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Nickel complexes featuring iminophosphorane-phenoxide ligands for catalytic ethylene dimerization

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Supporting Information Placeholder

ABSTRACT: A series of bidentate ligands associating an iminophosphorane and a phenoxide was synthesized and coordinated to nickel(II) leading initially to bimetallic KNi adducts. Replacement of the potassium by another metal allowed the isolation and characterization of bimetallic LiNi, and AlNi complexes, while addition of one equivalent of triphenylphosphine gave access to monometallic complexes. The same type of complex was obtained with the coordination of a tridentate ligand incorporating a supplementary amine donor. These paramagnetic complexes were characterized by elemental analysis and some of them by X-ray diffraction, evidencing a tetrahedral nickel center. They were shown to efficiently catalyze the oligomerization of ethylene in presence of Et_2AlCl (Al/Ni= 22.5) with TOF up to 72 000 mol(C_2H_4)/mol(Ni)/h, giving selectively butene (more than 97%) with at best 93% of 1- C_4 .

Introduction

Linear alpha olefins (LAOs) are important feedstocks for the chemical industry, that have found applications in various domains such as the preparation of lubricants, plasticizers, detergents and the synthesis of low-density polyethylene.¹ Their production is mainly achieved by the oligomerization of ethylene, for which different processes have been developed in the industry. Among them, the Phillips trimerization process based on chromium,² the Alphabutol process from IFP involving titanium,³ and the Shell Higher Olefin Process (SHOP) employing a phosphinoyl-enolato nickel complex⁴ are particularly remarkable. This latter catalytic system developed by Keim and coworkers has triggered further interest in nickel based catalytic systems, various ligands, either bidentate or tridentate,⁵ combining different heteroatoms were employed.⁶ A large diversity of bidentate ligand systems, which combine (N,N),⁷ (P,N),⁸ (P,P),⁹ (P,O),¹⁰ and (N,O)¹¹ donor groups, was described. Even if catalytic systems based on iminophosphorane (P=N) ligands are underdeveloped compared to their imine counterparts,¹² they have also been used to prepare nickel based ethylene oligomerization catalysts.¹³ Thus, in 2001, Réau and coworkers described the performances of nickel complexes featuring bis(iminophosphorane) ligand, which gave moderate productivity and selectivity in C_4 .^{13a} Later, Stephan and coworkers have shown that bidentate pyridine- or imidazole-iminophosphorane nickel complexes catalyze the dimerization of ethylene forming mainly 2- C_4 olefins.^{13b} More recently, we have demonstrated that mixed phosphine-iminophosphorane ligands led to efficient and selective nickel-based dimerization catalysts.^{13c}

As we recently developed tetradentate ligands associating iminophosphorane and phenoxide,¹⁴ we decided to prepare a bidentate version to evaluate phenoxide-iminophosphorane nickel complexes in ethylene oligomerization. Indeed, (N,O) based nickel catalysts (Figure 1) are well-known and generally favor ethylene polymerization.^{11a, 11b, 11c} Nevertheless, benzoquinone-monoimine nickel complexes (**I**), developed by the Braunstein's group,^{11c} achieved good selectivity in C_4 (up to 90%), but with a limited amount of α -olefins. Better selectivity was obtained with oxazolyl-methanol nickel complexes (**II**) developed by the same group.^{11d} In the same manner nickel catalysts based on phenyl-ether-pyrazol ligands (**III**) exhibited moderate to high activities with good selectivities in 1- C_4 (60-80 %).^{11f}

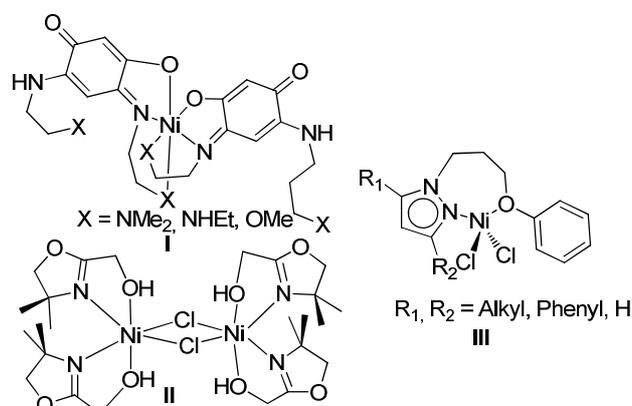


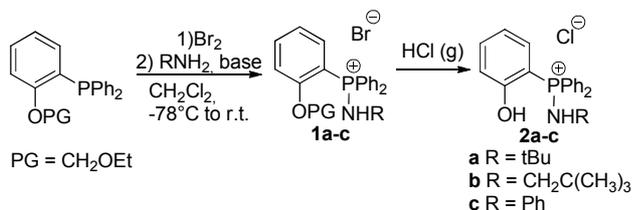
Figure 1. Examples of (N,O) nickel dimerization catalysts

In order to investigate if iminophosphoranes could be beneficial in such catalytic systems, we described in this paper the synthesis of bidentate phenoxide-iminophosphorane ligands, their coordination to Ni^{II} and their catalytic ability in ethylene oligomerization.

Results and discussion

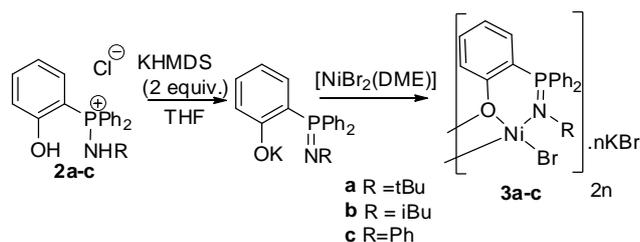
Some years ago, Zhang and coworkers¹⁵ synthesized such bidentate phenoxide-iminophosphorane ligands to prepare titanium and zirconium complexes. As they employed a synthesis based on the Staudinger reaction requiring an azide, only phenyl and trimethylsilyl derivatives were reported. In order to allow a facile variation of the nitrogen substituent, we preferred to rely on the Kirsanov reaction.¹⁶ This led us to prepare *o*-diphenylphosphinophenol protected as a methoxymethyl ether, following the procedure of Bianchi and coworkers.¹⁷

Aminophosphonium salts **1a-c** (Scheme 1) were then easily formed by bromination at low temperature followed by addition of a primary amine in presence of DABCO (diazabicyclooctane). The reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ spectroscopy; after completion, the reaction mixture was saturated with gaseous HCl to remove the methoxymethyl ether group. After workup, aminophosphonium salts **2a-c** were obtained in good yields (57 to 92% for the 2 steps). Interestingly they can be stored for days on the bench.



Scheme 1. Synthesis of aminophosphonium **2a-c**

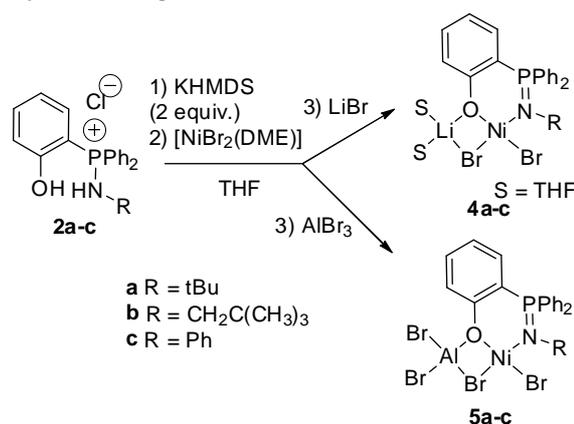
The iminophosphorane-phenoxide ligands were generated *in situ* before coordination (Scheme 2). The deprotonation was carried out with 2 equivalents of potassium hexamethyldisilazane (KHMDS) in THF, which allowed an easy removal of the insoluble KCl salts by centrifugation. The reaction is accompanied by a shielding of the phosphorus nucleus in $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy giving singlet at 12.0, 14.6, and 8.4 ppm for ligands **a-c** respectively.



Scheme 2. Coordination to nickel.

The ligands were not isolated and coordination to nickel(II) was realized in the same pot by adding one equivalent of $[\text{NiBr}_2(\text{DME})]$. This induced a rapid color change to purple for **3a,b** and blue-green for **3c**. The completeness of the reaction was ascertained by $^{31}\text{P}\{^1\text{H}\}$ NMR monitoring of the crude mixture showing the disappearance of the singlet corresponding to the ligand, no other signal was seen, which suggests the formation of paramagnetic complexes. Insoluble potassium salts were removed by centrifugation, followed by evaporation of THF, and washing of the obtained solid with petroleum ether to eliminate the amine side-product (HMDS) generated during the deprotonation step. All attempts to grow crystals of **3** failed whatever the solvent systems and temperatures employed, this precludes the determination of the precise structure of these adducts. However, elemental analysis seems to indicate the presence of one molecule of KBr for two $[(\text{Ni},\text{O})\text{NiBr}]$ moieties. Measurement of the magnetic moment of **3c** (as a representative example of this series of complexes) in solution¹⁸ gave a value of $3.3(1) \mu_{\text{B}}$ close to those reported in the literature for other nickel iminophosphorane complexes.^{13b}

Reasoning that substitution of potassium may avoid the formation of oligomers, and allow the characterization of the obtained nickel complexes, one equivalent of lithium bromide was added at the end of the coordination step. This led to complexes **4a-c** (Scheme 3), which precipitated out of the reaction mixture after concentration. These complexes were characterized by elemental analyses and X-ray diffraction. The magnetic moment of **4a** was measured in solution at $3.2(1) \mu_{\text{B}}$. Single crystals of **4a-c** were obtained by slow diffusion of petroleum ether at -40°C into THF solution of the complexes. The crystals were highly sensitive to temperature raising. The structures of **4a** and **4b** are displayed in Figures 2 and 3. For **4c**, the crystal structure was of low quality allowing only to confirm the connectivity, which is similar to that of **4a**. Detailed crystal data are given in Table S1 (see ESI).



Scheme 3. Synthesis of complexes **4a-c** and **5a-c**

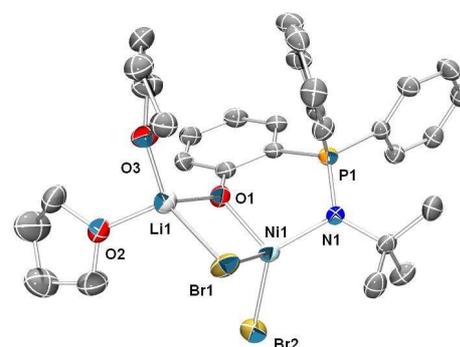


Figure 2. Ortep view of complex **4a**. Hydrogen atoms and a non-coordinated THF molecules have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected distances (Å) and angles ($^\circ$): Ni1-N1 1.977(2), Ni1-O1 1.954(2), Ni1-Br1 2.4526(5), Ni1-Br2 2.3799(5), Li1-O1 1.893(5), Li1-O2 1.915(6), Li1-O3 1.915(6), N1-P1 1.602(2), O1-C1 1.332(3), O1-Ni1-N1 98.30(8), N1-Ni1-Br2 116.17(7), Br2-Ni1-Br1 104.99(2), Br1-Ni1-O1 91.47(6), Li1-O1-Ni1 102.2(2), Li1-Br1-Ni1 73.8(1), Br1-Li1-O1 90.4(2), O1-Li1-O3 117.3(3), O3-Li1-O2 104.4(3), O2-Li1-Br1 16.5(2).

4a is a LiNi adduct, where both lithium and nickel exhibit a tetrahedral geometry. These atoms are bridged by a bromide and the oxygen. The four atoms form a nearly planar four-membered ring (O1-Ni1-Li1-Br1: 9.52°). As expected the Ni1-Br1 (2.453(1) Å) bond is longer than the Ni1-Br2 one (2.380(1) Å) in agreement with the bridging position of Br1. Other bonds and angles do not deserve special comments, for example the Br1-Li1 is comparable to that observed by Stephan *et al* for a NiLi adduct.¹⁹ Noteworthy the Ni1-N1 and Ni1-O1 bond lengths (1.977(2) Å and 1.954(2) Å respectively) observed in **4a** are longer than those observed in the

nickel phosphasalen complex featuring a tetradentate phenoxide-iminophosphorane ligand (1.905(4) and 1.881(3) Å for the longest Ni-N and Ni-O respectively).^{14d}

The lithium cation is solvated by two THF molecules, another non-coordinated solvent molecule is present in the cell and may explain the sensitivity of the crystals. The elemental analysis of **4a-c** are in agreement with this composition *i.e.* a bimetallic Ni complex solvated by two THF molecules.

However, X-ray analysis on single crystals of **4b** grown from THF evidenced a different structure: a dinuclear complex with no bromide in bridging position, and the lithium is, in this case, solvated by three THF molecules. Therefore, both Ni-Br bond lengths are similar (2.381(2) and 2.402(1) Å), moreover the Li1-O1 bond is longer in **4b** than in **4a** (1.945(7) and 1.893(5) Å respectively), the same observation is made for Ni1-O1 (1.975(2) Å *vs* 1.954(2) Å). Others parameters are similar to those observed for **4a**. Upon high vacuum drying, one THF molecule is probably released to form a four membered ring as observed for **4a**, explaining the composition obtained from elemental analysis.

Taking into account the ability of the oxygen atom of the phenoxide to coordinate electron deficient metal centers, and the role of AlNi adducts in oligomerization process,²⁰ we synthesized AlNi complexes (Scheme 3). The synthesis is similar to that of **4a-c**, AlBr₃ is added after the coordination step.

Complexes **5a-c** were isolated as blue solids which precipitated from the reaction mixture. These complexes were characterized by elemental analysis, since we were not able despite several attempts to grow single crystals. Complex **5c** exhibits a magnetic moment in solution of 3.4(1) μ_B.

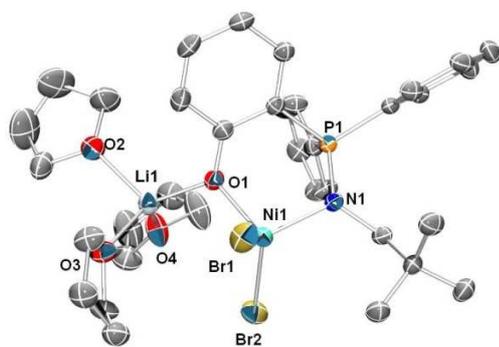
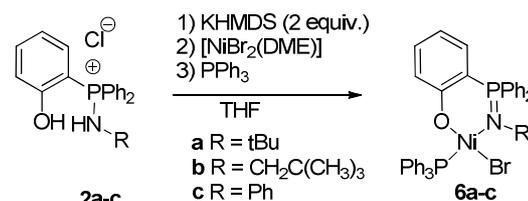


Figure 3. Ortep view of complex **4b**-THF. Hydrogen atoms and non-coordinated THF molecules have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Exchange between Br and Cl anions is observed for the coordinated halides, probably due to traces of KCl from the deprotonation step. Selected distances (Å) and angles (°): Ni1-N1 1.981(3), Ni1-O1 1.975(2), Ni1-Br1 2.402(8), Ni1-Br2 2.381(2), Li1-O1 1.930(7), Li1-O2 2.006(7), Li1-O3 1.945(7), Li1-O4 1.917(7), N1-P1 1.607(3), O1-C2 1.338(4); O1-Ni1-N1 98.9 (1), N1-Ni1-Br2 108.69(8), N1-Ni1-Br1 111.73(8), Li1-O1-Ni1 116.7(2).

In order to study the influence of the nuclearity on the catalytic performances, we also prepared monometallic complexes by introducing one equivalent of triphenylphosphine after the formation of adducts **3a-c** has been ascertained by ³¹P{¹H} NMR spectroscopy (Scheme 4). Complexes **6a-c** were isolated as paramagnetic green complexes (the mag-

netic moment of **6b** in solution was measured at 2.9(1) μ_B), suggesting a tetrahedral coordination around the nickel.



Scheme 4: Synthesis of complexes **6a-c**

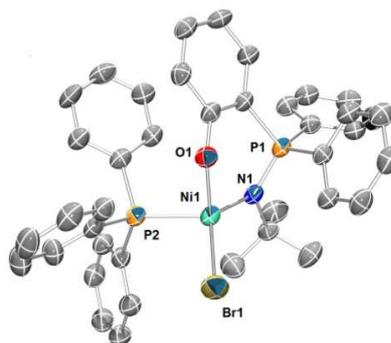
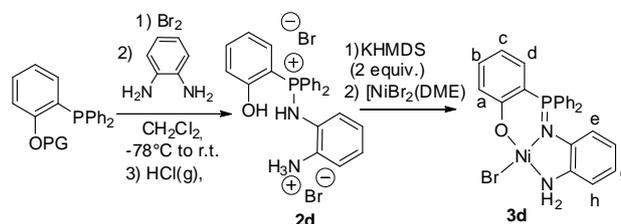


Figure 4. Ortep view of complex **6a**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected distances (Å) and angles (°): Ni1-N1 1.971(3), Ni1-O1 1.921(3), Ni1-Br1 2.371(1), Ni1-P2 2.321(1), P1-N1 1.616(4), O1-C2 1.314(5); O1-Ni1-N1 99.4(1), N1-Ni1-Br1 127.8(1), Br1-Ni1-P2 102.25(4), Ni1-N1-P1 113.7(2), O1-Ni1-P2 95.6(1).

This was confirmed by the X-ray analysis of single crystals of **6a** which were obtained by slow diffusion of petroleum ether onto THF solution of the complex at -40°C. An Ortep view of complex **6a** is presented Figure 4. The complex adopts a tetrahedral geometry, the Ni1-Br1, Ni1-N1, and Ni1-P1 bonds are comparable to those observed in **4a**, while the Ni1-O1 bond is significantly shorter 1.921(3) Å *vs* 1.954(2) Å in **4a**, which is explained by the non bridging position of the oxygen in **6a**.

To test a monomeric nickel complex having no phosphine ligand, we prepared a tridentate ligand featuring an additional amine group. The synthesis of the proligand **2d** is similar to that described for **2a-c** except that the Kirsanov reaction is conducted without addition of an extra base. Indeed, the acid formed is trapped by the anilino group to give the dicationic derivative (Scheme 5) which is directly deprotected using gaseous HCl leading to **2d**.



Scheme 5: Synthesis of complex **3d**

Table 1 Ethylene oligomerization with complexes 3-6^a

Entry	Complex	Co-catalyst	Al/Ni	Reaction Time (h)	TOF x 10 ⁻³ mol(C ₂ H ₄)/mol(Ni)/h ^b	%C ₄ (%1-C ₄)	(%1-C ₆)
1	[NiBr ₂ (DME)]	MAO	300	0.5	15.0	94.0 (85)	1.7 ^c
2	[NiBr ₂ (DME)]	Et ₂ AlCl	22.5	1	20.7	98.0 (78.2)	2.0
3	3b	MAO	300	1	20.1	98.1 (79.1)	1.9
4	3b	Et ₂ AlCl	22.5	1	36.9	98.4 (73.4)	1.6
5	3a	Et ₂ AlCl	22.5	1	39.6	98.2 (74.3)	1.8
6	3c	Et ₂ AlCl	22.5	1	68.1	98.2 (59.8)	1.8
7	3c	Et ₂ AlCl	22.5	0.5	67.5	97.9 (44.0)	2.1
8	3c	Et ₂ AlCl	45	1	72.1	97.0 (48.1)	3.0
9	3d	Et ₂ AlCl	22.5	1	41.2	97.0 (55.6)	3.0
10	4a	Et ₂ AlCl	22.5	1	23.7	97.6 (73.1)	2.4
11	4b	Et ₂ AlCl	22.5	1	30.3	98.4 (78.1)	1.6
12	4c	Et ₂ AlCl	22.5	1	17.0	98.1 (82.7)	1.9
13	5a	Et ₂ AlCl	22.5	1	18.5	98.7 (85.9)	1.3
14	5b	Et ₂ AlCl	22.5	1	28.9	98.5 (82.4)	1.5
15	5c	Et ₂ AlCl	22.5	1	7.3	98.7 (93.5)	1.3
16	6a	Et ₂ AlCl	22.5	1	13.9	99.6 (41.6)	0.6
17	6b	Et ₂ AlCl	22.5	1	14.5	99.4(48.9)	0.6
18	6c	Et ₂ AlCl	22.5	1	15.8	99.0 (55.6)	1.0

^a Conditions: T = 25 °C, 30 bar C₂H₄, 1h, 8 μmol Ni complex, solvent: toluene (20 mL).^b TOF = mol ethylene consumed per mol of Ni h⁻¹, TOF and selectivities are determined by GC chromatography, using heptane as internal reference; C_n, amount of olefin with n carbon atoms in the oligomers; α-C_n, amount of terminal alkene in the C_n fraction; as determined by quantitative GLC.^c Other isomers of hexene are formed

Its deprotonation with three equivalents of KHMDS in THF is monitored by ³¹P{¹H} NMR showing the disappearance of the singlet at 39 ppm corresponding to the aminophosphonium group and the appearance of a singlet at 15 ppm for the tridentate iminophosphorane ligand which was not isolated. Coordination was realized by adding one equivalent of [NiBr₂(DME)] to the reaction mixture giving a red solution and showing no signal by ³¹P{¹H} NMR spectroscopy. After workup, **3d** was isolated in 73% yield as a red solid. Its solution magnetic moment was measured at 3.1(1) μ_B in agreement with a paramagnetic complex that might be tetrahedral.²¹ However no single crystal was obtained precluding the determination of its crystal structure, we observed that THF or dichloromethane solution of this complex fades within days or weeks.

The nickel complexes **3-6**²² have been evaluated and compared in the catalytic ethylene oligomerization. Results are gathered in Table 1. Reactions were performed in toluene at 25°C under 30 bar of ethylene.

First experiments were done with **3b** and MAO (methylaluminoxane) as co-catalyst, nevertheless we found that Et₂AlCl gave better results, especially higher activity, with a much lower Al/Ni ratio (entries 3 and 4). Therefore all other experiments were carried out with this co-catalyst. For the sake of comparison, the performances of the nickel precursor are also indicated (entries 1-2).^{9b} All the complexes are active and selective for the formation of butene with satisfying to high activities

(TOF up to 72000 mol(C₂H₄)/mol(Ni)/h) and good selectivities (more than 97% of C₄). These performances outstrip those of the nickel precursor. No trace of polymer nor oligomers higher than C₆ was detected. Within the series of synthesized nickel complexes, for a given ligand, the best activities are observed with the NiK adduct. The presence of a strong coordinating ligand such as PPh₃ in the coordination sphere of the nickel dramatically reduces the productivity.²³

The activity increases when the coordinating ability of the auxiliary ligand decreases, which is probably explained by a better accessibility of the metal center. Within the series of adducts **3**, best TOF was observed for **3c** which bears a phenyl substituent on the nitrogen, which is therefore the less electron rich iminophosphorane. For this catalyst, a shorter experiment was conducted (entry 7), leading to similar performances suggesting a good stability of the active catalyst in the reaction medium. Moreover, using more aluminium co-catalyst did not have substantial effect on the catalytic ability (68x10³ to 72x10³ mol(C₂H₄)/mol(Ni)/h). **3d**, which features an aromatic substituent on the nitrogen atom, and does not contain potassium but an extra amine ligand which brings electron density to the metal, has an activity similar to alkyl-substituted adducts **3a-b** (entry 9). The selectivity in α-olefin varies greatly within the series and is related to the ability of the catalyst to isomerize 1-C₄ olefin.²⁴ Best selectivities in 1-C₄ were observed for NiLi and NiAl complexes (more than 70% and up to 93.5% for **5c**), whereas the less selec-

tive catalysts are those incorporating a supplementary coordinating ligand such as **6** and **3d**. From these results it clearly appears that the nature of the extra ligand influences the nature of the active species since both activities and selectivities are modified.

Contrary to most (N,O) nickel complexes described in the literature, which are ethylene polymerization catalysts, these complexes selectively dimerize ethylene. Compared to the Braustein's systems presented in Figure 1, higher proportion of 1-C₄ was formed. Results are roughly similar to those obtained with phenyl ether-pyrazolyl nickel complexes, nevertheless the latter were only tested over 20 min. In term of selectivity, we observed a higher proportion of C₄.

Therefore, the introduction of an iminophosphorane group seems to have a beneficial influence on the catalytic behavior. Moreover compared to other iminophosphorane dimerization catalysts, this series based on a phenoxide-iminophosphorane association are more active than the nickel complexes featuring a pyridine or oxazoline combined to an iminophosphorane, described by Stephan and coworkers,^{12c, 13b} but less efficient than phosphine-iminophosphorane nickel complexes.^{13c}

Conclusions

A series of nickel complexes featuring phenoxide-iminophosphorane ligands was prepared. The synthetic methodology based on the Kirsanov reaction allowed the introduction of alkyl, and aryl substituents on the N atom as well as the introduction of a supplementary amine donor group to give a tridentate ligand. Coordination of bidentate ligands afforded bimetallic NiK, NiLi, NiAl adducts, whereas monometallic complexes were obtained in presence of an extra L donor. These complexes are paramagnetic and were characterized by elemental analysis and in some cases by X-ray diffraction experiments, evidencing a tetrahedral nickel center. All these precursors (**3-6**) were shown to catalyze the selective dimerization of ethylene using Et₂AlCl as co-catalyst. Their performances (activity and selectivity) vary greatly with the substituent and the auxiliary ligand, best productivity being observed for the NiK complex **3c** (72x10³ mol(C₂H₄)/mol(Ni)/h) and better selectivity for the series of complex **5**. These performances compare favorably with other nickel complexes featuring (N,O) ligands, which motivated further studies on iminophosphorane catalysts.

Experimental Section

Synthesis

All experiments, unless otherwise stated, were performed under an atmosphere of dry nitrogen or argon using standard schlenk and glove box techniques. Solvents were taken directly from a ~~M-Braun~~ MB-SPS 800 Solvent Purification Machine. *O*-diphenylphosphinophenol,¹⁷ [NiBr₂(DME)]²⁵ were prepared according to the literature. We used methylaluminumoxane (10% wt in toluene), diethylaluminum chloride (0.9 M in toluene), and ethylene (N25 grade). All reagents and chemicals were obtained commercially and used without further purification.

Nuclear magnetic resonance spectra were recorded on a Avance 300 spectrometer operating at 300 MHz for ¹H, 75.5 MHz for ¹³C and 121.5 MHz for ³¹P. Solvent peaks were used as internal refer-

ences for ¹H and ¹³C chemical shifts (ppm). ³¹P{¹H} are relative to a 85% H₃PO₄ external reference. Coupling constant are expressed in hertz. The following abbreviations are used: br, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiple; v, virtual. The labeling used is indicated in Scheme 5. Elemental analyses were performed by the Elemental analysis service of the London Metropolitan University (United Kingdom). Analysis of the reaction mixture obtained after the catalytic run was performed by GC using a PR 2100 gas chromatograph equipped with a HP PONA column (50 m × 0.2 mm × 0.5 μm), first calibrated with authentic samples (except in the case of butene for which calibration was based upon the response factor of *n*-pentane).

Synthesis of 2a-c. Br₂ (200 μL, 3.883 mmol) was added dropwise to a solution of the protected phosphinophenol (1304 mg, 3.883 mmol) in CH₂Cl₂ (38 mL) at -78°C under nitrogen. The cold bath was removed and stirring was continued for 45 minutes at room temperature. The obtained suspension was then cooled again to -78°C and DABCO (218 mg, 1.942 mmol) was added, followed by the addition of the primary amine (3.883 mmol, 1 equiv.). Stirring was continued overnight at room temperature to give a white suspension. Dichloromethane was evaporated and the residue was taken in THF (50 mL). After removal of DABCO salts by centrifugation, the solvent was evaporated in vacuum, giving white solids. The products were solubilized in CH₂Cl₂ (15 mL) and verified in ³¹P{¹H} NMR spectrum. The solution was then saturated with gaseous HCl. After 15 minutes of stirring, a cloudy pale yellow solution has formed.

For **2a**, the reaction mixture was washed with water (2x10 mL). After drying the organic phase on MgSO₄, dichloromethane was removed. THF (5 mL) was then added, the mixture was sonicated for few minutes. Filtration and washing with pentane (10 mL) yielded a white powder. **2a** (0.87 g, 2.2 mmol, 57%). ³¹P{¹H} NMR (CDCl₃): δ 35.2 (s, P^V); ¹H NMR (CDCl₃): δ 7.96 (1H, ddd, ³J_{H,H}=7.5 Hz, ⁴J_{H,H}=2.0 Hz, ⁴J_{P,H}=5.5 Hz, H_a), 7.75 (4H, dd, ³J_{H,H}=7.5 Hz, ³J_{P,H}=13.0 Hz, *o*-CH(PPh₂)), 7.70 (2H, vt, ³J_{H,H}=7.5 Hz, *p*-CH(PPh₂)), 7.58 (4H, vtd, ³J_{H,H}=³J_{H,H}=7.5 Hz, ⁴J_{P,H}=2.5 Hz, *m*-CH(PPh₂)), 7.41 (1H, vtd, ³J_{H,H}=³J_{H,H}=7.5 Hz, ⁴J_{H,H}=3.0 Hz, H_b), 6.80 (2H, m, H_c, H_d), 4.94 (1H, s, NH), 1.15 (9H, s, CH₃); ¹³C{¹H} NMR (CDCl₃): δ 161.6 (d, ²J_{P,C}=2.0 Hz, OC^{IV}), 136.7 (d, ⁴J_{P,C}=1.5 Hz, C_b), 134.8 (d, ⁴J_{P,C}=3.0 Hz, *p*-CH(PPh₂)), 134.0 (d, ²J_{P,C}=11.4 Hz, *o*-CH(PPh₂)), 132.1 (d, ²J_{P,C}=10.5 Hz, C_d), 129.8 (d, ³J_{P,C}=13.5 Hz, *m*-CH(PPh₂)), 128.8 (d, ³J_{P,C}=12.4 Hz, C_{a(c)}), 122.7 (d, ¹J_{P,C}=101.8 Hz, C^{IV}(PPh₂)), 120.2 (d, ³J_{P,C}=13.9 Hz, C_{a(c)}), 107.1 (d, ¹J_{P,C}=107.3 Hz, PC^{IV}), 55.8 (d, ²J_{P,C}=4.8 Hz, C^{IV}(CH₃)₃), 32.1 (d, ³J_{P,C}=4.4 Hz, CH₃)

2b-2c were obtained after evaporation of dichloromethane and HCl and solubilization of the residue in THF (20 mL) giving a yellow slurry. The white solid was separated by centrifugation, washed again with THF (5 mL) and dried in vacuum.

2b (1.24 g, 2.8 mmol, 72%). ³¹P{¹H} NMR (CDCl₃): δ 36.4 (s, P^V); ¹H NMR (CDCl₃): δ 8.15 (s, b, OH), 8.02 (1H, dd, ³J_{H,H}=7.5 Hz, ⁴J_{P,H}=6.5 Hz, H_a), 7.80 (4H, ddd, ³J_{H,H}=7.5 Hz, ⁴J_{H,H}=1.0 Hz, ³J_{P,H}=13.5 Hz, *o*-CH(PPh₂)), 7.75 (2H, vtt, ³J_{H,H}=7.5 Hz, ⁴J_{H,H}=1.0 Hz, *p*-CH(PPh₂)), 7.62 (4H, vtd, ³J_{H,H}=³J_{H,H}=7.5 Hz, ⁴J_{P,H}=3.0 Hz, *m*-CH(PPh₂)), 7.46 (1H, vtd, ³J_{H,H}=³J_{H,H}=7.5 Hz, ⁴J_{H,H}=2.0 Hz, H_b), 6.88 (2H, m, H_c, H_d), 4.96 (1H, d, ²J_{P,H}=2.0 Hz, NH),

1.46 (2H, s, CH₂), 1.19 (9H, s, CH₃); ¹³C{¹H} NMR (CDCl₃): δ 161.4 (d, ²J_{P,C}=2.0 Hz, OC^{IV}), 136.7 (d, ⁴J_{P,C}=2.0 Hz, C_b), 134.8 (d, ⁴J_{P,C}=3.0 Hz, *p*-CH(PPh₂)), 133.9 (d, ²J_{P,C}=11.5 Hz, *o*-CH(PPh₂)), 132.4 (d, ^{2/3}J_{P,C}=11.0 Hz, C_{dic}), 129.8 (d, ³J_{P,C}=12.0 Hz, *m*-CH(PPh₂)), 122.7 (d, ¹J_{P,C}=102.0 Hz, C^{IV}(PPh₂)), 120.3 (d, ^{2/3}J_{P,C}=13.5 Hz, C_{ad}), 119.4 (d, ²J_{P,C}=7.4 Hz, C_a), 107.2 (d, ¹J_{P,C}=106.3 Hz, PC^{IV}), 55.8 (d, ²J_{P,C}=5.0 Hz, CH₂), 53.5 (s, C^{IV}(CH₃)₃), 32.1 (d, ³J_{P,C}=4.3 Hz, CH₃).

2c (1.35 g, 3.01 mmol, 78%). ³¹P{¹H} NMR (CDCl₃): δ 39.9 (s, P^V); ¹H NMR (CDCl₃): δ 7.97 (1H, ddd, ³J_{H,H}=6.5 Hz, ⁴J_{H,H}=1.0 Hz, ⁴J_{P,H}=8.5 Hz, H_a), 7.68 (2H, vtt, ³J_{H,H}=7.5 Hz, ⁴J_{H,H}=1.0 Hz, *p*-CH(PPh₂)), 7.66 (4H, ddd, ³J_{H,H}=7.5 Hz, ⁴J_{H,H}=1.0 Hz, ³J_{P,H}=14.0 Hz, *o*-CH(PPh₂)), 7.54 (4H, vtd, ³J_{H,H}=³J_{H,H}=7.5 Hz, ⁴J_{P,H}=3.0 Hz, *m*-CH(PPh₂)), 7.54 (1H, m, H_b), 7.10 (2H, vt, ³J_{H,H}=³J_{H,H}=7.5 Hz, *m*-CH(NPh)), 7.02 (1H, vtd, ³J_{H,H}=³J_{H,H}=6.5 Hz, ⁴J_{H,H}=1.0 Hz, H_c), 7.00 (1H, t, ³J_{H,H}=7.5 Hz, *p*-CH(PPh₂)), 6.93 (1H, ddd, ³J_{H,H}=6.5 Hz, ⁴J_{H,H}=1.0 Hz, ³J_{P,H}=3.5 Hz, H_d), 6.85 (2H, d, ³J_{H,H}=7.5 Hz, *o*-CH(NPh)); ¹³C{¹H} NMR (CDCl₃): δ 161.8 (d, ²J_{P,C}=2.5 Hz, OC^{IV}), 137.8 (d, ²J_{P,C}=3.0 Hz, C^{IV}(NPh)), 137.6 (d, ⁴J_{P,C}=2.0 Hz, C_b), 135.2 (d, ⁴J_{P,C}=3.0 Hz, *p*-CH(PPh₂)), 133.8 (d, ²J_{P,C}=11.5 Hz, *o*-CH(PPh₂)), 133.1 (d, ³J_{P,C}=10.5 Hz, C_c), 130.0 (d, ³J_{P,C}=13.6 Hz, *m*-CH(PPh₂)), 129.6 (s, *m*-CH(NPh)), 124.5 (s, *p*-CH(NPh)), 121.6 (d, ³J_{P,C}=6.0 Hz, *o*-CH(NPh)), 120.6 (d, ³J_{P,C}=14.0 Hz, C_a), 120.3 (d, ¹J_{P,C}=104.0 Hz, C^{IV}(PPh₂)), 119.5 (d, ²J_{P,C}=7.5 Hz, C_d), 105.9 (d, ¹J_{P,C}=105.0 Hz, PC^{IV}).

Synthesis of 2d. Br₂ (200 μL, 3.883 mmol) was added dropwise to a solution of the protected phosphinophenol (1304 mg, 3.883 mmol) in CH₂Cl₂ (38 mL) at -78 °C under nitrogen. The cold bath was removed and stirring was continued for 45 minutes at room temperature. The obtained suspension was then cooled again to -78 °C and *o*-phenylenediamine (420 mg, 3.883 mmol) was added. Stirring was continued overnight at room temperature to give a pale yellow slurry. Dichloromethane was evaporated and the residue was washed with THF (2x10 mL), giving a white solid, which was dissolved in CH₂Cl₂ (15 mL), and verified in ³¹P{¹H} NMR spectrum. The solution was then saturated with gaseous HCl. After 15 minutes of stirring, a cloudy pale yellow solution has formed. Dichloromethane and HCl were evaporated. The residue was taken in THF (20 mL) giving a yellow slurry. The white solid was separated by centrifugation, washed again with THF (5 mL) and dried in vacuum (1.95 g, 3.56 mmol, 92%).

³¹P{¹H} NMR (MeOD-*d*₄): δ 39.0 (s); ¹H NMR (MeOD-*d*₄): δ 7.93 (4H, ddd, ³J_{H,H}=7.5 Hz, ⁴J_{H,H}=1.0 Hz, ³J_{P,H}=14.0 Hz, *o*-CH(PPh₂)), 7.85 (2H, ttd, ³J_{H,H}=8.0 Hz, ⁴J_{H,H}=1.0 Hz, ⁵J_{P,H}=2.0 Hz, *p*-CH(PPh₂)), 7.79 (1H, dtvd, ³J_{H,H}=³J_{H,H}=8.0 Hz, ⁴J_{H,H}=1.0 Hz, ⁵J_{P,H}=1.5 Hz, H_b), 7.71 (4H, vtd, ³J_{H,H}=³J_{H,H}=7.5 Hz, ⁴J_{P,H}=4.0 Hz, *m*-CH(PPh₂)), 7.53 (1H, ddd, ³J_{H,H}=8.0 Hz, ⁴J_{H,H}=1.0 Hz, ³J_{P,H}=15.0 Hz, H_d), 7.46 (1H, dvt, ³J_{H,H}=8.0 Hz, ⁴J_{H,H}=1.0 Hz, ⁴J_{P,H}=1.0 Hz, H_c), 7.26 (1H, vtd, ³J_{H,H}=³J_{H,H}=8.0 Hz, ⁴J_{H,H}=1.0 Hz, H_f), 7.20 (1H, dtdd, ³J_{H,H}=³J_{H,H}=8.0 Hz, ⁴J_{H,H}=1.0 Hz, ⁴J_{P,H}=3.0 Hz, H_c), 7.15 (ddd, ³J_{H,H}=8.0 Hz, ⁴J_{H,H}=1.0 Hz, ⁴J_{P,H}=6.0 Hz, 1H, H_a), 7.15 (vtd, ³J_{H,H}=³J_{H,H}=8.0 Hz, ⁴J_{H,H}=1.0 Hz, 1H, H_e), 6.93 (dd, ³J_{H,H}=8.0 Hz, ⁴J_{H,H}=1.0 Hz, 1H, H_i); ¹³C{¹H} NMR (MeOD-*d*₄): δ 162.8 (d, ²J_{P,C}=3.5 Hz, C^{IV}-O), 140.0 (d, ⁴J_{P,C}=2.0 Hz, C_b), 136.8 (d, ⁴J_{P,C}=3.0 Hz, *p*-CH(PPh₂)), 136.3 (d, ²J_{P,C}=9.5 Hz, C_d), 135.4 (d, ²J_{P,C}=11.5 Hz, *o*-CH(PPh₂)),

133.3 (d, ²J_{P,C}=1.0 Hz, PNC^{IV}), 132.7 (d, ³J_{P,C}=14.0 Hz, *m*-CH(PPh₂)), 130.9 (s, C_j), 128.4 (s, C_g), 127.7 (d, ³J_{P,C}=8.0 Hz, NC^{IV}), 127.1 (d, ³J_{P,C}=4.0 Hz, C_e), 126.4 (s, C_h), 122.7 (d, ³J_{P,C}=13.5 Hz, C_c), 121.6 (d, ¹J_{P,C}=106.0 Hz, C^{IV}(PPh₂)), 118.8 (d, ³J_{P,C}=7.5 Hz, C_a), 107.8 (d, ¹J_{P,C}=104.5 Hz, C^{IV}(PPh₂)).

Synthesis of complexes 3a-d. KHMDS (200 mg, 1 mmol and 300 mg, 1.5 mmol in the case of **3d**) was added into a slurry of the phenolaminophosphonium salt (0.5 mmol) in THF (10 mL). After 30 min stirring at room temperature, the insoluble potassium salts were removed by centrifugation. [NiBr₂(DME)] (154 mg, 0.5 mmol) was added resulting immediately in a color change. Stirring was continued for 2h. Insoluble potassium salts were removed by centrifugation. THF was evaporated to give the product as a pale solid which is washed with petroleum ether to remove traces of HMDS. **3a** (220 mg, 0.21 mmol, 82%), pale purple solid. Anal. Calcd for C₄₄H₄₆Br₃KN₂Ni₂O₂P₂: C, 48.35; H, 4.24; N, 2.56. Found: C, 48.82; H, 5.38; N, 2.73. **3b** (195 mg, 0.18 mmol, 74%), pale blue solid. Anal. Calcd for C₄₆H₅₀Br₃KN₂Ni₂O₂P₂: C, 49.28; H, 4.50; N, 2.50. Found: C, 49.38; H, 4.39; N, 2.51. **3c** (230 mg, 0.21 mmol, 84%), pale green solid. μ_{eff}=3.3(1) μ_B. Anal. Calcd for C₄₈H₃₈Br₃KN₂Ni₂O₂P₂: C, 50.89; H, 3.38; N, 2.47. Found: C, 49.22; H, 4.82; N, 2.97. **3d** (200 mg, 0.39 mmol, 78%) deep red solid. μ_{eff}=3.1(1) μ_B. Anal. Calcd for C₂₄H₂₀Br₃NiO₂P: C, 55.22; H, 3.86; N, 5.37. Found: C, 55.15; H, 3.75; N, 5.28.

Synthesis of complexes 4a-c. KHMDS (200 mg, 1 mmol) was added into a slurry of the phenolaminophosphonium salt (0.5 mmol) in THF (10 mL). After 30 min stirring at room temperature, insoluble potassium salts were removed by centrifugation. [NiBr₂(DME)] (154 mg, 0.5 mmol) was added resulting immediately in a color change. Stirring was continued for 2h, insoluble potassium salts were removed by centrifugation, and LiBr (44 mg, 0.5 mmol) was added. The solution changed immediately giving a deep blue/purple color. After 2h the reaction mixture was concentrated (to 0.2 mL) leading to the precipitation of a crystallized solid, which was washed with petroleum ether to remove traces of HMDS. **4a** (329 mg, 0.46 mmol, 92%), blue purple solid. μ_{eff}=3.2(1) μ_B. Anal. Calcd for C₃₀H₃₇Br₂LiNiO₃P: C, 50.32; H, 5.21; N, 1.96. Found: C, 49.91; H, 5.61; N, 1.80. **4b** (300 mg, 0.42 mmol, 84%), blue solid. Anal. Calcd for C₃₁H₃₉Br₂LiNiO₃P: C, 51.00; H, 5.38; N, 1.92. Found: C, 50.76; H, 5.63; N, 1.83. **4c** (300 mg, 0.41 mmol, 82%), green solid. Anal. Calcd for C₃₂H₃₃Br₂LiNiO₃P: C, 52.22; H, 4.52; N, 1.90. Found: C, 51.87; H, 4.68; N, 1.79.

Synthesis of complexes 5a-c. KHMDS (200 mg, 1 mmol) was added into a slurry of the phenolaminophosphonium salt (0.5 mmol) in THF (10 mL). After 30 min stirring at room temperature, insoluble potassium salts were removed by centrifugation. [NiBr₂(DME)] (154 mg, 0.5 mmol) was added resulting immediately in a color change. Stirring was continued for 2h and the insoluble potassium salts were removed by centrifugation. AlBr₃ (134 mg, 0.5 mmol) was added. The solution changed immediately to a deep blue/purple one. After one night stirring, a dark solid precipitated out. THF was reduced in volume (2 mL) to favor the precipitation. The solid was separated by centrifugation, washed with petroleum ether to remove traces of HMDS, dried in vacuum. **5a** (240 mg, 0.32 mmol, 64%), brown solid. Anal. Calcd for C₂₂H₂₃AlBr₄NNiOP: C, 35.06; H, 3.08; N, 1.86. Found: C, 35.15;

H, 3.12; N, 1.76. **5b**, (230 mg, 0.31 mmol, 62%), brown solid. Anal. Calcd for $C_{23}H_{25}AlBr_4NNiOP$: C, 35.98; H, 3.28; N, 1.82. Found: C, 36.08; H, 3.40; N, 1.92. **5c** (240 mg, 0.31 mmol, 62%), brown solid. $\mu_{\text{eff}} = 3.4(1) \mu_B$. Anal. Calcd for $C_{24}H_{19}AlBr_4NNiOP$: C, 37.26; H, 2.48; N, 1.81. Found: C, 37.33; H, 2.55; N, 1.75.

Synthesis of complexes 6a-c. KHMDs (200 mg, 1 mmol) was added into a slurry of the phenolaminophosphonium salt (0.5 mmol) in THF (10 mL). After 30 min of stirring at room temperature, insoluble potassium salts (KCl) was removed by centrifugation. $[NiBr_2(DME)]$ (154 mg, 0.5 mmol) was added resulting immediately in a change of color. Stirring was continued for 2h. PPh_3 (122 mg, 0.5 mmol) was added. The solution changed immediately to a deep green one. After stirring overnight, insoluble potassium salts were removed by centrifugation. and THF was reduced in volume (1 mL) allowing the precipitation of a green solid. The solid was separated by centrifugation and washed with petroleum ether to remove traces of HMDS, dried in vacuum. **6a**. (260 mg, 0.35 mmol, 70%). green solid. Anal. Calcd for **6a** ($C_{40}H_{38}BrNNiOP_2$): C, 64.12; H, 5.11; N, 1.87. Found: C, 63.98; H, 5.22; N, 1.76. **6b**. (280 mg, 0.37 mmol, 73 %). Green solid. $\mu_{\text{eff}} = 2.9(1) \mu_B$. Anal. Calcd for **6b** ($C_{41}H_{40}BrNNiOP_2$): C, 64.51; H, 5.28; N, 1.84. Found: C, 65.08; H, 4.40; N, 1.92. **6c**. (315 mg, 0.41 mmol, 83%). green solid. Anal. Calcd for **6c** ($C_{42}H_{34}BrNNiOP_2$): C, 65.58; H, 4.45; N, 1.82. Found: C, 65.44; H, 4.52; N, 1.90.

General procedure for ethylene oligomerization

All catalytic reactions were carried out in a glass container placed in a magnetically stirred stainless steel autoclave (40 mL), equipped with a pressure gauge and needle valves for injections. The interior of the autoclave was protected from corrosion by a Teflon protective coating. A typical reaction was performed by introducing in the reactor under nitrogen atmosphere a suspension of the complex (8 μmol) in toluene (20 mL). After injection of the cocatalyst solution (in toluene), the reactor was immediately brought to the desired working pressure, and continuously fed with ethylene using a reserve bottle. The reaction was stopped by closing the ethylene supply and cooling down the system to -70°C . After release of residual pressure, the reaction was quenched by adding methanol (5 mL). *n*-heptane (1.2 mL) used as internal standard was also introduced and the mixture was analyzed by quantitative GC.

X-ray crystallography

Data were collected at 150 K on a Bruker Kappa APEX II diffractometer using a Mo $K\alpha$ ($\lambda = 0.71069 \text{ \AA}$) X-ray source and a graphite monochromator. The crystal structure was solved using SIR 97²⁶ and Shelxl-97 or Shelxl-2013.²⁷ ORTEP drawings were made using ORTEP III for Windows.²⁸

ASSOCIATED CONTENT

Supporting Information

Crystallographic data for **4a-b** and **6a** as cif and a with refinement details are given as supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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REFERENCES

1. Forestiere, A.; Olivier-Bourbigou, H.; Saussine, L., *Oil Gas Sci. Technol.* **2009**, *64*, 649-667.
2. McGuinness, D. S., *Chem. Rev.* **2011**, *111*, 2321-2341.
3. (a) Chauvin, Y., *Angew. Chem. Int. Edit.* **2006**, *45*, 3740-3747; (b) Commereuc, D.; Chauvin, Y.; Gaillard, J.; Leonard, J.; Andrews, J., *Hydrocarb. Process.* **1984**, *63*, 118-120.
4. (a) Keim, W., *Angew. Chem. Int. Edit. Engl.* **1990**, *29*, 235-244; (b) Skupinska, J., *Chem. Rev.* **1991**, *91*, 613-648; (c) Keim, W., *Angew. Chem. Int. Edit.* **2013**, *52*, 12492-12496.
5. (a) Ajellal, N.; Kuhn, M. C. A.; Boff, A. D. G.; Horner, M.; Thomas, C. M.; Carpentier, J. F.; Casagrande, O. L., *Organometallics* **2006**, *25*, 1213-1216; (b) Speiser, F.; Braunstein, P.; Saussine, L., *Dalton Trans.* **2004**, 1539-1545; (c) Sun, W. H.; Wang, K. F.; Wedeking, K.; Zhang, D. H.; Zhang, S.; Cai, J. J.; Li, Y., *Organometallics* **2007**, *26*, 4781-4790.
6. Wang, S.; Sun, W.-H.; Redshaw, C., *J. Organomet. Chem.* **2014**, *751*, 717-741.
7. (a) Gao, H. Y.; Guo, W. J.; Bao, F.; Gui, G. Q.; Zhang, J. K.; Zhu, F. M.; Wu, Q., *Organometallics* **2004**, *23*, 6273-6280; (b) Mukherjee, S.; Patel, B. A.; Bhaduri, S., *Organometallics* **2009**, *28*, 3074-3078; (c) Nelkenbaum, E.; Kapon, M.; Eisen, M. S., *J. Organomet. Chem.* **2005**, *690*, 3154-3164; (d) Svejda, S. A.; Brookhart, M., *Organometallics* **1999**, *18*, 65-74; (e) Tayade, K. N.; Mane, M. V.; Sen, S.; Murthy, C. N.; Tembe, G. L.; Pillai, S. M.; Vanka, K.; Mukherjee, S., *J. Mol. Catal. A-Chem.* **2013**, *366*, 238-246; (f) Yu, J. G.; Hu, X. Q.; Zeng, Y. N.; Zhang, L. P.; Ni, C. H.; Hao, X. A.; Sun, W. H., *New J. Chem.* **2011**, *35*, 178-183.
8. (a) de la Tabla, L. O.; Matas, I.; Palma, P.; Alvarez, E.; Campora, J., *Organometallics* **2012**, *31*, 1006-1016; (b) Kermagoret, A.; Braunstein, P., *Organometallics* **2008**, *27*, 88-99; (c) Speiser, F.; Braunstein, P.; Saussine, L., *Acc. Chem. Res.* **2005**, *38*, 784-793; (d) Speiser, F.; Braunstein, P.; Saussine, L.; Welter, R., *Organometallics* **2004**, *23*, 2613-2624; (e) Speiser, F.; Braunstein, P.; Saussine, L.; Welter, R., *Inorg. Chem.* **2004**, *43*, 1649-1658; (f) Weng, Z. Q.; Teo, S.; Hor, T. S. A., *Organometallics* **2006**, *25*, 4878-4882.
9. (a) Lejeune, M.; Semeril, D.; Jeunesse, C.; Matt, D.; Peruch, F.; Lutz, P. L.; Ricard, L., *Chem. Eur. J.* **2004**, *10*, 5354-5360; (b) Mora, G.; van Zutphen, S.; Klemp, C.; Ricard, L.; Jean, Y.; Le Floch, P., *Inorg. Chem.* **2007**, *46*, 10365-10371.
10. (a) Kuhn, P.; Semeril, D.; Jeunesse, C.; Matt, D.; Lutz, P.; Welter, R., *Eur. J. Inorg. Chem.* **2005**, 1477-1481; (b) Kuhn, P.; Semeril, D.; Jeunesse, C.; Matt, D.; Neuburger, M.; Mota, A., *Chem. Eur. J.* **2006**, *12*, 5210-5219.
11. (a) Younkin, T. R.; Conner, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A., *Science* **2000**, *287*, 460-462; (b) Hicks, F. A.; Brookhart, M., *Organometallics* **2001**, *20*, 3217-3219; (c) Yang, Q. Z.; Kermagoret, A.; Agostinho, M.; Siri, O.; Braunstein, P.,

- Organometallics* **2006**, *25*, 5518-5527; (d) Kermagoret, A.; Braunstein, P., *Dalton Trans.* **2008**, 1564-1573; (e) Radlauer, M. R.; Day, M. W.; Agapie, T., *Organometallics* **2012**, *31*, 2231-2243; (f) Ulbrich, A.; Campedelli, R. R.; Milani, J. L. S.; dos Santos, J. H. Z.; Casagrande, O. D., *Appl. Catal. A-Gen.* **2013**, *453*, 280-286.
- 12.(a) Buchard, A.; Komly, B.; Auffrant, A.; Le Goff, X. F.; Le Floch, P., *Organometallics* **2008**, *27*, 4380-4385; (b) Garcia-Alvarez, J.; Garcia-Garrido, S. E.; Cadierno, V., *J. Organomet. Chem.* **2014**, *751*, 792-808; (c) LePichon, L.; Stephan, D. W.; Gao, X. L.; Wang, Q. Y., *Organometallics* **2002**, *21*, 1362-1366; (d) Yadav, K.; McCahill, J. S. J.; Bai, G.; Stephan, D. W., *Dalton Trans.* **2009**, 1636-1643.
- 13.(a) Sauthier, M.; Leca, F.; de Souza, R. F.; Bernardo-Gusmao, K.; Queiroz, L. F. T.; Toupet, L.; Reau, R., *New J. Chem.* **2002**, *26*, 630-635; (b) Spencer, L. P.; Altwer, R.; Wei, P. R.; Gelmini, L.; Gauld, J.; Stephan, D. W., *Organometallics* **2003**, *22*, 3841-3854; (c) Buchard, A.; Auffrant, A.; Klempe, C.; Vu-Do, L.; Boubekeur, L.; Le Goff, X. F.; Le Floch, P., *Chem. Commun.* **2007**, 1502-1504; (d) Klempe, C.; Buchard, A.; Houdard, R.; Auffrant, A.; Mezailles, N.; Le Goff, X. F.; Ricard, L.; Saussine, L.; Magna, L.; Le Floch, P., *New J. Chem.* **2009**, *33*, 1748-1752; (e) Tognetti, V.; Buchard, A.; Auffrant, A.; Ciofini, I.; Le Floch, P.; Adamo, C., *Journal of Molecular Modeling* **2013**, *19*, 2107-2118.
- 14.(a) Bakewell, C.; Cao, T. P. A.; Le Goff, X. F.; Long, N. J.; Auffrant, A.; Williams, C. K., *Organometallics* **2013**, *32*, 1475-1483; (b) Bakewell, C.; Cao, T. P. A.; Long, N.; Le Goff, X. F.; Auffrant, A.; Williams, C. K., *J. Am. Chem. Soc.* **2012**, *134*, 20577-20580; (c) Cao, T. P. A.; Buchard, A.; Le Goff, X. F.; Auffrant, A.; Williams, C. K., *Inorg. Chem.* **2012**, *51*, 2157-2169; (d) Cao, T. P. A.; Labouille, S.; Auffrant, A.; Jean, Y.; Le Goff, X. F.; Le Floch, P., *Dalton Trans.* **2011**, *40*, 10029-10037.
- 15.Qi, C. H.; Zhang, S. B.; Sun, J. H., *J. Organomet. Chem.* **2005**, *690*, 3946-3950.
- 16.Horner, L.; Oediger, H., *Annalen Der Chemie-Justus Liebig* **1959**, *627*, 142-162.
- 17.Bianchi, A.; Bernardi, A., *J. Org. Chem.* **2006**, *71*, 4565-4577.
- 18.(a) Evans, D. F., *Journal of the Chemical Society* **1959**, 2003-2005; (b) Deutsch, J. L.; Poling, S. M., *J. Chem. Educ.* **1969**, *46*, 167-168; (c) Loliger, J.; Scheffol, R., *J. Chem. Educ.* **1972**, *49*, 646-647.
- 19.Masuda, J. B.; Wei, P.; Stephan, D. W., *Dalton Trans.* **2003**, 3500-3505.
- 20.(a) Wilke, G., *Angew. Chem. Int. Edit. Engl.* **1988**, *27*, 185-206; (b) Eisch, J. J.; Ma, X.; Singh, M.; Wilke, G., *J. Organomet. Chem.* **1997**, *527*, 301-304; (c) Weng, Z. Q.; Teo, S.; Koh, L. L.; Hor, T. S. A., *Chem. Commun.* **2006**, 1319-1321; (d) Albahily, K.; Al-Baldawi, D.; Gambarotta, S.; Koc, E.; Duchateau, R., *Organometallics* **2008**, *27*, 5943-5947; (e) Thapa, I.; Gambarotta, S.; Korobkov, I.; Murugesu, M.; Budzelaar, P., *Organometallics* **2012**, *31*, 486-494.
- 21.As nickel bromide complexes with a tridentate ligand are generally square planar considering the Cambridge Database, we performed DFT calculations showing that starting from a square planar complex, optimization in a triplet state led to a pseudo tetrahedral complex, which was found 5.4 kcal.mol⁻¹ lower in energy than the optimized singlet square planar complex.
- 22.To calculate the quantity of nickel using adducts **3**, which could not be satisfactorily characterized, we assumed a dimer with one KBr molecule as indicated by elemental analysis. .
- 23.About the detrimental role of PPh₃ was already reported by others see for example (a) Stapleton, R. L.; Chai, J.; Nuanthanom, A.; Fliksak, Z.; Nele, M.; Ziegler, T.; Rinaldi, P. L.; Soares, J. B. P.; Collins, S., *Macromolecules* **2007**, *40*, 2993-3004; (b) Stapleton, R. L.; Chai, J.; Taylor, N. J.; Collins, S., *Organometallics* **2006**, *25*, 2514-2524.
- 24.The longer the reaction mixture is kept at low temperature after stopping the feeding in ethylene and before the quench with methanol, the higher the proportion of 2-C4 is. Therefore it was important to reduce as much as possible this time in order to reduce this isomerization due to handling and to correctly represent the composition after the catalytic run.
- 25.King, R. B., *Organometallic Syntheses*. Academic Press: New York, 1965; Vol. 1, p 170.
- 26.Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R., *J. Appl. Crystallogr.* **1999**, *32*, 115-119.
- 27.Sheldrick, G. M., *SHELXL-97*. Universität Göttingen: Göttingen, Germany, 1997.
- 28.Farrugia, L. J. *ORTEP-3 program*, Department of Chemistry, University of Glasgow: 2001.

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