASC) (3.3 mL of a 25 wt % solution in toluene); the ethylene pressure was 30 bar (No. 29, p = 24 bar). [b] The yield and the 1-olefin content C_4−C_{26} were determined by GC and a flame ionization detector using calibration curves with standard solutions. [c] α is the probability of the chain propagation.

Table 2. Yield (%) of Oligomers in the Experiments 1, 2, and 4−6

	expt no.				
	1	2	4	5	6
C_4	100	95.9	100	89.1	95.9
C_6		4.1		9.9	4.1
C_8				0.9	
C_{10}				0.1	

Table 3. Yield (%) of Oligomers in the Experiments 18−21, 23, 25, and 29

	expt no.						
	18	19	20	21	23	25	29
C_4	92.5	100	98.2	89.5	91.7	92.2	88.7
C_6	6.5		1.8	9.5	7.7	7.1	9.9
C_8	1.0			1.0	0.6	0.7	1.2
C_{10}	0.06			0.04			0.14
C_{12}	0.02						0.03
C_{14}	0.01						0.01
C_{16}							0.01

Ni1−C18 bond length measures 1.882(7) Å. The bite angle O1−Ni1−N1 is 90.4°. The metallacycle is planar, and the metal center shows a distorted-square-planar coordination sphere. The plane of the mesityl ring is oriented perpendicularly to the metallacycle plane, the dihedral angle being 90.0°.

The complexes **2a**−**e** and **4** were prepared in an analogous manner by reaction of the anions with $[(PPh_3)_2Ni(Mes)Br]$[27] (Schemes 6−8).

Catalytic Oligomerizations with Ethylene and Propylene. The precatalysts **1a**−**d** are effective for ethylene oligomerization when activated with MAO (Table 1, runs 2−6), mostly giving dimeric products. Without MAO the activity is very low (Table 1, run 1). Youkin et al.[15a] have shown that N,O ligand Ni complexes can be active for olefin polymerization without MAO, with bulky substituents close to the chelating O atom. The bulky surroundings seem to ease up dissociation of the PPh_3 ligand. Since our system does not have much steric bulk at this site, activation is necessary. On the other hand, activation with EASC does not take place in this case. In other experiments with alkylaluminum-based cocatalysts (Et_3Al, Bu_3Al) activation only takes place within a very small range of Al/Ni ratios.[15b] The complexes **1a**,**c** bearing the isopropyl substituents at the aryl rings are the most active among the nitrile-bound complexes **1**, thus indicating the importance of bulky substituents in the ligand. Though these bulky substituents are far away from the active metal center, their steric demand has an impact on the position of the PPh_3 groups and, thus, the active metal center is affected indirectly. The higher the activity, the lower the selectivity for the produced olefins. **1a** (Table 1, run 2) only yields C_4−C_6 with 95.9% butenes, while **1c** (Table 1, run 5) gives C_4−C_{10} with 89.1% butenes. The selectivity for α-olefins is rather poor, 25% for **1c**, but reaches 71% in the case of the less active **1b**. The choice of the cocatalyst is important. A good catalytic activity is observed in the presence of MAO, whereas the precatalyst is about 100 times less active in the absence of any cocatalyst. EASC is not a suitable cocatalyst to be used with the precatalysts **1a**−**d** in the reactions with ethylene, since all nickel complexes tested in the presence of this organoaluminum compound did not perform any oligomerization (Table 1). Complexes of type **2** showed no activity either with MAO or with EASC as cocatalyst.

Table 4. Dimerization of Propene with Nickel(II) Catalysts

no.	cat[a]	amt (μmol)	cocat.	time (h)	p (bar)	T (°C)	yield (g)[b]	TON ($\times 10^3$)	TOF ($\times 10^3$/h)
31	**1a**	10	MAO	1	8	25			
32	**1a**	10	EASC	0.8	8	26−52	12.6	30.00	36.15
33	**1b**	10	EASC	1	8	24−36	9.7	23.09	23.09
34	**1c**	10	MAO	1	8	25			
35	**1c**	10	EASC	1	8	25−50	7.8	18.56	18.56
36	**1d**	10	EASC	1	8	25−49	14.0	33.25	33.25
37	**2a**	10	EASC	1	8	27−50	5.4	12.88	12.88
38	**2a**	10	EASC	1	9.5	25−52	17.1	40.73	40.73
39	**2b**	10	EASC	1	8	26−43	15.7	37.41	37.41
40	**2f**	10	EASC	1	8	25−44	22.0	52.41	52.41
41	**3a**	10	EASC	1	8	25	11.8	28.09	28.09
42	**3b**	14	EASC	1	9.5	25−54	23.4	39.76	39.76
43	**3c**	10	EASC	1	8	26−44	19.0	45.25	45.25
44	**3e**	10	EASC	1	8	24−44	8.0	18.93	18.93
45	**3f**	10	MAO	1	8	25			
46	**3f**	10	EASC	1	8	25	11.5	27.43	27.43
47	**3g**	10	EASC	1	9.5	25−54	26.5	63.09	63.09
48	**3h**	10	EASC	1	8	26−42	7.7	18.34	18.34
49	**3i**	10	EASC	1.2	9.5	25−43	15.5	36.93	36.93
50	**4**	10	EASC	1	8	25−50	11.5	27.34	27.34

[a] All precatalysts were first dissolved in 30 mL of toluene in an ultrasonic bath and then activated either with 100 equiv of MAO (0.6 mL of a 10 wt % MAO solution in toluene) or with 300 equiv of $Et_2AlCl{\cdot}EtAlCl_2$ (3.3 mL of a 25 wt % solution in toluene). [b] The yield and the 1-olefin content C_6-C_{18} were determined by GC and a flame ionization detector using calibration curves with standard solutions.

The N,O-chelated complexes **3a**−**i** exhibit very different catalytic properties for the oligomerization of ethylene. While **3a**−**c** and **3i** are completely inactive (Table 1, runs 13−17 and 27 and 28), **3d**−**h** oligomerize ethylene with good turnover frequencies (Table 1, runs 18−26). Apparently, the presence of the noncoordinating cyano group in place of an ester group is an inhibiting factor in the catalysis.

The chelate complexes **3d**−**f** are active with MAO as cocatalyst at 30 bar (runs 18, 19, and 21). The precursor **3f** bears the most bulky groups (i.e. isopropyl) at the 2,6-positions of the aryl ring and is the most active among the N,O-chelate complexes **3** for the oligomerization reaction. The main products are butenes ranging from 89.5% for **3f** (C_4-C_{10}) to 100% for **3e** (only C_4). The precatalyst **3d** produces the brightest range of oligomers (C_4-C_{14}), although it is more selective for butenes than **3f** (92.5% vs 89.5%). Selectivity toward α-olefins varies in the range of 24−58%. The precatalyst **3f** maintains a good catalytic activity even in the absence of any cocatalyst (Table 1, run 20), its TOF being just half of the value reached in the presence of MAO (4.7×10^4 vs 9.3×10^4 h^{-1}). **3f** is fully inactive when EASC is employed (Table 1, run 22).

When activated with MAO, both complexes **3g**,**h** oligomerize ethylene to C_4-C_{14} oligomers (Table 1, runs 23 and 25), where the main fraction consists of butenes (92%). The length of the alkyl chain R^3 of **3g**,**h** influences the activity: in fact, the turnover frequency of **3h** (R^3 = *n*-propyl) is twice as much as **3g** (R^3 = methyl, 5.1×10^4 vs 2.4×10^4 h^{-1}). The selectivities are very similar to each other. ESAC does not give active catalytic species with **3g**,**h** (Table 1, runs 22 and 24).

2f and **3i** with ligands bearing one or two imidazo-[1,5-*a*]pyridines were inactive for catalytic oligomerizations with ethylene (Table 1, runs 12, 27, and 28) in the presence of both MAO and EASC as cocatalyst. The amidoiminomalonate complex **4** shows good performances in the presence of MAO as cocatalyst, yielding oligomers in the range of C_4-C_{16} with prevailing dimers (Table 1, run 29). It possesses one of the best α-selectivities with MAO (54%) of all procatalysts tested herein, although the selectivity for dimerization is not very satisfactory (88.7%).

In summary, 3-aminoacrylate, 3-aminoiminoacrylate, and amidoiminomalonate nickel(II) complexes **1**−**4** form a versatile class of successful ethylene oligomerization catalysts. The catalytic properties are strongly affected by many factors such as coordination mode of the ligand (chelate or monodentate), the steric hindrance of substituents at the aryl rings, electronic characteristics of functional groups at the backbone (ester, nitrile, or simply hydrogen), and the groups sideways to the coordinating atoms (ester, ketone, imino ester, or imidazopyridine). The best results were obtained in the presence of MAO as cocatalyst. The best activity for ethylene oligomerization was shown by the CN-coordinated 2-cyano-3-aminoacrylate nickel(II) complex **1c** (TOF 1.13×10^5 h^{-1}), followed by the chelate ester-substituted 3-aminoacrylate **3f** (TOF 9.3×10^4 h^{-1}). The most selective catalysts for generating *n*-olefins were the nonchelate 2-cyano-3-aminoiminoacrylate nickel(II) complex **1b** (71%) and the chelate ester-substituted 3-aminoacrylate **3e** (58%).

Some of the described nickel(II) complexes were also tested for the reaction with propylene. The precatalysts tested were not catalytically active when treated with MAO (Table 4, runs 31, 34, and 45). Nevertheless, they exhibited good performances when activated with EASC; the turnover frequency was ranging from 7500 to 63 000 h^{-1}. The influence of the organoaluminum activator corresponds to literature published about the dimerization of propylene by β-ketiminate nickel(II) complexes (TOF up to 1.3×10^5 h^{-1}).[15c]

All catalysts tested behaved similarly to each other and the main products mostly consisted of dimers, ranging between 85 and 95% (Tables 5−7). The tendency of the nickel(II) catalysts to dimerize propylene rather than to form higher oligomers is due to their strong propensity for β-elimination.[14,34]

Methylpentenes were the main products (Table 5), followed by hexenes. Mostly internal olefins were produced. The GC spectra of the fractions C_6 usually showed the presence of many different isomers, thus

Table 5. Distribution of Dimers (mol %)

no.	cat.	dimer[a]	1-hexene[b]	hexenes[c]	methyl-pentenes	dimethyl-butenes
32	**1a**	93.0	0.06	39.4	58.1	2.5
33	**1b**	84.8	0.06	38.0	61.6	0.4
35	**1c**	87.5	0.07	43.0	53.9	3.1
36	**1d**	87.6	0.07	38.0	59.3	2.7
37	**2a**	95.2	0.06	20.1	73.9	6.0
38	**2a**	92.5		33.2	65.0	1.8
39	**2b**	89.6	0.06	35.7	63.1	1.2
40	**2f**	91.6		32.7	66.5	0.8
41	**3a**	95.7		41.0	50.9	8.1
42	**3b**	91.5		28.9	67.9	3.2
43	**3c**	89.8		33.0	65.8	1.2
44	**3e**	86.0	0.08	39.4	60.1	0.5
46	**3f**	92.2		30.2	68.3	1.5
47	**3g**	92.0		32.9	65.5	1.6
48	**3h**	95.2		31.1	67.7	1.2
49	**3i**	91.4		32.7	66.5	0.8
50	**4**	84.7		33.6	64.5	1.9

[a] Values for higher oligomers can be found in Tables S1 and S2 in the supplement. [b] Calculated over the whole amount. [c] 1-Hexene included.

Table 6. Results of 1-Hexene Oligomerization with Nickel(II) Catalysts

no.	cat.[a]	amt (μmol)	cocat.	t (h)	T (°C)	solvent	yield (g)[c]	TON ($\times 10^3$)	TOF ($\times 10^3$/h)
51	**3i**[a]	10	EASC	1	25−29		0.7	0.84	0.84
52	**3b**[a]	10	EASC	1	24−28		1.3	1.58	1.58
53	**3b**[b]	10	EASC	1	23−28	toluene	0.3	0.32	0.32

[a] The precatalysts were first dissolved in 30 mL of 1-hexene in an ultrasonic bath and then activated with 360 equiv of EASC. [b] The precatalyst was first dissolved in 30 mL of toluene in an ultrasonic bath; then 5 mL of 1-hexene was added and the catalysis was activated with 360 equiv of EASC. [c] The yield and the olefin content of C_6−C_{24} were determined by FID-GC using calibration curves with standard solutions.

Table 7. Yield (%) of Oligomers in Experiments 51−53

	expt		
fraction	51	52	53
C_{12}	41.6	88.4	68.2
C_{18}	32.3	7.0	27.0
C_{24}	26.2	4.6	4.8

indicating that the catalysts are able to isomerize the olefin produced. When the propylene pressure was increased, catalytic activity was improved, too (Table 4, runs 37 and 38). As shown in the case of complex **2a**, the higher pressure also influences the ratio of the dimers produced: at lower pressure the catalyst is more selective for generating methylpentenes.

Even complexes not active for ethylene oligomerization provided good results with propylene. For example, complexes **2a**,**b** were not effective in oligomerizing ethylene, but they worked well with propylene and exhibited good activities (1.3×10^4 and 3.7×10^4 h^{-1}, respectively, at 8 bar of pressure). The increased steric hindrance of the isopropyl groups at the aryl substituents of the precatalyst **2b** provides a better catalytic performance compared to **2a**, which bears less bulky methyl groups. However, **2a** exhibited the highest selectivity for methylpentenes of all tested precatalysts.

Some other catalysts have a different behavior toward ethylene and propylene oligomerization. For example, the imidazo[1,5-*a*]pyridyl chelate complexes **2f** and **3i** also exhibit high activities in dimerizing propylene (5.2×10^4 and 3.7×10^4 h^{-1}, respectively). **2f** gave oligomers in the range of C_6−C_{18}, while **3i** yielded olefins up to C_{24}. Among the C_6 fraction, the main products consisted of methylpentenes (Tables 5−7).

The cyano-coordinated complexes **1a**,**b** and **1c**,**d** also mostly produced dimers in good yields (Table 4, runs 32, 33, 35, and 36) and exhibited moderately better selectivities for the generation of linear hexenes (Table 5, runs 32, 33, 35, and 36). Among this class of compounds, **1a** was the most active and most selective catalyst to produce dimers (93.0%, Table S1 in the supplement): this trend is inverted to that of the ethylene oligomerization—there, **1c** was the most active and selective precatalyst.

The precatalysts **3a**−**c** did not work for ethylene oligomerization, but they reacted with propylene when activated with EASC (Table 4, runs 41−43). The most selective precatalyst to generate dimers was **3a**, producing only olefins in the range of C_6−C_{12}. Hence, also in this case the catalytic activity was influenced by the steric hindrance of the substituents at the aryl groups. The behaviors of the chelate complexes **3a**−**c** and the nonchelate complexes **1a**−**d** were very similar in the propylene dimerization with regard to both the activity and selectivity (Tables 4−7). With **4**, a lower tendency to generate dimers was observed (84.7%, Table S2 in the Supporting Information), but the distribution of the formed dimers did not change significantly in comparison with the other precatalysts tested (Table 5).

At 8 bar of ethylene pressure, the most active nickel catalyst was the imidazopyridyl complex **2f** (5.2×10^4 h^{-1}, Table 4), while the best selectivity to generate dimers was observed with the 3-aminoacrylate complex **3a** (95.7%, Table S1). **1c** exhibited the highest selectivity for the formation of linear hexenes (43.0%, Table 5), while **2a** and **3f** were the most selective for the formation of methylpentenes (74 and 68%, respectively).

Additionally, a few tests with 1-hexene were performed to verify if some complexes are active for the oligomerization of higher α-olefins (Table 6). **3b**,**i** were tested in the presence of EASC and gave oligomers consisting of C_{12}, C_{18}, and C_{24} with rather low yields. The main products were dimers, and the oligomer distribution depended on the ligands used (runs 51 and 52) and on the reaction conditions (runs 52 and 53): more dimers were obtained when the reaction was performed only in 1-hexene and fewer dimers in a diluted solution of 1-hexene in toluene.

When the oligomerization was performed in bulk, the complexes **3b**,**i** also worked as isomerization catalysts for 1-hexene and gave a mixture of internal olefins. Less than 10% of the 1-hexene was oligomerized under these test conditions, while most of it underwent isomerization.

3. Conclusions

Novel 3-aminoiminoacrylate, 3-aminoacrylate, and amidoiminomalonate ligands have been synthesized and coordinated with nickel(II) ions to give active precatalysts **1**−**4** suitable for dimerization reactions with small

(34) (a) Johnson, L. K.; Killian, C. M.; Brookhart M. *J. Am. Chem. Soc.* **1995**, *117*, 6414−6415. (b) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267−268. (c) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 11664−11665. (d) Tempel, D.; Brookhart, M. *Organometallics* **1998**, *17*(11), 2290−2296.

olefins: e.g., ethylene, propylene, and 1-hexene. The ligands **IVa**,**b** and **Vd**,**e** did not act as chelating units but instead coordinated to the nickel(II) ion through the cyano group to give **1a**−**d**. If the cyano group was replaced by less suitable coordinating groups such as esters, only bidentate chelate complexes **2a**−**e** and **3d**−**h** were obtained.

Catalytic properties of the precatalysts **1**−**4** for the dimerization and oligomerization of ethylene and propylene depend on the coordination mode and the substituted backbone of the ligand, the steric hindrance of the substituents at the aryl rings, and the nickel(II)-coordinated functional groups. For the dimerization of ethylene, the best results were obtained with MAO as cocatalyst. The highest activity in the reaction with ethylene provided **1c** and **3f**, whereby **1b** acted as the most selective precatalyst. Some nickel(II) complexes did not work for ethylene oligomerization, but they reacted with propylene when activated with EASC (e.g. **2a**,**b**,**f,** **3a**−**c**,**i**). **2f** and **3g** were the most active precatalysts with EASC and propylene, while the best selectivity to generate dimers was observed with **3a**. **1c** showed the highest selectivity for the formation of linear hexenes, while **2a** and **3f** are most selective for the formation of methylpentenes. **3b**,**i** were also active for the oligomerization of 1-hexene with EASC as cocatalyst. The main products were isomerized internal dodecenes.

4. Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of argon using standard Schlenk techniques. NMR spectra were recorded on Bruker 250 MHz (^{1}H) and 62.9 MHz (^{13}C) spectrometers at 293 K. Mass spectra were obtained using electron ionization (EI), electron spray ionization (ESI), or field ionization (FI). FI and EI spectra were recorded with Micromass GCT and Finnigan MAT GCQ spectrometers, ESI spectra were recorded with a Hewlett-Packard 1100 MSD spectrometer. Melting points were either determined by using capillaries and a Büchi apparatus or with differential scanning calorimetry (DSC) with a Mettler Toledo DSC822e instrument. IR spectra were recorded with a Perkin-Elmer System 2000 FT-IR. Oligomer products were analyzed by GC with a flame ionization detector, using a 50 m DB1 column, injector temperature 40 °C, and the following temperature program: 40 °C/5 min, 40−300 °C, 5 °C/10 min^{-1}. The individual products were integrated, using *n*-tridecane as internal standard.

Materials. MAO (10% solution in toluene), EASC (25% solution in toluene), and all other anilines were purchased commercially and used as received.

3. Synthesis of Nickel(II) Complexes 1−4. General Procedure. The corresponding ligand was dissolved in absolute toluene. Then a 0.6 M solution of sodium bis(trimethylsilyl)amide in toluene was added. The resulting solution was added dropwise to a solution of $[(PPh_3)_2Ni(Mes)Br]$[27] in absolute toluene. If not otherwise noted, the mixture was stirred under argon at room temperature for 16−24 h, and then it was filtered on Celite under argon and the filtrate was concentrated under vacuum to 1−5 mL. After that, 15−50 mL of an absolute pentane/hexane mixture was added and the precipitate was filtered, dried under vacuum, and finally stored under argon.

[Ethyl 2-cyano-3-[(2,6-diisopropylphenyl)amino]-*N*-(2,6-diisopropylphenyl)prop-2-enimidoatemesityl]bis(triphenylphosphino)nickel(II) (1a) was obtained from ethyl 2-cyano-3-[(2,6-diisopropylphenyl)-amino]-*N*-(2,6-diisopropylphenyl)prop-2-enimidoate (**IVa**; 0.38 g, 0.8 mmol) in 20 mL of absolute toluene, sodium bis(trimethylsilyl)amide solution in toluene (1.23 g, 0.8 mmol), $[(PPh_3)_2Ni(Mes)Br]$[27] (0.66 g, 0.8 mmol) in 35 mL of absolute toluene. Yield: 0.27 g (0.2 mmol, 27%). ^{1}H NMR (DMSO-d_6): δ 7.49−7.17 (m, 37H, H_{Phenyl} + NC*H*), 6.08 (s, 2H, H_{Mes}), 3.32 (s, 24H, CH_3), 2.86 (bs, 4H, C*H*), 2.72 (bs, 2H, CH_2), 2.29 (bs, 6H, CH_3), 2.02 (bs, 3H, CH_3), 1.23 (bs, 3H, CH_3). IR (KBr): ν 3436 cm^{-1} (C═N), 3054 (C−H, *aryl*), 2961, 2911 (C−H, CH_3), 2198 (C≡N, w), 1618 (C═C), 1456 (C═C), 1434 (P−Ph, PPh_3), 1363 (C−H, $C(CH_3)_2$), 1262 (C−O−C), 1093 (C−O), 1028 (C−O−C), 846 (C−H, *mesityl*), 803 (C−H, *aryl*), 693 (C−H, *phenyl*). ESI$^+$-MS: *m/z* 1161 (M$^+$). Anal. Calcd for $C_{75}H_{81}N_3NiOP_2$: C, 77.58; H, 7.03; N, 3.62. Found: C, 77.43; H, 6.91; N, 3.32.

[Ethyl 2-Cyano-3-[(2,6-dimethylphenyl)amino]-*N*-(2,6-diisopropylphenyl)prop-2-enimidoatetoluyl]bis(triphenylphosphino)nickel(II) (1b) was obtained from ethyl 2-cyano-3-[(2,6-dimethylphenyl)amino]-*N*-(2,6-diisopropylphenyl)prop-2-enimidoate (**IVb**; 0.13 g, 0.3 mmol) in 10 mL of absolute toluene, sodium bis(trimethylsilyl)amide solution in toluene (0.50 g, 0.3 mmol), and $[(PPh_3)_2Ni(Mes)Br]$[27] (0.26 g, 0.3 mmol) in 10 mL of absolute toluene. Yield: 0.14 g (0.1 mmol, 38%). ^{1}H NMR ($CDCl_3$): δ 7.56−7.07 (m, 37H, H_{Phenyl} + NC*H*), 6.10 (s, 2H, H_{Mes}), 4.34 (q, 2H, CH_2), 3.10 (s, 6H, CH_3), 2.94 (m$_7$, 2H, C*H*), 2.16 (s, 6H, CH_3), 1.98 (s, 3H, CH_3), 1.38 (t, 3H, CH_3), 1.20 (d, 6H, CH_3), 1.17 (d, 6H, CH_3). IR (KBr): ν 3448 cm^{-1} (C═N), 3058 (C−H, *aryl*), 2964 (C−H, CH_3), 2204 (C≡N, w), 1647 (C═C), 1621 (C═C), 1589 (C═C, *phenyl*), 1478 (C═C), 1435 (P−Ph, PPh_3), 1370 (C−H, $C(CH_3)_2$), 1273 (C−O−C), 1095 (C−O), 1027 (C−O−C), 847 (C−H, *mesityl*), 796 (C−H, *aryl*), 773 (C═C−H), 693 (C−H, *phenyl*). ESI$^+$-MS: *m/z* 1105 (M$^+$).

[Ethyl 2-cyano-3-[(2,6-diisopropylphenyl)amino]acrylatemesityl]bis(triphenylphosphino)nickel(II) (1c) was obtained from ethyl 2-cyano-3-[(2,6-diisopropylphenyl)amino]-acrylate (**Vd**; 0.21 g, 0.7 mmol) in 15 mL of absolute toluene, sodium bis(trimethylsilyl)amide solution in toluene (1.06 g, 0.7 mmol), and $[(PPh_3)_2Ni(Mes)Br]$[27] (0.55 g, 0.7 mmol) in 30 mL of absolute toluene. Yield: 0.17 g (0.2 mmol, 24%). ^{1}H NMR (DMSO-d_6): δ 7.47−7.14 (m, 34H, H_{Aryl} + NC*H*), 6.19 (s, 2H, H_{Mes}), 3.32 (s, 12H, CH_3), 2.86 (bs, 4H, C*H*), 2.77 (bs, 2H, CH_2), 2.28 (bs, 6H, CH_3), 2.02 (bs, 3H, CH_3), 0.62 (t, 3H, CH_3). IR (KBr): ν 3434 cm^{-1} (C═N), 3055 (C−H, *aryl*), 2962 (C−H, CH_3), 2207 (C≡N, w), 1615 (C═C), 1480 (C═C), 1435 (P−Ph, PPh_3), 1370 (C−H, $C(CH_3)_2$), 1262 (C−O−C), 1094 (C−O), 1027 (C−O−C), 844 (C−H, *mesityl*), 694 (C−H, *phenyl*). ESI$^+$-MS: *m/z* = 1001 (M$^+$). Anal. Calcd for $C_{63}H_{64}N_2NiO_2P_2$: C, 75.53; H, 6.44; N, 2.80. Found: C, 75.20; H, 6.10; N, 2.47.

[Ethyl 2-cyano-3-[(4-methylphenyl)amino]acrylatemesityl]bis(triphenylphosphino)nickel(II) (1d) was obtained from ethyl 2-cyano-3-[(4-methylphenyl)amino]acrylate (**Ve**; 0.29 g, 1.3 mmol) in 20 mL of absolute toluene and sodium bis(trimethylsilyl)amide solution in toluene (1.86 g, 1.3 mmol), with $[(PPh_3)_2Ni(Mes)Br]$[27] (1.00 g, 1.3 mmol) in 50 mL of absolute toluene being added dropwise to the solution. Yield: 0.69 g (0.7 mmol, 58%). ^{1}H NMR ($CDCl_3$): δ 7.60 (bs, 1H, NC*H*), 7.52−7.16 (m, 30H, H_{Phenyl}), 6.54 (d, 2H, H_{Aryl}), 6.43 (d, 2H, H_{Aryl}), 5.75 (s, 2H, $H_{Mesityl}$), 2.82 (q, 2H, CH_2), 2.64 (q, 2H, CH_2), 2.06 (s, 3H, CH_3), 1.84 (s, 3H, CH_3), 0.75 (t, 3H, CH_3). IR (KBr): ν 3463 cm^{-1} (C═N), 3042 (C−H, *aryl*), 2963 (C−H, CH_3), 2200 (C≡N, w), 1671 (C═C), 1629 (C═C), 1479 (C═C), 1434 (P−Ph, PPh_3), 1379 (C−H, CH_3), 1261 (C−O−C), 1094 (C−O), 1027 (C−O−C), 843 (C−H, *mesityl*), 817 (C−H, *aryl*), 694 (C−H, *phenyl*). ESI$^+$-MS: *m/z* 932 (M$^+$). $C_{54}H_{54}N_2NiO_2P_2$: C, 73.40; H, 6.16; N, 3.17. Found: C, 73.13; H, 6.04; N, 3.54.

[Ethyl 2-{ethoxy[(2,6-dimethylphenyl)imino]-methyl}-3-[(2,6-dimethylphenyl)amino]acrylatemesityl](triphenylphosphino)nickel(II) (2a) was obtained from ethyl 2-{ethoxy[(2,6-dimethylphenyl)imino]methyl}-3-[(2,6-dimethylphenyl)amino]acrylate (**Xa**; 0.29 g, 0.7 mmol) in 15 mL of absolute toluene, sodium bis(trimethylsilyl)amide solution in toluene (1.15 g, 0.8 mmol), and $[(PPh_3)_2Ni(Mes)Br]$[27] (0.58 g,

0.7 mmol) in 15 mL of absolute toluene. Yield: 0.33 g (0.4 mmol, 53%). ^{1}H NMR ($CDCl_3$): δ 7.32−7.06 (m, 15H, H_{Phenyl}), 6.94 (t, 1H, H_{Aryl}), 6.67 (d, 2H, H_{Aryl}), 6.63 (bs, 1H, NC*H*), 5.79 (s, 2H, $H_{Mesityl}$), 4.28 (q, 2H, CH_2), 2.61 (q, 2H, CH_2), 2.45 (s, 6H, CH_3), 2.23 (s, 6H, CH_3), 2.08 (s, 6H, CH_3), 1.92 (s, 3H, CH_3), 1.31 (t, 3H, CH_3), 0.53 (t, 3H, CH_3). IR (KBr): ν 3449 cm^{-1} (C═N), 3058 (C−H, *aryl*), 2968, 2923 (C−H, *CH$_3$*), 1642 (C═O), 1610 (C═C), 1465 (C−H, *CH$_3$*), 1435 (P−Ph, *PPh$_3$*), 1379 (C−H, *CH$_3$*), 1238 (C−O−C), 1086 (C−O), 1037 (C−O−C), 844 (C−H, *mesityl*), 804 (C−H, *aryl*), 693 (C−H, *phenyl*). ESI$^+$-MS: *m/z* = 834 (M$^+$). Anal. Calcd for $C_{51}H_{55}N_2NiO_3P$: C, 73.48; H, 6.65; N, 3.36. Found: C, 73.12; H, 6.38; N, 3.10.

[Ethyl 2-{ethoxy[(2,6-diisopropylphenyl)imino]methyl}-3-[(2,6-diisopropylphenyl)amino]acrylate-mesityl](triphenylphosphino)nickel(II) (2b) was obtained from ethyl 2-{ethoxy[(2,6-diisopropylphenyl)imino]methyl}-3-[(2,6-diisopropylphenyl)amino]acryl-ate (**Xb**; 0.23 g, 0.4 mmol) in 20 mL of absolute toluene, sodium bis(trimethylsilyl)amide solution in toluene (0.68 g, 0.5 mmol), and [$(PPh_3)_2$Ni(Mes)Br][27] (0.35 g, 0.4 mmol) in 10 mL of absolute toluene. Yield: 0.12 g (0.1 mmol, 28%). ^{1}H NMR (DMSO-d_6): δ 7.62 (s, 1H, NC*H*), 7.63−7.16 (m, 21H, H_{Aryl}), 6.08 (s, 2H, H_{Mes}), 3.32 (s, 24H, CH_3), 2.97 (bs, 4H, C*H*), 2.88 (bs, 2H, CH_2), 2.72 (bs, 2H, CH_2), 2.28 (bs, 6H, CH_3), 1.93 (bs, 3H, CH_3), 1.22 (bs, 3H, CH_3), 1.08 (bs, 3H, CH_3). ESI$^+$-MS: *m/z* 946 (M$^+$). Anal. Calcd for $C_{59}H_{71}N_2NiO_3P$: C, 74.92; H, 7.57; N, 2.96. Found: C, 74.72; H, 7.53; N, 2.91.

[Ethyl 3-[(2,6-diethylphenyl)amino]-2-{ethoxy[(4-methylphenyl)imino]methyl}acrylatemesityl](triphenylphosphino)nickel(II) (2c) was obtained from ethyl 3-[(2,6-diethylphenyl)amino]-2-{ethoxy[(4-methylphenyl)imino]-methyl}acrylate (**Xc**; 0.10 g, 0.3 mmol) in 20 mL of absolute toluene, sodium bis(trimethylsilyl)amide solution in toluene (0.37 g, 0.3 mmol), and [$(PPh_3)_2$Ni(Mes)Br][27] (0.20 g, 0.3 mmol) in 5 mL of absolute toluene. Yield: 0.20 g (0.2 mmol, 91%). ^{1}H NMR ($CDCl_3$) δ 7.32−6.54 (m, 23H, $H_{Phenyl+Aryl}$ + NC*H*), 5.73 (s, 2H, $H_{Mesityl}$), 3.98 (q, 2H, CH_2), 2.61 (q, 2H, CH_2), 2.43 (q, 4H, CH_2), 2.41 (s, 6H, CH_3), 2.29 (s, 3H, CH_3), 1.83 (s, 3H, CH_3), 1.06 (t, 3H, CH_3), 0.89 (t, 3H, CH_3), 0.67 (t, 3H, CH_3). IR (KBr): ν 3459 cm^{-1} (C═N), 3054 (C−H, *aryl*), 2964 (C−H, *CH$_2$, CH$_3$*), 1646 (C═O), 1479 (C−H, *CH$_2$, CH$_3$*), 1435 (P−Ph, *PPh$_3$*), 1094 (C−O), 1029 (C−O−C), 847 (C−H, *mesityl*), 804 (C−H, *aryl*), 692 (C−H, *phenyl*). ESI$^+$-MS: *m/z* 847 (M$^+$).

[Ethyl 2-{ethoxy[(2,6-dimethylphenyl)imino]-methyl}-3-[(4-methylphenyl)amino]acrylatemesityl](triphenylphosphino)nickel(II) (2d) was obtained from ethyl 2-{ethoxy[(2,6-dimethylphenyl)imino]methyl}-3-[(4-methylphenyl)amino]acrylate (**Xd**; 0.14 g, 0.4 mmol) in 20 mL of absolute toluene, sodium bis(trimethylsilyl)amide solution in toluene (0.54 g, 0.4 mmol), and [$(PPh_3)_2$Ni(Mes)Br][27] (0.29 g, 0.4 mmol) in 20 mL of absolute toluene. Yield: 0.07 g (0.1 mmol, 23%). ^{1}H NMR ($CDCl_3$): δ 7.29−6.91 (m, 15H, H_{Phenyl}), 6.70−6.49 (m, 8H, H_{Aryl} + NC*H*), 5.79 (s, 2H, $H_{Mesityl}$), 4.30 (q, 2H, CH_2), 2.63 (q, 2H, CH_2), 2.45 (s, 6H, CH_3), 2.33 (s, 3H, CH_3), 2.18 (s, 6H, CH_3), 1.90 (s, 3H, CH_3), 1.33 (t, 3H, CH_3), 0.54 (t, 3H, CH_3). IR (KBr): ν 3456 cm^{-1} (C═N), 3054 (C−H, *aryl*), 2964 (C−H, *CH$_3$*), 1636 (C═O), 1480 (C−H, *CH$_3$*), 1435 (P−Ph, *PPh$_3$*), 1095 (C−O), 1029 (C−O−C), 847 (C−H, *mesityl*), 804 (C−H, *aryl*), 744 (C−H, *aryl*), 693 (C−H, *phenyl*). ESI$^+$-MS: *m/z* 819 (M$^+$).

[Ethyl 2-[[(2,6-diisopropylphenyl)imino](ethoxy)methyl]-3-[(2,6-dimethylphenyl)amino]acrylatemesityl](triphenylphosphino)nickel(II) (2e) was obtained from ethyl 2-[[(2,6-diisopropylphenyl)imino]-(ethoxy)methyl]-3-[(2,6-dimethylphenyl)amino]acryl-ate (**Xe**; 0.09 g, 0.2 mmol) in 20 mL of absolute toluene, sodium bis(trimethylsilyl)amide solution in toluene (0.34 g, 0.2 mmol), and [$(PPh_3)_2$Ni(Mes)Br][27] (0.15 g, 0.2 mmol) in 20 mL of absolute toluene. The mixture was stirred under argon at room temperature for 2 days. Yield: 0.07 g (0.1 mmol, 41%). ^{1}H NMR ($CDCl_3$): δ 7.03−6.55 (m, 22H, $H_{Phenyl+Aryl}$ + NC*H*), 5.80 (s, 2H, $H_{Mesityl}$), 4.22 (q, 2H, CH_2), 3.55 (m$_7$, 2H, C*H*), 2.71 (q, 2H, CH_2), 2.46 (s, 6H, CH_3), 1.91 (s, 6H, CH_3), 1.84 (s, 3H, CH_3), 1.14 (t, 3H, CH_3), 0.86 (s, 6H, CH_3), 0.82 (s, 6H, CH_3), 0.79 (t, 3H, CH_3). IR (KBr): ν 3455 cm^{-1} (C═N), 3054 (C−H, *aryl*), 2963 (C−H, *CH$_3$*), 1635 (C═O), 1481 (C−H, *CH$_3$*), 1435 (P−Ph, *PPh$_3$*), 1095 (C−O), 1029 (C−O−C), 847 (C−H, *mesityl*), 805 (C−H, *aryl*), 693 (C−H, *phenyl*). ESI$^+$-MS: *m/z* 889 (M$^+$).

[1-Methyl-3-[(1-methylimidazo[1,5-a]pyridin-3-yl)methyl]imidazo[1,5-a]pyridylmesityl](triphen-ylphosphino)-nickel(II) (2f) was obtained from 1-methyl-3-[(1-methylimidazo-[1,5-*a*]pyridin-3-yl)methyl]imidazo[1,5-*a*]pyridine (**Xf**; 0.08 g, 0.3 mmol) in 25 mL of absolute toluene, sodium bis(trimethylsilyl)amide solution in toluene (0.51 g, 0.4 mmol), and [$(PPh_3)_2$Ni(Mes)Br][27] (0.24 g, 0.3 mmol) in 15 mL of absolute toluene. Yield: 0.10 g (1 mmol, 45%). ^{1}H NMR ($CDCl_3$): δ 8.06 (bs, 2H, H_{Aryl}), 7.68 (bs, 2H, H_{Aryl}), 7.56−7.10 (m, 15H, H_{Phenyl}), 6.53 (bs, 2H, H_{Aryl}), 6.43 (bs, 2H, H_{Aryl}), 4.79 (s, 2H, $H_{Mesityl}$), 3.11 (bs, 1H, C*H*), 2.50 (s, 6H, CH_3), 1.69 (s, 6H, CH_3), 1.27 (s, 3H, CH_3). IR (KBr): ν 3455 cm^{-1} (C═N), 2963, 2917 (C−H, *CH$_3$*), 1631 (C═C), 1435 (P−Ph, *PPh$_3$*), 1102 (C−N), 847 (C−H, *mesityl*), 738 (C−H, *heterocycle*), 707 (C−H, *heterocycle*). ESI$^+$-MS: *m/z* 715 (M$^+$). Anal. Calcd for $C_{44}H_{41}N_4NiP$: C, 73.86; H, 5.78; N, 7.83. Found: C, 73.53; H, 5.49; N, 8.18.

[Ethyl 2-cyano-3-[(4-methoxyphenyl)amino]acrylatemesityl](triphenylphosphino)nickel(II) (3a) was obtained from ethyl 2-cyano-3-[(4-methoxyphenyl)amino]acrylate (**Va**; 0.17 g, 0.7 mmol) in 15 mL of absolute toluene, sodium bis-(trimethylsilyl)amide solution in toluene (1.00 g, 0.7 mmol), and [$(PPh_3)_2$Ni(Mes)Br][27] (0.52 g, 0.7 mmol) in 20 mL of absolute toluene. Yield: 0.32 g (0.5 mmol, 71%). ^{1}H NMR ($CDCl_3$): δ 7.61 (d, 1H, NC*H*), 7.40−7.20 (m, 15H, H_{Aryl}), 6.44 (d, 2H, H_{Aryl}), 6.28 (d, 2H, H_{Aryl}), 5.78 (d, 2H, H_{Mes}), 3.59 (s, 3H, CH_3), 2.83 (q, 2H, CH_2), 2.63 (s, 6H, CH_3), 1.86 (s, 3H, CH_3), 0.75 (t, 3H, CH_3). IR (KBr): ν 3465 cm^{-1} (C═N), 3055 (C−H, *aryl*), 2960, 2911 (C−H, *CH$_3$*), 2832 (C−H, *OCH$_3$*), 2198 (C≡N, s), 1664, 1618 (C═C), 1479 (C═C, *phenyl*), 1429 (P−Ph, *PPh$_3$*), 1372 (C−H, *CH$_3$*), 1095 (C−O), 1029 (C−O−C), 843 (C−H, *mesityl*), 832 (C−H, *aryl*), 749 (C−H, *phenyl*), 696 (C−H, *phenyl*). ESI$^+$-MS: *m/z* 685 (M$^+$). Anal. Calcd for $C_{40}H_{39}N_2NiO_3P$: C, 70.09; H, 5.74; N, 4.09. Found: C, 69.89; H, 5.79; N, 4.12.

[Ethyl 2-cyano-3-[(2,6-dimethylphenyl)amino]acrylatemesityl](triphenylphosphino)nickel(II) (3b) was obtained from ethyl 2-cyano-3-[(2,6-dimethylphenyl)amino]-acrylate (**Vb**; 0.17 g, 0.7 mmol) in 15 mL of absolute toluene, sodium bis(trimethylsilyl)amide solution in toluene (1.10 g, 0.8 mmol), and [$(PPh_3)_2$Ni(Mes)Br][27] (0.55 g, 0.7 mmol) in 30 mL of absolute toluene. Yield: 0.23 g (0.3 mmol, 48%). ^{1}H NMR (DMSO-d_6): δ 7.50−7.15 (m, 16H, H_{Phenyl} + NC*H*), 6.73−6.62 (m, 3H, H_{Aryl}), 5.77 (s, 2H, H_{Mes}), 3.32 (s, 6H, CH_3), 3.01 (q, 2H, CH_2), 2.09 (s, 6H, CH_3), 1.87 (s, 3H, CH_3), 0.67 (t, 3H, CH_3). IR (KBr): ν 3456 cm^{-1} (C═N), 3057 (C−H, *aryl*), 2962, 2914 (C−H, *CH$_3$*), 2205 (C≡N, s), 1703 (C═O), 1615 (C═C), 1435 (P−Ph, *PPh$_3$*), 1371 (C−H, *CH$_3$*), 1267 (C−O−C), 1094 (C−O), 1019 (C−O−C), 844 (C−H, *mesityl*), 747 (C−H, *phenyl*), 695 (C−H, *phenyl*). ESI$^+$-MS: *m/z* 684 (M$^+$). Anal. Calcd for $C_{41}H_{41}N_2NiO_2P$: C, 72.05; H, 6.05; N, 4.10. Found: C, 71.84; H, 5.91; N, 3.94.

[Ethyl 2-cyano-3-[(2,6-diethylphenyl)amino]acrylatemesityl](triphenylphosphino)nickel(II) (3c) was obtained from ethyl 2-cyano-3-[(2,6-diethylphenyl)amino]acrylate (**Vc**; 0.20 g, 0.7 mmol) in 20 mL of absolute toluene, sodium bis-(trimethylsilyl)amide solution in toluene (1.08 g, 0.7 mmol), and [$(PPh_3)_2$Ni(Mes)Br][27] (0.56 g, 0.7 mmol) in 15 mL of absolute toluene. Yield: 0.30 g (0.4 mmol, 58%). ^{1}H NMR ($CDCl_3$): δ 7.41−7.16 (m, 16H, H_{Phenyl} + NC*H*), 6.82 (t, 1H, H_{Aryl}), 6.66 (d, 2H, H_{Aryl}), 5.78 (s, 2H, $H_{Mesityl}$), 2.99 (q, 2H, CH_2), 2.57 (q, 2H, CH_2), 2.50 (s, 6H, CH_3), 1.89 (s, 3H, CH_3), 1.03 (t, 3H, CH_3), 0.79 (t, 3H, CH_3). IR (KBr): ν 3461 cm^{-1} (C═N), 3064 (C−H, *aryl*), 2960, 2933 (C−H, *CH$_3$, CH$_3$*), 2206 (C≡N, s), 1614 (C═C), 1498 (C═C), 1431 (P−Ph, *PPh$_3$*), 1367 (C−H,

CH$_3$), 1273 (C−O−C), 1094 (C−O), 1019 (C−O−C), 845 (C−H, *mesityl*), 745 (C−H, *phenyl*), 694 (C−H, *phenyl*). ESI$^+$-MS: *m/z* 711 (M$^+$). Anal. Calcd for $C_{43}H_{45}N_2NiO_2P$: C, 72.59; H, 6.37; N, 3.94. Found: C, 72.24; H, 6.13; N, 3.63.

[Diethyl {[(4-methylphenyl)amino]methylene}malonatemesityl](triphenylphosphino)nickel(II) (3d) was obtained from diethyl {[(4-methylphenyl)amino]methylene}-malonate (**VIa**; 0.08 g, 0.3 mmol) in 25 mL of absolute toluene, sodium bis(trimethylsilyl)amide solution in toluene (0.47 g, 0.3 mmol), and [(PPh$_3$)$_2$Ni(Mes)Br][27] (0.22 g, 0.3 mmol) in 10 mL of absolute toluene. The mixture was stirred under argon at room temperature for 48 h. Yield: 0.10 g (0.1 mmol, 48%). ^{1}H NMR (CDCl$_3$): *δ* 8.23 (d, 1H, NC*H*), 7.32−7.07 (m, 15H, *H*$_{Phenyl}$), 6.97 (d, 2H, *H*$_{Aryl}$), 6.83 (d, 2H, *H*$_{Aryl}$), 5.78 (s, 2H, *H*$_{Mesityl}$), 4.11 (q, 2H, C*H*$_2$), 3.09 (q, 2H, C*H*$_2$), 2.93 (s, 6H, C*H*$_3$), 2.46 (s, 6H, C*H*$_3$), 1.83 (s, 3H, C*H*$_3$), 1.16 (t, 3H, C*H*$_3$), 0.72 (t, 3H, C*H*$_3$). ESI$^+$-MS: *m/z* 717 (M$^+$). Anal. Calcd for $C_{42}H_{44}NNiO_4P$: C, 70.41; H, 6.19; N, 1.95. Found: C, 70.19; H, 5.99; N, 1.73.

[Diethyl {[(2,6-diethylphenyl)amino]methylene}malonatemesityl](triphenylphosphino)nickel(II) (3e) was obtained from diethyl {[(2,6-diethylphenyl)amino]methylene}-malonate (**VIb**; 0.14 g, 0.4 mmol) in 10 mL of absolute toluene, sodium bis(trimethylsilyl)amide solution in toluene (0.66 g, 0.4 mmol), and [(PPh$_3$)$_2$Ni(Mes)Br][27] (0.35 g, 0.4 mmol) in 10 mL of absolute toluene. Yield: 0.14 g (0.2 mmol, 40%). ^{1}H NMR (CDCl$_3$): *δ* 7.92 (d, 1H, NC*H*), 7.42−7.10 (m, 15H, *H*$_{Phenyl}$), 6.75 (t, 1H, *H*$_{Aryl}$), 6.61 (d, 2H, *H*$_{Aryl}$), 5.72 (s, 2H, *H*$_{Mesityl}$), 4.03 (q, 2H, C*H*$_2$), 2.91 (q, 2H, C*H*$_2$), 2.78 (q, 2H, C*H*$_2$), 2.50 (q, 2H, C*H*$_2$), 2.41 (s, 6H, C*H*$_3$), 1.82 (s, 6H, C*H*$_3$), 1.10 (t, 3H, C*H*$_3$), 0.96 (t, 3H, C*H*$_3$), 0.75 (t, 3H, C*H*$_3$). IR (KBr): *ν* 3443 cm^{-1} (C═N), 3056 (C−H, *aryl*), 2965, 2933 (C−H, *CH*$_2$, *CH*$_3$), 1698 (C═O), 1600 (C═C), 1462 (C−H, *CH*$_2$, *CH*$_3$), 1435 (P−Ph, *PPh*$_3$), 1381 (C−H, *CH*$_3$), 1241 (C−O−C), 1071 (C−O), 1027 (C−O−C), 845 (C−H, *mesityl*), 789 (C−H, *aryl*), 747 (C−H, *phenyl*), 722 (C−H, *CH*$_2$), 695 (C−H, *phenyl*). ESI$^+$-MS: *m/z* 758 (M$^+$). Anal. Calcd for $C_{45}H_{50}NNiO_4P$: C, 71.25; H, 6.64; N, 1.85. Found: C, 70.89; H, 6.51; N, 1.77.

[Diethyl {[(2,6-diisopropylphenyl)amino]methylene}-malonatemesityl](triphenylphosphino)nickel(II) (3f) was obtained from diethyl {[(2,6-diisopropylphenyl)amino]methylene}malonate (**VIc**; 0.22 g, 0.6 mmol) in 10 mL of absolute toluene, sodium bis(trimethylsilyl)amide solution in toluene (1.00 g, 0.7 mmol), and [(PPh$_3$)$_2$Ni(Mes)Br][27] (0.48 g, 0.6 mmol) in 10 mL of absolute toluene. Yield: 0.16 g (0.2 mmol, 34%). ^{1}H NMR (CDCl$_3$): *δ* 7.86 (d, 1H, NC*H*), 7.33−7.09 (m, 15H, *H*$_{Phenyl}$), 6.93 (t, 1H, *H*$_{Aryl}$), 6.81 (d, 2H, *H*$_{Aryl}$), 5.80 (s, 2H, *H*$_{Mesityl}$), 4.03 (q, 2H, C*H*$_2$), 3.61 (m$_7$, 2H, C*H*), 3.05 (q, 2H, C*H*$_2$), 2.46 (s, 6H, C*H*$_3$), 1.84 (s, 3H, C*H*$_3$), 1.09 (t, 3H, C*H*$_3$), 0.91 (d, 6H, C*H*$_3$), 0.89 (d, 6H, C*H*$_3$), 0.67 (t, 3H, C*H*$_3$). IR (KBr): *ν* 3468 cm^{-1} (C═N), 3057 (C−H, *aryl*), 2962 (C−H, *CH*$_3$), 1697 (C═O), 1599 (C═C), 1461 (C−H, *CH*$_3$), 1436 (P−Ph, *PPh*$_3$), 1381 (C−H, *C(CH*$_3$*)*$_2$), 1260 (C−O−C), 1070 (C−O), 1029 (C−O−C), 846 (C−H, *mesityl*), 802 (C−H, *aryl*), 744 (C−H, *phenyl*), 693 (C−H, *phenyl*). ESI$^+$-MS: *m/z* 787 (M$^+$). Anal. Calcd for $C_{47}H_{54}NNiO_4P$: C, 71.77; H, 6.92; N, 1.78. Found: C, 71.61; H, 6.43; N, 1.63.

[Ethyl 2-acetyl-3-[(2,6-dimethylphenyl)amino]acrylatemesityl](triphenylphosphino)nickel(II) (3g) was obtained from ethyl 2-acetyl-3-[(2,6-dimethylphen-yl)amino]-acrylate (**VIIIa**; 0.17 g, 0.6 mmol) in 10 mL of absolute toluene, sodium bis(trimethylsilyl)amide solution in toluene (1.03 g, 0.7 mmol), and [(PPh$_3$)$_2$Ni(Mes)Br][27] (0.50 g, 0.6 mmol) in 15 mL of absolute toluene. Yield: 0.08 g (0.1 mmol, 19%). ^{1}H NMR (CDCl$_3$): *δ* 7.80 (d, 1H, NC*H*), 7.39−7.16 (m, 15H, *H*$_{Phenyl}$), 6.78−6.67 (m, 3H, *H*$_{Aryl}$), 5.83 (s, 2H, *H*$_{Mesityl}$), 4.14 (q, 2H, C*H*$_2$), 2.47 (s, 6H, C*H*$_3$), 2.11 (s, 6H, C*H*$_3$), 1.92 (s, 3H, C*H*$_3$), 1.20 (t, 3H, C*H*$_3$), 0.89 (t, 3H, C*H*$_3$). IR (KBr): *ν* 3441 cm^{-1} (C═N), 3055 (C−H, *aryl*), 2964, (C−H, *CH*$_3$), 1688 (C═C), 1635 (C═C), 1480 (C−H, *CH*$_3$), 1435 (P−Ph, *PPh*$_3$), 1262 (C−O−C), 1094 (C−O), 1022 (C−O−C), 843 (C−H, *mesityl*), 803 (C−H, *aryl*), 740 (C−H, *phenyl*), 694 (C−H, *phenyl*). ESI$^+$-MS: *m/z* 700 (M$^+$). Anal. Calcd for $C_{42}H_{44}NNiO_3P$: C, 72.02; H, 6.33; N, 2.00. Found: C, 71.67; H, 5.98; N, 1.79.

[Ethyl 2-butyryl-3-[(2,6-dimethylphenyl)amino]acrylatemesityl](triphenylphosphino)nickel(II) (3h) was obtained from ethyl 2-butyryl-3-[(2,6-dimethylphen-yl)amino]-acrylate (**VIIIb**; 0.20 g, 0.7 mmol) in 10 mL of absolute toluene, sodium bis(trimethylsilyl)amide solution in toluene (1.04 g, 0.7 mmol), and [(PPh$_3$)$_2$Ni(Mes)Br][27] (0.52 g, 0.7 mmol) in 10 mL of absolute toluene. The mixture was stirred under argon at room temperature for 5 days. Yield: 0.08 g (0.1 mmol, 16%). ^{1}H NMR (CDCl$_3$): *δ* 7.79 (d, 1H, NC*H*), 7.38−7.16 (m, 15H, *H*$_{Phenyl}$), 6.79−6.65 (m, 3H, *H*$_{Aryl}$), 5.84 (s, 2H, *H*$_{Mesityl}$), 4.14 (q, 2H, C*H*$_2$), 2.50 (t, 2H, C*H*$_2$), 2.46 (s, 6H, C*H*$_3$), 2.10 (s, 6H, C*H*$_3$), 1.94 (s, 3H, C*H*$_3$), 1.22 (t, 3H, C*H*$_3$), 0.74 (m$_6$, 2H, C*H*$_2$), 0.49 (t, 3H, C*H*$_3$). IR (KBr): *ν* 3446 cm^{-1} (C═N), 3054 (C−H, *aryl*), 2964, 2935 (C−H, *CH*$_2$, *CH*$_3$), 1706 (C═O), 1583 (C═C), 1457 (C−H, *CH*$_2$, *CH*$_3$), 1434 (P−Ph, *PPh*$_3$), 1387 (C−H, *CH*$_3$), 1272 (C−O−C), 1072 (C−O), 1035 (C−O−C), 846 (C−H, *mesityl*), 786 (C−H, *aryl*), 693 (C−H, *phenyl*). ESI$^+$-MS: *m/z* 728 (M$^+$). Anal. Calcd for $C_{44}H_{48}NNiO_3P$: C, 72.54; H, 6.64; N, 1.92. Found: C, 72.18; H, 6.33; N, 1.68.

[Ethyl cyano(1-methylimidazo[1,5-*a*]pyridin-3(2*H*)ylidene)acetatemesityl](triphenylphosphino)nickel(II) (3i) was obtained from ethyl cyano(1-methylimidazo[1,5-*a*]pyridin-3(*2H*)-ylidene)acetate (**VIIIc**; 0.11 g, 0.4 mmol) in 15 mL of absolute toluene, sodium bis(trimethylsilyl)amide solution in toluene (0.70 g, 0.5 mmol), and [(PPh$_3$)$_2$Ni(Mes)Br][27] (0.33 g, 0.4 mmol) in 20 mL of absolute toluene. The mixture was stirred at room temperature for 3 days. Yield: 0.09 g (0.1 mmol, 31%). ^{1}H NMR (CDCl$_3$) *δ* 7.39−7.06 (m, 18H, *H*$_{Phenyl+Pyr}$), 6.59 (t, 1H, *H*$_{Pyr}$), 6.05 (s, 2H, *H*$_{Mes}$), 4.27 (q, 2H, C*H*$_2$), 2.75 (s, 6H, C*H*$_3$), 2.01 (s, 3H, C*H*$_3$), 1.27 (s, 3H, C*H*$_3$), 0.62 (t, 3H, C*H*$_3$). IR (KBr): *ν* 3437 cm^{-1} (C═N), 3055 (C−H, *aryl*), 2964, 2923 (C−H, *CH*$_3$), 2174 (C≡N, s), 1742 (C═O), 1581 (C═C), 1497 (C═C), 1435 (P−Ph, *PPh*$_3$), 1374 (C−H, *CH*$_3$), 1261 (C−O), 1094 (C−O), 1029 (C−O−C), 846 (C−H, *mesityl*), 729 (C−H, *heterocycle*), 694 (C−H, *heterocycle*). ESI$^+$-MS: *m/z* 682 (M$^+$). Anal. Calcd for $C_{40}H_{38}N_3NiO_2P$: C, 70.40; H, 5.61; N, 6.16. Found: C, 70.03; H, 5.30; N, 5.82.

[*N*-(2,6-Diisopropylphenyl)-3-[(2,6-diisopropyl-phenyl)amino]-3-oxopropanimidoatemesityl](tri-phenylphosphino)nickel(II) (4) was obtained from ethyl *N*-(2,6-diisopropylphenyl)-3-[(2,6-diisopropylphen-yl)amino]-3-oxopropanimidoate (**XII**; 0.21 g, 0.4 mmol) in 20 mL of absolute toluene, sodium bis(trimethylsilyl)amide solution in toluene (0.65 g, 0.4 mmol), and [(PPh$_3$)$_2$Ni(Mes)Br][27] (0.35 g, 0.4 mmol) in 20 mL of absolute toluene. Yield: 0.16 g (0.2 mmol, 41%). ^{1}H NMR (CDCl$_3$): *δ* 7.77−6.91 (m, 21H, *H*$_{Aryl+Phenyl}$), 6.10 (s, 2H, *H*$_{Mes}$), 3.10 (s, 6H, C*H*$_3$), 3.03 (bs, 1H, C*H*), 2.92 (bs, 1H, C*H*), 2.62 (bs, 2H, C*H*$_2$), 2.36 (s, 2H, C*H*$_2$), 1.98 (s, 3H, C*H*$_3$), 1.20 (bs, 12H, C*H*$_3$), 1.09 (bs, 12H, C*H*$_3$), 0.97 (bs, 3H, 1.20 (bs, 12H, C*H*$_3$). IR (KBr): *ν* 3359 cm^{-1} (C═N), 3054 (C−H, *aryl*), 2964 (C−H, *CH*$_3$), 2869 (C−H, *CH*), 1595 (C═C), 1550 (C(O)−N), 1480 (C═C), 1459 (C−H, *CH*$_2$, *CH*$_3$), 1435 (P−Ph, *PPh*$_3$), 1385 (C−H, *C(CH*$_3$*)*$_2$), 1260 (C−O−C), 1095 (C−O), 846 (C−H, *mesityl*), 801 (C−H, *aryl*), 744 (C−H, *phenyl*), 693 (C−H, *phenyl*). ESI$^+$-MS: *m/z* 889 (M$^+$). Anal. Calcd for $C_{56}H_{67}N_2NiO_2P$: C, 75.59; H, 7.59; N, 3.15. Found: C, 75.21; H, 7.23; N, 2.78.

Oligomerization Procedure. (a) Oligomerizations with Propylene (8−9.5 bar). The precatalyst was dissolved in 30 mL of solvent in a Schlenk flask under argon. A complete solution was obtained by leaving the flask in an ultrasonic bath for several minutes. A 150 mL glass reactor was evacuated and then filled with argon. The precatalyst solution was added under argon into the reactor vessel. The cocatalyst (MA, approximately 100 equiv, 0.6 mL of a 10 wt % MAO solution in toluene; EASC, approximately 300 equiv, 3.3 mL of a 25 wt % solution in toluene) and *n*-tridecane standard solution were added with stirring under argon. For several minutes propyl-

Table 8. Crystallographic Data

	1a	1b	3a	3c	3g	3h
empirical formula	$C_{77}H_{85.80}N_3NiOP_2$	$C_{71}H_{73}N_3NiOP_2$	$C_{40}H_{39}N_2NiO_3P$	$C_{43}H_{45}N_2NiO_2P$	$C_{42}H_{44}NNiO_3P$	$C_{44}H_{47}NNiO_3P$
CCDC no.	256362	256366	256364	256367	256363	256365
fw	1189.94	1104.97	685.41	711.49	700.46	727.51
temp (K)	240(2)	200(2)	200(2)	200(2)	200(2)	200(2)
wavelength, λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	triclinic	monoclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
unit cell dimens						
a, Å	12.674(1)	14.978(1)	15.220(1)	10.822(5)	20.493(1)	10.749(10)
b, Å	14.702(1)	24.131(1)	9.616(1)	12.157(6)	17.590(1)	13.812(13)
c, Å	18.808(1)	17.469(1)	24.915(1)	14.632(7)	10.144(1)	14.233(14)
α, deg	101.815(1)	90	90	99.202(7)	90	100.826(17)
β, deg	91.609(1)	101.839(1)	106.896(1)	94.050(7)	91.436(1)	99.922(16)
γ, deg	102.356(1)	90	90	98.805(7)	90	104.049(15)
V (Å^3)	3341.3(4)	6179.6(7)	3489.2(3)	1868.9(1)	3655.3(4)	1960(3)
Z	2	4	4	2	4	2
ρ_{calcd} (g cm^{-3})	1.183	1.188	1.305	1.264	1.273	1.233
μ (mm^{-1})	0.384	0.411	0.642	0.600	0.614	0.575
F(000)	1270	2344	1440	752	1480	770
cryst size (mm^3)	0.3 × 0.25 × 0.1	0.3 × 0.2 × 0.2	0.25 × 0.07 × 0.07	0.25 × 0.2 × 0.1	0.4 × 0.4 × 0.3	0.30 × 0.05 × 0.05
θ range for data collecn (deg)	1.63−28.31	1.39−28.32	1.40−28.28	1.42−28.45	1.53−28.30	1.50−28.61
index ranges	$-16 \le h \le 16$, $-19 \le k \le 19$, $-25 \le l \le 25$	$-19 \le h \le 19$, $-31 \le k \le 32$, $-23 \le l \le 23$	$-20 \le h \le 20$, $-12 \le k \le 12$, $-32 \le l \le 33$	$-14 \le h \le 14$, $-15 \le k \le 16$, $-19 \le l \le 19$	$-27 \le h \le 27$, $-23 \le k \le 23$, $-13 \le l \le 13$	$-14 \le h \le 14$, $-18 \le k \le 18$, $-18 \le l \le 18$
no. of rflns collected	40 555	74 003	41 775	18 820	43 174	24 010
no. of indep rflns	16 042 (R(int) = 0.0741)	15 125 (R(int) = 0.0741)	8602 (R(int) = 0.1978)	8853 (R(int) = 0.0731)	8977 (R(int) = 0.0282)	9499 (R(int) = 0.1733)
no. of data/restraints/params	16 042/6/777	15 125/0/724	8602/0/437	8853/2/472	8977/0/448	9499/0/467
goodness of fit on F^2	0.856	0.941	0.776	0.924	1.063	0.868
final R indices ($I > 2\sigma(I)$][a]	R1 = 0.0480, wR2 = 0.1157	R1 = 0.0413, wR2 = 0.0915	R1 = 0.0500, wR2 = 0.0921	R1 = 0.0725, wR2 = 0.1675	R1 = 0.0368, wR2 = 0.0966	R1 = 0.1058, wR2 = 0.2405
R indices (all data)[a]	R1 = 0.1495, wR2 = 0.1326	R1 = 0.0921, wR2 = 0.1087	R1 = 0.1967, wR2 = 0.1232	R1 = 0.1366, wR2 = 0.1971	R1 = 0.0516, wR2 = 0.1032	R1 = 0.2670, wR2 = 0.3194

[a] $R1 = [\sum||F_o| - |F_c||]/\sum|F_o|$, $wR2 = [[\sum w(|F_o^2 - F_c^2|)^2]/[\sum w(F_o^2)]]^{1/2}$, $w = 1/[(\sigma F_o)^2 + (aP)^2]$. The value of aP was obtained from structure refinement.

ene was introduced while streaming through the reactor to displace the argon. Then the reactor was closed and pressurized to 8 bar (or 9.5 bar) with propylene. The reactor pressure was maintained constant throughout the oligomerization run by manually controlled addition of propylene. Runs were terminated by venting off volatiles and extracting the solution with dilute hydrochloric acid and water. Quantitative GC analysis of the organic layer was performed immediately after the extraction.

(b) Oligomerizations with Ethylene (30 bar). The precatalyst was dissolved in 30 mL of solvent in a Schlenk flask under argon. A complete solution was obtained by leaving the flask in an ultrasonic bath for several minutes. A 150 mL stainless steel reactor with cooling mantle was evacuated and then filled with argon. The precatalyst solution was added under argon into the reactor vessel. The cocatalyst (MAO, approximately 100 equiv, 0.6 mL of a 10 wt % MAO solution in toluene; EASC, approximately 300 equiv, 3.3 mL of a 25 wt % solution in toluene) and *n*-tridecane standard solution were added with stirring under argon. For several minutes ethylene was introduced while streaming through the reactor to displace the argon. Then the reactor was closed and pressurized to 30 bar with ethylene. The reactor pressure was maintained constant throughout the oligomerization run by manually controlled addition of ethylene. The temperature of the reaction was controlled by cooling the reactor vessel with water. Runs were terminated by venting off volatiles and extracting the solution with dilute hydrochloric acid and water. Quantitative GC analysis of the organic layer was performed immediately after the extraction.

Crystal Structure Determination. The intensity data for the compounds were collected by a Siemens Smart 1000 CCD diffractometer using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects but not for absorption.[35,36]

The structures were resolved by direct methods (SHELXS[37]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[38]). The hydrogen atoms were localized by difference Fourier synthesis and refined isotropically. The data are deposited in the Cambridge Crystallographic Data Centre.[39]

All non-hydrogen atoms were refined anisotropically.[38] XP (SIEMENS Analytical X-ray Instruments, Inc.) and Ortep[40] were used for structure representations. Crystal data for all compounds are given in Table 8.

Supporting Information Available: Text giving synthetic details and characterization data for the ligands used in this study and tables giving additional yield data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(39) The files CCDC 256362−256367 contain the supplementary crystallographic data of the structure analyses given in this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax (+44) 1223-336-033; deposit@ccdc.cam.ac.uk).

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