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Iminobisphosphines to (Non-)Symmetrical Diphosphinoamine Ligands: Metal-Induced Synthesis of Diphosphorus Nickel Complexes and Application in Ethylene Oligomerisation Reactions

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We describe the synthesis of a range of novel iminobisphosphine ligands based on a sulfonamido moiety [R^1SO_2-N=$P(R^2)_2$-$P(R^3)_2$]. These molecules rearrange in the presence of nickel by metal-induced breakage of the P–P bond to yield symmetrical and nonsymmetrical diphosphinoamine nickel complexes of general formula Ni{[$P(R^2)_2$]N(SO_2R^1)$P(R^3)_2$}Br_2. The complexes can be isolated and are very stable. Upon activation by MAO, these complexes oligomerise ethylene to small chain oligomers (mainly C_4–C_8) with high productivity. Surprisingly fast codimerisation reactions of ethylene with butenes is observed, leading to a high content of branched C_6 products.

Introduction

The demand for short-chain olefins has been increasing and the need to develop robust and selective oligomerisation catalytic systems, pushed by the recent upswing in ethylene production, is of prime importance. Over the past 60 years, a great number of homogeneous nickel catalysts for olefin oligomerisation have been reported.[1] Among others, monophosphine ligands, studied in the 1960s, were shown to have significant positive effects on the selectivity of olefin oligomerisation, leading to industrial successes.[2] At that time, disphosphine ligands were scarce and the use of well-known 1,2-bis(diphenylphosphanyl)ethane (DPPE) led to nickel-based catalysts that display low activity in ethylene transformation.[3] An unusual four-membered nickel complex containing a η^3-diphosphaallyl ligand η^3-[P(Ar)-C($OSiMe_3$)-P(Ar), Ar = 2,4,6-triisopropylphenyl] was reported by Keim et al. as a moderately active catalyst for ethylene polymerisation.[4] A renewed interest in bidentate ligands, triggered by the advances in their synthesis, allowed an evaluation of symmetrical diphosphines with different bite angles and electronic properties. In the field of nickel-catalysed olefin oligomerisation, symmetrical carbon-bridged diphosphines ligands have shown activity leading to the formation of oligomeric/polymeric products.[5,6] In addition, the groups of Le Floch[7] and Matt,[8] respectively, reported xanthene- and calixarene-based diphosphine nickel complexes associated with methylaluminoxane (MAO) as active catalytic systems for ethylene dimerisation (butenes > 90%). Symmetrical diphosphinoamine Ph_2P-NR-PPh_2 nickel complexes [with R = Ph, CH_2-C_6H_5, CH_2-(C_4H_3O), CH_2-(C_4H_3S), CH_2-(C_5H_4N),CH_2-CH_2-(C_4H_3S)] were shown to oligomerise ethylene to light olefins with moderate activity when activated by MAO.[9,10] Introducing bulky groups (OMe, Me, Et, *i*Pr) on the *ortho* position of the arylphosphines switched the catalyst selectivity from oligomerisation to production of polyethylene.[11,12] So far the evaluation of ligands in this important reaction is limited to symmetrical bisphosphine ligated nickel complexes, mainly because of the lack of synthetic routes of nonsymmetric diphosphines. As such, we developed a synthetic route that allows the formation of nickel complexes based on nonsymmetrical bidentate ligands. Herein, we report a metal-induced rearrangement strategy from iminobisphosphine ligands to symmetrical and nonsymmetrical diphosphine nickel complexes. These nickel precatalysts can be activated by using MAO, providing fast catalysts for ethylene oligomerisation reactions.

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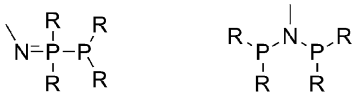
Results and Discussion

Iminobisphosphines (N=P–P) were described for the first time by Schmidpeter et al. in 1969.[13,14] However, the tendency of such compounds to form oils ("schwer kristallisierbare Öle") and to decompose were an obstacle to their isolation and characterisation. Bulky and electron-rich N-tosylamine derivatives have been described, leading to isolable iminobisphosphines $TsN{=}PR_2{-}PR_2$ (with R = Et or *i*Pr).[15] More recently, Dyson et al. reported the preparation and isolation of stable aryl-substituted iminobisphosphines.[16] Generally, these compounds are synthesised by reacting two equivalents of chlorophosphine with an amine. Iminobisphosphines may coexist with their diphosphinoamine P–N–P isomer, in a ratio that depends on the nitrogen substitution (Scheme 1). Although homo-*P*-substituted iminobisphosphines are now well described, the literature on hetero-*P*-substituted iminobisphosphine ligands is scarce and limited to NMR observations in situ.[15] In the presence of Pt or Pd precursors, Dyson et al. pointed out that iminobisphosphine completely rearranges to the bidentate P–N–P system, in which both phosphorus atoms are coordinated to the metal centre.[9,17,18] Recently, Shell also patented the synthesis of homo- and hetero-*P*-substituted iminobisphosphine mixtures and their applications in chromium-catalysed ethylene oligomerisation.[19]



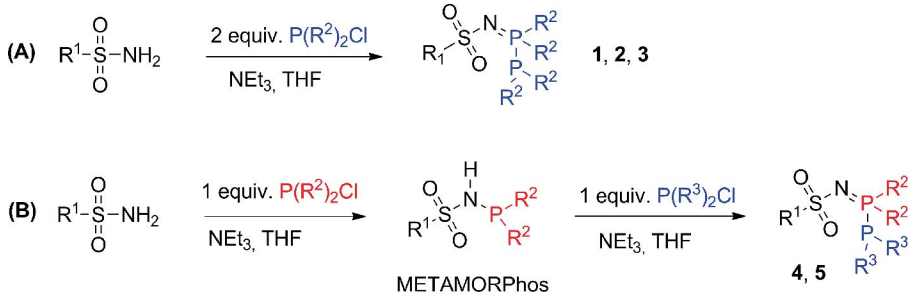
Scheme 1. Isomeric structures of iminobisphosphines (N=P–P) and diphosphinoamines (P–N–P).

We recently introduced METAMORPhos as a new ligand scaffold that consists of a sulfonamide-based phosphoramidite ligand.[20] The same sulfonamide building blocks were used in this work to prepare new iminobisphosphines, which were isolated as powders in moderate to good yields (up to 79%). The two different synthesis pathways (A and B) explored are depicted in Table 1. Homo-*P*-substituted iminobisphosphines were selectively obtained by reacting two equivalents of a chlorophosphine with a sulfonamide in the presence of NEt_3 in tetrahydrofuran (THF) (A). On the other hand, hetero-*P*-substituted iminobisphosphines were afforded in a two-step synthesis (B). First, the sulfonamide reacted with a chlorophosphine to give a phosphinoamine, which represents a typical METAMORPhos ligand. In a second step, the phosphinoamine reacted with a different chlorophosphine to yield the hetero-*P*-substituted iminobisphosphine.

Single crystals were grown for homo- and hetero-*P*-substituted ligands **1** and **4** by slow diffusion of pentane into a toluene solution of the ligand. The X-ray crystal structures confirmed the ligand structures. Importantly, the order of addition of chlorophosphines in the stepwise route during the synthesis of the hetero-*P*-substituted product, determines the final structure: i.e., the $P(i\text{Pr})_2$ at the terminal P^{III} position and PPh_2 at the central P^V (Figure 1 and Figure 2). The formation of iminobisphosphines is likely due to a nucleophilic attack of the METAMORPhos phosphorus (route B) on the chlorophosphine, in agreement with the reaction and mechanism reported by Foss and coworkers.[21] P(1)–N(1) and P(1)–P(2) distances for both ligands in the solid state are close to reported values.[16,18] The P(2)–P(1)–N(1) angle in ligand **2** is in the range of reported iminobisphosphines [115.00(5)°]. However, for hetero-*P*-substituted ligand **4**, the P(2)–P(1)–N(1) angle is much less [99.5(1)°].

The iminobisphosphines bear a central P^V and a terminal P^{III} atom, resulting in two characteristic doublets in the ^{31}P NMR spectrum, with $^1J_{P,P}$ coupling constants of ca. 300 Hz. From 2D $^{31}P\{^1H\}$ experiments on the hetero-*P*-substituted ligand **4**, we assigned the upfield doublet at δ = 2.80 ppm to terminal $P(i\text{Pr})_2$ and the downfield chemical shift at δ = 20.13 ppm to central PPh_2, leading to comprehensive ^{31}P NMR characterisation of all ligands. The $^{31}P\{^1H\}$ chemical shifts and the $^1J_{P,P}$ values for ligands **1**–**5** are reported in Table 2. Basic substituents on the phos-

Table 1. Synthesis of homo- and hetero-*P*-substituted iminobisphosphines.



Ligand	R^1	R^2	R^3	Isolated yield [%]
1	(4-Br)C_6H_4	Ph	–	68
2	(4-*n*Bu)C_6H_4	Ph	–	79
3	(4-Br)C_6H_4	*i*Pr	–	58
4	(4-*n*Bu)C_6H_4	Ph	*i*Pr	34
5	(4-*n*Bu)C_6H_4	Ph	Cy	51

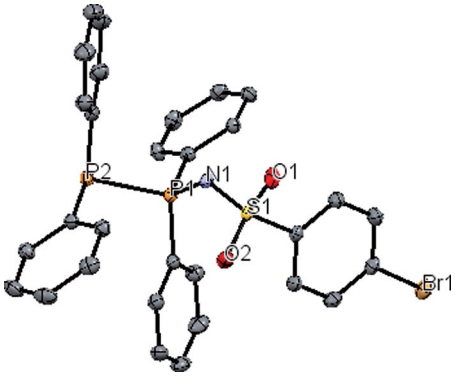


Figure 1. ORTEP plot (50% probability displacement ellipsoids) of ligand **1**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: S(1)–O(1) 1.4446(11); S(1)–O(2) 1.4448(11); S(1)–N(1) 1.5726(12); P(1)–P(2) 2.2221(5); P(1)–N(1) 1.6000(12); O(1)–S(1)–O(2) 116.50(7), O(1)–S(1)–N(1) 106.98(6); O(1)–S(1)–C(1) 105.97(7); O(2)–S(1)–N(1) 112.83(6); P(2)–P(1)–N(1) 115.00(5).

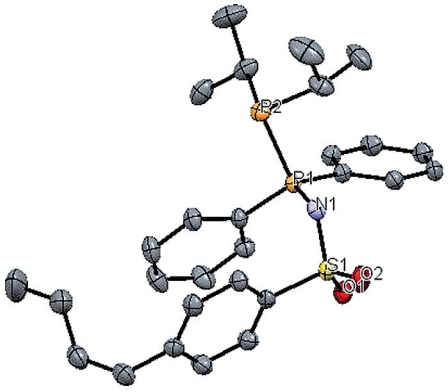


Figure 2. ORTEP plot (50% probability displacement ellipsoids) of ligand **4**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]:S(1)–O(1) 1.441(3); S(1)–O(2) 1.446(3); S(1)–N(1) 1.591(2); P(1)–P(2) 2.200(1); P(1)–N(1) 1.615(2); O(1)–S(1)–O(2) 116.6(1), O(1)–S(1)–N(1) 107.5(1); O(1)–S(1)–C(25) 106.7(1); O(2)–S(1)–N(1) 113.0(1); P(2)–P(1)–N(1) 99.5(1).

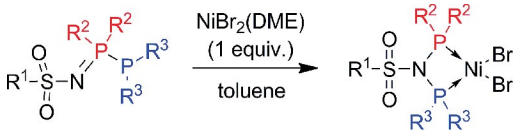
phines induce a chemical shift displacement downfield. In addition, $^1J_{P,P}$ coupling constants increase with the phosphine basicity. Indeed, iminobisphosphines with basic substituents such as **3** ($^1J_{P,P}$ = 329 Hz) have larger coupling constants compared with the aryl-substituted compounds ($^1J_{P,P}$ = 281 Hz for **1**).

Table 2. ^{31}P Chemical shifts and coupling constants of ligands **1**–**5** in CD_2Cl_2.

Ligand	P^V δ [ppm]		P^{III} δ [ppm]		$^1J_{P,P}$ [Hz]
1	Ph	19.72	Ph	–18.74	281
2	Ph	19.47	Ph	–17.90	278
3	*i*Pr	50.39	*i*Pr	–6.32	329
4	Ph	20.13	*i*Pr	2.80	312
5	Ph	20.44	Cy	–4.98	315

Upon reaction of ligands **1**–**5** with $NiBr_2$(DME) (DME = 1,2-dimethoxyethane) as the metal precursor, complete conversion into diphosphinoamine-chelated nickel complexes **6**–**10**, respectively, was observed. Accordingly, the ^{31}P NMR spectra display a singlet for the symmetrical complexes **6**–**8** and two doublets with a small coupling constant ($^2J_{P,P}$ = 119.6 and 118.6 Hz for **9** and **10**, respectively), typical for *cis*-oriented ligands in nickel complexes. The red, diamagnetic complexes were obtained in moderate to good isolated yields (up to 80%; Table 3). This approach constitutes an elegant way to generate unprecedented symmetrical P-alkyl and nonsymmetrical diphosphine nickel complexes. Crystals of complexes **6** (symmetrical), **9** and **10** (unsymmetrical) that were suitable for X-ray diffraction were grown from slow vapour diffusion of pentane into dichloromethane/toluene solutions. ORTEP diagrams are shown in Figures 3, 4 and 5 along with selected bond lengths and bond angles. All three nickel complexes adopt a square-planar geometry with a constrained *cis*-coordination of the ligand, similar to the published diphosphinamine nickel complexes. The bond lengths and angles of the various complexes in the solid state are very similar. The substitution only slightly affects the P–N bond length, which is longer for basic phosphines; in complex **9**, N-PPh_2: 1.727(3) Å and N-P(*i*Pr)$_2$: 1.752(3) Å and in complex **10**, N-PPh_2: 1.7449(15) Å and N-PCy_2: 1.7512(15) Å. The bite angles of all the complexes are in the same range [97.16(8) < P–N–P < 97.37(15) and 75.54(2) < P–Ni–P < 75.976(19)].

Table 3. Synthesis of diphosphinoamine-$NiBr_2$ complexes.



Complex	R^1	R^2	R^3	Isolated yield [%]
6	(4-Br)C_6H_4	Ph	Ph	80
7	(4-*n*Bu)C_6H_4	Ph	Ph	68
8	(4-Br)C_6H_4	*i*Pr	*i*Pr	57
9	(4-*n*Bu)C_6H_4	Ph	*i*Pr	61
10	(4-*n*Bu)C_6H_4	Ph	Cy	54

We were interested in the mechanism of the metal-induced rearrangement of these ligands and, to this end, we performed some additional experiments. Upon mixing ligand **3** with $NiBr_2$(DME), the signals of the free ligand disappeared and two new resonances were observed at $\delta(CD_2Cl_2)$ = 133.6 and 36.6 ppm. The resonance at δ = 133.6 ppm is characteristic for di(isopropyl)phosphine bromide and is also observed when the synthesis is performed in halogen-free solvents such as toluene, showing that the halogen source is most likely the nickel precursor. The resonance at δ = 36.6 ppm is in the range of the R–NH–PR_2 fragment. These observations are in line with the proposed metal-induced rearrangement reported by Dyson et al. for Pd and Pt.[15] In this mechanism, the P–P bond of the iminobisphosphine is proposed to cleave homolytically, releasing a chlorophosphine among unidentified fragments. We reasoned that this rearrangement may also involve intermolecular processes. Therefore, an experiment was con-

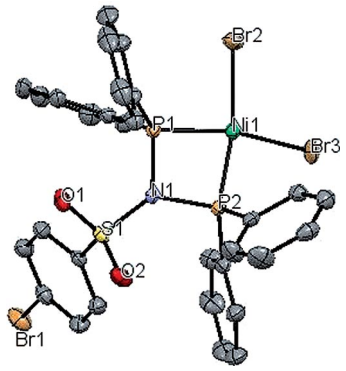


Figure 3. ORTEP plot (50% probability displacement ellipsoids) of complex **6**. Hydrogen atoms and CH_2Cl_2 solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Br(2)–Ni(1) 2.3230(4); Br(3)–Ni(1) 2.3307(4); Ni(1)–P(1) 2.1277(6); Ni(1)–P(2) 2.1212(6); P(1)–N(1) 1.7316(18); P(2)–N(1) 1.7385(18); Br(2)–Ni(1)–Br(3) 99.703(13); Br(2)–Ni(1)–P(1) 91.250(19); Br(2)–Ni(1)–P(2) 163.48(2); Br(3)–Ni(1)–P(1) 164.82(2); Br(3)–Ni(1)–P(2) 95.203(19); P(1)–Ni(1)–P(2) 75.54(2); Ni(1)–P(1)–N(1) 93.33(6); Ni(1)–P(2)–N(1) 93.36(6); P(1)–N(1)–P(2) 97.17(9).

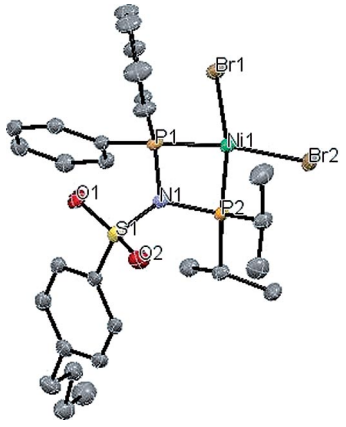


Figure 4. ORTEP plot (50% probability displacement ellipsoids) of complex **9**.4CH_2Cl_2. Hydrogen atoms and CH_2Cl_2 solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Br(1)–Ni(1) 2.3334(6); Br(2)–Ni(1) 2.3275(6); Ni(1)–P(1) 2.1189(10); Ni(1)–P(2) 2.1284(10); P(1)–N(1) 1.727(3); P(2)–N(1) 1.752(3); Br(1)–Ni(1)–Br(2) 98.87(2); Br(1)–Ni(1)–P(1) 92.91(3); Br(1)–Ni(1)–P(2) 168.24(3); Br(2)–Ni(1)–P(1) 168.00(3); Br(2)–Ni(1)–P(2) 92.44(3); P(1)–Ni(1)–P(2) 75.93(4); Ni(1)–P(1)–N(1) 93.85(10); Ni(1)–P(2)–N(1) 92.79(10); P(1)–N(1)–P(2) 97.37(15).

ducted in which the homo-*P*-substituted iminobisphosphines **2** (Ph, Ph) and **3** (*i*Pr, *i*Pr) were mixed with 2 equiv. $NiBr_2$(DME). After 5 min, complete conversion of ligand **2** into the symmetrical complex **7** was observed, in addition to free ligand **3**. After 4 d stirring, a mixture of homo- and hetero-substituted complexes was observed, along with by-products (Scheme 2). Surprisingly, the addition of one equivalent of ligand **3** (*i*Pr, *i*Pr) to a solution of isolated complex **7** (Ph, Ph), resulted in the formation of only a single nonsymmetrical complex ($^2J_{P,P}$ = 120 Hz) along with the starting materials, and the formation of homocomplex **8** (*i*Pr, *i*Pr) was not observed. This demonstrates that the P–P bond is likely cleaved in *P*-alkyl-based systems and that the P–N bond, as in the diphosphinoamine complex **7**, may

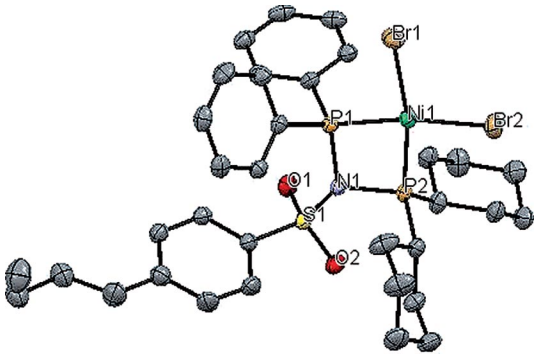
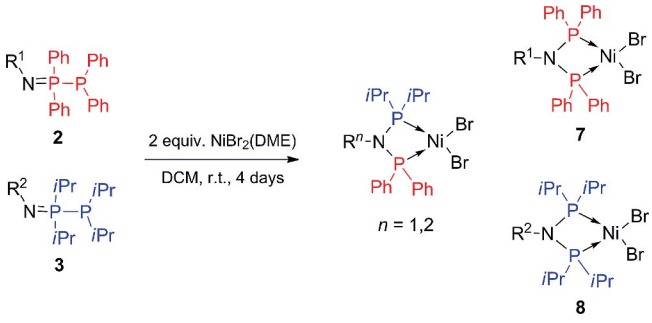


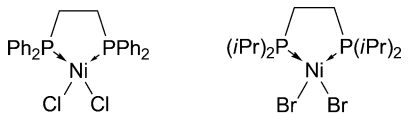
Figure 5. ORTEP plot (50% probability displacement ellipsoids) of complex **10**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Br(1)–Ni(1) 2.3314(3); Br(2)–Ni(1) 2.3200(3); Ni(1)–P(1) 2.1194(5); Ni(1)–P(2) 2.1401(5); P(1)–N(1) 1.7449(15); P(2)–N(1) 1.7512(15); Br(1)–Ni(1)–Br(2) 97.109(12); Br(1)–Ni(1)–P(1) 92.018(16); Br(1)–Ni(1)–P(2) 167.949(18); Br(2)–Ni(1)–P(1) 170.843(18); Br(2)–Ni(1)–P(2) 94.884(16); P(1)–Ni(1)–P(2) 75.976(19); Ni(1)–P(1)–N(1) 93.78(5); Ni(1)–P(2)–N(1) 92.88(5); P(1)–N(1)–P(2) 97.16(8).

also be broken. Importantly, mixing the two isolated complexes **7** (Ph, Ph) and **8** (*i*Pr, *i*Pr) did not lead to the formation of nonsymmetrical complexes, indicating that the complexes themselves are sufficiently stable (in absence of triggers) for catalysis. Some decomposition products and paramagnetic compounds were, however, formed after 4 d.



Scheme 2. Scrambling experiment on complex formation performed with two symmetrical iminobisphosphines and $NiBr_2$(DME) (2 equiv.) in CH_2Cl_2.

The symmetrical and nonsymmetrical bidentate P–N–P nickel complexes **7**–**10** were evaluated in ethylene oligomerisation using methylaluminoxane (MAO; 10 wt.-% in toluene) as activator. Three diphosphine nickel complexes $NiCl_2$(DPPE) and $NiBr_2$(D*i*PrPE) were prepared to evaluate the electronic and chelating effects on the catalytic outcome (Scheme 3). Ethylene oligomerisation reactions were carried out under two sets of conditions: 30 bar/45 °C and



Scheme 3. Reference diphosphine nickel complexes for ethylene oligomerisation: $NiCl_2$(DPPE) and $NiBr_2$(D*i*PrPE).

Table 4. Results of catalytic tests of ethylene oligomerisation at 30 bar C_2H_4, 45 °C for complexes **7**–**10** and references $NiCl_2$(DPPE) and $NiBr_2$(D*i*PrPE).[a]

Complex	T_{max} [°C]	Mass of product [g]	Productivity[b]	Product distribution[c] C_4	C_6	C_8^+	1-C_4[d]
7	52	8.4	14	92.4	6.6	1.0	57.7
8[e]	77	36.1	80	71.5	18.3	10.2	22.3
9[e]	65	36.2	81	71.7	17.9	10.4	20.9
10[e]	70	33.1	70	68.1	19.4	12.5	22.2
$NiCl_2$(DPPE)	51	2.9	5	93.2	5.3	1.6	38.0
$NiBr_2$(D*i*PrPE)	50	1.3	2	79.1	15.3	5.6	67.7

[a] Reaction conditions (unless stated otherwise): n_{Ni} = 10 µmol, MAO (300 equiv.), toluene (50 mL), 1 h. [b] Productivity in $kg_{oligomer}\cdot(g_{Ni}\cdot h)^{-1}$. [c] Product analysis performed by GC (wt.-%). [d] Wt.-% 1-C_4 in C_4 cut. [e] Reaction stopped at 45 min.

Table 5. Results of catalytic tests of ethylene oligomerisation at 5 bar C_2H_4, 30 °C for complexes **7**–**10**.[a]

	T_{max} [°C]	Mass of product [g]	Productivity[b]	Product distribution[c] C_4	C_6	C_8^+	1-C_4[d]
7	30	3.0	5	94.4	4.8	0.8	11.9
8	34	23.9	41	66.5	22.4	11.2	10.7
9	30	17.0	29	67.0	21.8	11.3	10.1
10	30	25.9	36	60.4	24.9	14.7	9.4

[a] Reaction conditions: n_{Ni} = 10 µmol, MAO (300 equiv.), toluene (50 mL), 1 h. [b] Productivity in $kg_{oligomer}\cdot(g_{Ni}\cdot h)^{-1}$. [c] Product analysis performed by GC (wt.-%). [d] Wt.-% 1-C_4 in C_4 cut.

5 bar/30 °C. All the reactions were conducted in duplicate and found to be reproducible (see Tables 4 and 5).

Upon activation with MAO at 30 bar and 45 °C, complex **7** is moderately productive for short chain oligomers [14 $kg_{oligomer}\cdot(g_{Ni}\cdot h)^{-1}$; see Table 4]. The deactivation, observed experimentally by a decrease in ethylene uptake in time, is attributed to an unstable active species was recovered as a black deposit at the end of the reaction. Interestingly, the novel alkyl-substituted (PNP′)$NiBr_2$ complexes **8**–**10** were very active [70–81 $kg_{oligomer}\cdot(g_{Ni}\cdot h)^{-1}$] and the exothermic reaction resulted in a temperature change (up to +23 °C). Compared with the aryl-disubstituted complex **7**, complexes **8**–**10** were five times more active, showing that basic phosphorus moieties are beneficial for the activity. In contrast, the ethylene-bridged diphosphine nickel complexes $NiCl_2$(DPPE) and $NiBr_2$(DP*i*PrE) gave oligomers with low activity and no exotherm. The activity and selectivity displayed by $NiCl_2$(DPPE) and $NiBr_2$(DP*i*PrE) is similar to the methylene-bridged diphosphine complexes reported by the group of Pringle and Wass.[4]

Performing the catalytic experiments under milder conditions (5 bar and 30 °C) allowed the reaction temperature to be fully controlled. By applying these conditions it was possible to keep the ethylene uptake linear, and catalysts were still active after 60 min. The symmetrical diphenyl-*P*-substituted complex **7** was barely active at 5 bar and 30 °C, affording mainly dimers (Table 5) The nitrogen substitution of all the complexes, namely the -SO_2- moiety did not have a crucial impact on the catalysis because *N*-alkyl-substituted complexes of general formula R-CH_2-N(PPh_2)$_2$, developed by the group of Wu,[7] were equivalent in terms of activity to the symmetrical diphenyl-*P*-substituted complex **7**. Although not directly impacting catalysis, the sulfonyl group enhanced the stability of the synthetic intermediates and allowed the possibility to access a variety of homo- and hetero-substituted nickel complexes, especially some with basic phosphines. The corresponding isopropyl-disubstituted analogue **8** showed high productivity and moderate selectivity for butenes (66.5%) and low alpha selectivity (10.7%). The nonsymmetric complexes **9** (Ph, *i*Pr) and **10** (Ph, Cy) activated by MAO were also very active and moderately selective towards butene formation (67.0 and 60.4%, respectively).

The moderate selectivity for the terminal olefins in the C_4 and C_6 fractions obtained when complexes **7**–**10** were used as catalysts (see Table 5) is likely to result from two different processes, i.e., isomerisation that converts, for instance, 1-C_4 into 2-C_4 and/or codimerisation of butenes and ethylene to branched hexenes. We therefore looked in detail at the C_6 products in an attempt to understand the mechanistic pathways. The identification of all the C_6 isomers [1-hexene, 2-hexene (*cis* + *trans*), 3-hexene (*cis* + *trans*), 3-methylpent-1-ene, 3-methylpent-2-ene (*cis* + *trans*), 2-ethylbut-1-ene] was possible by coupling GC and GC–MS analyses and is presented for complexes **7**–**10** in Table 6.

Table 6. Isomer distribution in the C_6 cut for complexes **7**–**10** determined by GC analysis.[a]

% of C6	HEX1	HEX2	HEX3	M3P1	M3P2	E2B1
7	4.4	24.5	9.3	12.0	35.6	14.2
8	0.7	6.2	1.6	12.2	59.6	19.7
9	0.7	7.2	1.6	12.1	61.6	17.3
10	0.5	5.4	1.3	10.9	63.5	18.4

[a] Reaction conditions: see Table 5. HEX1: 1-hexene; HEX2: 2-hexenes; HEX3: 3-hexenes; M3P1: 3-methylpent-1-ene; M3P2: 3-methylpent-2-enes; E2B1: 2-ethylbut-1-ene.

Analysis of the C_6 products formed from the experiment in which precatalyst **7** was used, revealed the presence of up to 38.2% linear C6 olefins compared with 9.6% maximum for precatalysts **8**–**10** containing *P*-alkyl moieties. Remarkably, the symmetrical and nonsymmetrical precatalysts **8**–**10** present the same product distribution pattern in C_6 oligomers, with methylpentenes being the predominant isomers with up to 74.4 wt.-% in the C_6 fraction. Whereas linear isomers are expected to be formed from ethylene polyaddition reactions, branched products are likely formed from consecutive codimerisation reactions of ethylene and butenes. To gain an understanding of the codimerisation process, we monitored the product formation in the liquid phase using **8** as the precatalyst. Samples of the reaction mixture taken after 12 min showed that the linear-C_6/branched-C_6 ratio was identical to that quantified after 1 h reaction time. This demonstrates that codimerisation is not only observed when butenes are accumulated in the medium but also at the start of the reaction. Considering the very high content of branched isomers at different reaction times, we conclude that, for our alkyl-based diphosphinoamine nickel catalysts, the codimerisation reactions are competitive with ethylene oligomerisation.

Conclusions

Starting from sulfonamide moieties, we prepared several stable iminobisphosphines bearing P-aryl, P-alkyl, or mixtures of both groups. We have shown that the metal-induced rearrangement to diphosphinoamine complexes is likely initiated by P–P bond cleavage and that the ligand redistribution can involve an intermolecular process. This path allows new alkylphosphine-substituted complexes (PNP)-$NiBr_2$ and nonsymmetrical complexes (PNP′)$NiBr_2$ to be easily generated. Activated by MAO, the alkyl-P-containing catalysts are efficient for ethylene oligomerisation. Besides displaying high productivity, these systems present a product distribution of butenes along with mainly branched oligomers (C6 and C8+) that are favoured by competitive codimerisation processes.

Experimental Section

General: All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Sulfonamides and reference ligands were purchased from commercial suppliers and used without further purification. Chlorophosphines were distilled trap-to-trap under reduced pressure. MAO (10% in toluene) was purchased from Chemtura and stored cold. THF, pentane and Et_2O were distilled from sodium benzophenone ketyl. CH_2Cl_2, chlorobenzene and triethylamine were distilled from CaH_2, toluene from sodium, under nitrogen. NMR spectra [^1H, $^1H(^{31}P)$, ^{31}P, $^{31}P(^1H)$ and $^{13}C(^1H)$] were measured with a Varian Mercury 300 MHz, or a Bruker 300 MHz spectrometer at 25 °C. High-resolution fast atom bombardment (FAB) mass spectra were recorded with a JEOL JMS SX/SX102A four-sector mass spectrometer. Calculated spectra were obtained with a JEOL Isotopic Simulator (version 1.3.0.0). Analyses of liquid phases were performed with a GC Agilent 6850 Series II equipped with a PONA column. The gas phases for ethylene oligomerisation were analysed by gas GC on HP 6890.

Synthesis of Ligands

Synthesis of 4-Butylbenzene-1-sulfonamide-bisphenyl-phosphine (METAMORPhos): Prepared according to a reported procedure.[18] Commercially available 4-butylbenzene-1-sulfonamide (9.38 mmol, 1 equiv.) was dissolved in THF (20 mL) and triethylamine (25 mmol), leading to a clear colourless solution. Distilled chlorodiphenylphosphine (9.38 mmol, 1.0 equiv.) was added dropwise under strong magnetic stirring at room temperature. The suspension was stirred overnight at room temperature, then the suspension was filtered under nitrogen atmosphere and the resulting clear solution was evaporated to a white solid. The product was dissolved in dichloromethane (10 mL) to give a clear solution. Pentane (40 mL) was added dropwise to the solution, causing a white solid to precipitate out. The organic layer was removed by using a syringe, and the white solid obtained was washed with pentane (2× 20 mL). The product was obtained as a white solid (isolated yield: 74%). The product was characterised by ^1H and ^{31}P and $^{31}P\{^1H\}$ NMR spectroscopic analysis and the data were consistent with reported values.

Synthesis of 4-Bromo-*N*-(1,1,2,2-tetraphenyldiphosphanylidene)-benzenesulfonamide 1: 4-Bromobenzene-1-sulfonamide (500 mg, 2.12 mmol, 1 equiv.) was dissolved in THF (10 mL) and triethylamine (1.6 mL, 11.2 mmol, 5.3 equiv.), leading to a clear colourless solution. Distilled diphenylchlorophosphine (0.760 mL, 4.24 mmol, 2 equiv.) was added dropwise under strong magnetic stirring at room temperature. The suspension was stirred for 5 min at room temperature then the suspension was filtered under nitrogen atmosphere and the resulting clear solution was evaporated to give a white solid. The solid was dissolved in a minimum of dichloromethane, and pentane (20 mL) was added. Upon evaporation under reduced pressure, a precipitate formed. The liquid was removed by using a syringe and the powder was washed with pentane (2× 10 mL). Finally the product was dried under reduced pressure, affording a white powder (isolated yield: 870 mg, 68%). Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a saturated dichloromethane solution of the product. ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.82–6.89 (m, 24 H) ppm. ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 19.72 (d, $^1J_{P,P}$ = 281.1 Hz), –18.74 (d, $^1J_{P,P}$ = 281.1 Hz) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ = 19.72 (d, $^1J_{P,P}$ = 279.9 Hz), –18.74 (d, $^1J_{P,P}$ = 281.2 Hz) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 124.96 (s, C_{quat}, C-Br), 127.42 [dd, $^1J_{C,P}$ = 81.8, $^2J_{C,P}$ = 10.2 Hz, 4 C, C_{quat} (PPh_2 *ipso*)], 127.81 (s, 2 C, CH_{ArSO2}); 129.00 (d, $^3J_{C,P}$ = 12.3 Hz, 4 C, *meta*-CH_{Ar}), 129.17 (dd, $^3J_{C,P}$ = 7.9, $^4J_{C,P}$ = 1.1 Hz, 4 C, *meta*-CH_{Ar}), 130.95 (d, $^4J_{C,P}$ = 2.4 Hz, 2 C, *para*-CH_{Ar}), 131.56 (s, 2 C, CH_{ArSO2}), 133.22 (d, $^4J_{C,P}$ = 3.1 Hz, 2 C, *para*-CH_{Ar}), 133.47 (dd, $^2J_{C,P}$ = 9.71, $^3J_{C,P}$ = 4.54 Hz, 4 C, *ortho*-CH_{Ar}), 135.75 (dd, $^2J_{C,P}$ = 21.1, $^3J_{C,P}$ = 7.2 Hz, 4 C, *ortho*-CH_{Ar}), 145.90 (d, $^3J_{C,P}$ = 3.2 Hz, C_{quat}, C-SO_2) ppm. MS (FAB$^+$): *m*/*z* calcd. for $C_{30}H_{25}NO_2P_2BrS$ $[MH]^+$ 606.0248; found 606.0255. $C_{30}H_{25}NO_2P_2BrS$: calcd. C 59.61, H 4.00, N 2.32; found C 59.53, H 3.85, N 2.26.

Synthesis of 4-Butyl-*N*-(1,1,2,2-tetraphenyldiphosphanylidene)benzenesulfonamide (2): 4-Butylbenzene-1-sulfonamide (500 mg, 2.34 mmol, 1 equiv.) was dissolved in THF (20 mL) and triethylamine (1 mL, 7.17 mmol, 3 equiv.), giving a clear colourless solution. Distilled diphenylchlorophosphine (0.945 mL, 4.98 mmol, 2.1 equiv.) was added dropwise under strong magnetic stirring at room temperature. The suspension was stirred for 5 min at room temperature, then the suspension was filtered under a nitrogen atmosphere and the resulting clear solution was evaporated to give an

oil. The oil was dissolved in Et_2O (10 mL) and evaporated without heating. This step was repeated four times until the combined increase in concentration and loss in temperature caused the product to precipitate. The solid was vacuum-dried to obtain a white powder (isolated yield: 1.07 g, 79%). ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.91–6.33 (m, 24 H, ArH), 2.59 (t, $^3J_{H,H}$ = 7.7 Hz, 2 H, $CH_3CH_2CH_2CH_2CAr$), 1.57 (m, 2 H, $CH_3CH_2CH_2CH_2CAr$), 1.33 (m, 2 H, $CH_3CH_2CH_2CH_2CAr$), 0.93 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, $CH_3CH_2CH_2CH_2Ar$) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 14.09 (CH_3), 22.63 (CH_2CH_3), 33.87 ($CH_2CH_2CH_3$), 35.72 ($ArCH_2$), 125.98 ($C_{Ar–SO2}$, 2 C), 127.89 (dd, $^1J_{P,C}$ = 81.5, $^2J_{C,P}$ = 10.2 Hz, 4 C, *ipso*-$C_{quat\ PPh2}$), 128.80 ($C_{Ar–SO2}$, 2 C), 128.88 (d, $^3J_{C,P}$ = 12.3 Hz, 4 C, *meta*-$CH_{\ PPh2}$), 129.08 (dd, $^3J_{C,P}$ = 7.8, $^4J_{C,P}$ = 0.9 Hz, 4 C, *meta*-$CH_{\ PPh2}$), 130.81 (d, $^4J_{C,P}$ = 2.3 Hz, 2 C, *para*-$CH_{\ PPh2}$), 133.03 (d, $^4J_{C,P}$ = 3.0 Hz, 2 C, *para*-$CH_{\ PPh2}$), 133.46 (dd, $^2J_{C,P}$ = 9.6, $^3J_{C,P}$ = 4.4 Hz, 2 C, *ortho*-$CH_{\ PPh2}$), 135.76 (dd, $^2J_{C,P}$ = 21.05, $^3J_{C,P}$ = 7.3 Hz, 2 C, *ortho*-$CH_{\ PPh2}$), 144.20 (d, $^3J_{C,P}$ = 3.3 Hz, C_{quat} C-SO_2), 145.99 (C_{quat}, C-*n*Bu) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ = 19.47 (d, $^1J_{P,P}$ = 277.9 Hz), –17.90 (d, $^1J_{P,P}$ = 278.0 Hz) ppm. MS (FAB+): *m/z* calcd. for $C_{34}H_{34}O_2NP_2S$ $[M + H]^+$ 582.1786; found 582.1790. $C_{34}H_{34}O_2NP_2S$ calcd. C 70.21, H 5.72, N 2.41; found C 70.11, H 5.93, N 2.50.

Synthesis of 4-Bromo-*N*-(1,1,2,2-tetraisopropyldiphosphanylidene)-benzenesulfonamide (3): 4-Bromobenzene-1-sulfonamide (2 g, 8.47 mmol, 1 equiv.) was dissolved in THF (20 mL) and triethylamine (3.6 mL, 25.4 mmol, 3 equiv.) to give a clear colourless solution. Commercial diisopropylchlorophosphine (2.95 mL, 18.5 mmol, 2.2 equiv.) was added dropwise under strong magnetic stirring at room temperature. The suspension was stirred for 2 d at room temperature, then the suspension was filtered under a nitrogen atmosphere and the resulting clear solution was evaporated to a white solid. The solid was suspended in pentane (10 mL) and evaporated without heating. This step was repeated once. The solid was dissolved in a minimum of dichloromethane (4 mL), and pentane (60 mL) was added causing a solid to form. The liquid was removed by using a syringe and the powder was washed twice with pentane (10 mL). Finally the product was dried under reduced pressure to afford a white powder (isolated yield: 2.3 g, 58%). ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.87–7.30 (m, 4 H, ArH), 2.72 (m, 2 H, H_3CCHCH_3), 2.49 (m, 2 H, H_3CCHCH_3), 1.63–0.97 (m, 24 H, CH_3) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ = 50.39 (d, $^1J_{P,P}$ = 329.5 Hz), –6.30 (d, $^1J_{P,P}$ = 329.8 Hz) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 17.50 (m, 4 C, $CH_{3\ iPr}$), 21.09 (dd, $^2J_{C,P}$ = 9.6, $^3J_{C,P}$ = 7.9 Hz, 2 C, $CH_{3\ iPr}$), 22.33 (dd, $^1J_{C,P}$ = 21.8, $^2J_{C,P}$ = 4.15 Hz, 2 C, $CH_{\ iPr}$), 23.15 (dd, $^2J_{C,P}$ = 20.9, $^3J_{C,P}$ = 6.9 Hz, 2 C, $CH_{3\ iPr}$), 28.86 (dd, $^1J_{C,P}$ = 42.14, $^2J_{C,P}$ = 6.9 Hz, 2 C, $CH_{\ iPr}$), 124.73 (C_{quat}, C-Br), 127.65 ($CH_{\ Ar–SO2}$, 2 C), 131.69 ($CH_{\ Ar–SO2}$, 2 C), 146.69 (C_{quat}, C-SO_2) ppm. . $C_{18}H_{32}BrNO_2P_2S$ calcd. C 46.16, H 6.89, N 2.99; found C 46.11, H 6.98, N 3.01.

Synthesis of 4-Butyl-*N*-(1,1-diisopropyl-2,2-diphenyldiphosphanylidene)benzenesulfonamide (4): 4-Butylbenzene-1-sulfonamide-bisphenyl-phosphine (1 g, 4.68 mmol, 1 equiv.) was dissolved in THF (20 mL) and triethylamine (1.3 mL, 9.36 mmol, 2 equiv.) to give a clear colourless solution. Commercial diisopropylphosphine (0.746 mL, 4.68 mmol, 1 equiv.) was added dropwise under strong magnetic stirring at room temperature. The suspension was stirred for 10 min at room temperature, then the suspension was filtered under a nitrogen atmosphere and the resulting clear solution was evaporated to an oil. Pentane (20 mL) was added to the oil under strong stirring then, after decantation, the upper layer was removed by using a syringe. The oil was suspended in pentane (10 mL) and evaporated without heating. This step was repeated once with pentane (10 mL) and twice with Et_2O (10 mL). The combined increase in concentration and loss in temperature caused the product to precipitate. Pentane (20 mL) was added to wash the powder and was removed by using a syringe and the solvent was removed under vacuum to afford a white solid (isolated yield: 808 mg, 34%). ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.98–7.83 (m, 4 H, PPh_2), 7.76–7.64 (m, 2 H, CH_2ArSO_2), 7.60–7.35 (m, 6 H, PPh_2), 7.23–7.12 (m, 2 H, CH_2ArSO_2), 2.69–2.57 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, $CH_3CH_2CH_2CH_2Ar$), 2.44 (m, 2 H, CH_3CHCH_3), 1.69–1.48 (m, 2 H, $CH_3CH_2CH_2CH_2Ar$), 1.35 (m, 2 H, $CH_3CH_2CH_2CH_2Ar$), 1.18–0.99 (m, 12 H CH_3CHCH_3), 0.93 (t, *J* = 7.3 Hz, 3 H, $CH_3CH_2CH_2CH_2Ar$) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ = 20.13 (d, *J* = 311.6 Hz), 2.80 (d, *J* = 311.6 Hz) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 14.10 (CH_3), 20.70 (dd, $J_{C,P}$ = 10.6, 9.2 Hz, CH_3 *i*Pr), 22.67 (CH_2CH_3), 22.75 (d, $J_{C,P}$ = 3.0 Hz, CH *i*Pr), 23.01 (CH *i*Pr), 23.18 (dd, $^2J_{C,P}$ = 18.1, $^3J_{C,P}$ = 7.6 Hz, CH_3 *i*Pr), 33.86 ($CH_2CH_2CH_3$), 35.77 ($ArCH_2$), 126.02 ($C_{Ar–SO2}$, 2 C), 128.63 ($C_{Ar–SO2}$, 2 C), 129.11 (d, $^3J_{C,P}$ = 12.4 Hz, 2 C, *meta*-CH_{PPh2}), 130.78 (dd, $^1J_{C,P}$ = 83.6, $^2J_{C,P}$ = 9.7 Hz, 4 C_{quat}, *ipos*-C_{PPh2}), 132.61 (dd, $J_{C,P}$ = 9.4, 6.0 Hz, 6 C, *ortho*/*para*-CH_{PPh2}), 144.60 (d, *J* = 4.9 Hz, C_{quat}, C-SO_2), 146.15 (C_{quat}, C-*n*Bu) ppm. $C_{28}H_{37}NO_2P_2S$ calcd. C 65.48, H 7.16, 2.73; found 65.53, H 7.34, 2.060

Synthesis of 4-Butyl-*N*-(1,1-dicyclohexyl-2,2-diphenyldiphosphanylidene)benzenesulfonamide (5): 4-Butylbenzene-1-sulfonamide-bisphenyl-phosphine (360 mg, 0.91 mmol, 1 equiv.) was dissolved in THF (10 mL) and triethylamine (0.126 mL, 1.82 mmol, 2 equiv.) to give a clear colourless solution. Commercial dicyclohexylylphosphine (0.200 mL, 0.91 mmol, 1 equiv.) was added dropwise under strong magnetic stirring at room temperature. The suspension was stirred for 5 min at room temperature, then the suspension was filtered under a nitrogen atmosphere and the resulting clear solution was evaporated to an oil. The oil was suspended in pentane (10 mL) and evaporated without heating. This step was repeated once with pentane (10 mL) and twice with Et_2O (10 mL). The combined increase in concentration and loss in temperature caused the product to precipitate. Pentane (20 mL) was added to wash the powder, which was vacuum-dried to afford a white solid (isolated yield: 273 mg, 51%). ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.90 (dd, *J* = 12.5, 7.6 Hz, 4 H, PPh_2), 7.78–7.67 (dd, *J* = 8.4, 2.0 Hz, 2 H, Ar-SO_2), 7.61–7.40 (m, 6 H, PPh_2), 7.18 (dd, *J* = 8.4, 2.0 Hz, 2 H, Ar-SO_2), 2.63 (t, $J_{H,H}$ = 7.6 Hz, 2 H, CH_2-Ar), 2.30–2.01 (m, 2 H, Cy), 1.81 (m, 2 H, Cy), 1.73–1.49 (m, 8 H, Cy), 1.73–1.49 (m, 2 H, CH_2CH_2Ar), 1.33 (dt, $J_{H,H}$ = 16.3, 7.3 Hz, 2 H, $CH_2CH_2CH_2$-Ar), 1.17 (m, 10 H, Cy), 0.93 (t, $J_{H,H}$ = 7.3 Hz, 3 H, $H_3CCH_2CH_2$) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ = 20.44 (d, $^1J_{P,P}$ = 314.9 Hz), –4.98 (d, $^1J_{P,P}$ = 314.4 Hz) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 4.08 (CH_3), 22.65 (CH_2CH_3), 26.31 (d, $J_{C,P}$ = 0.8 Hz, 2 C, CH_2 Cy), 27.47 (d, $J_{C,P}$ = 8.9 Hz, 2 C, CH_2 Cy), 27.74 (d, $J_{C,P}$ = 12.4 Hz, 2 C, CH_2 Cy), 30.88 (m, $J_{C,P}$ = 8.9 Hz, 2 C, CH_2 Cy), 32.81 (dd, $^1J_{C,P}$ = 20.54, $^2J_{C,P}$ = 2.91 Hz, 2 C, CH-P Cy), 33.30 (dd, $J_{C,P}$ = 15.8, *J* = 7.4 Hz, 2 C, CH_2 Cy), 33.88 ($CH_2CH_2CH_3$), 35.71 ($ArCH_2CH_2$), 126.02 ($CH_{Ar–SO2}$, 2 C), 128.59 ($CH_{Ar–SO2}$, 2 C), 129.03 (d, $^3J_{C,P}$ = 12.2 Hz, 4 C, *meta*-CH_{PPh2}), 131.30 (dd, $^1J_{C,P}$ = 84.0, $^2J_{C,P}$ = 9.2 Hz, 2 C, *ipso*-$C_{quat\ PPh2}$), 132.51 (d, $^4J_{C,P}$ = 3.1 Hz, 2 C, *para*-CH_{PPh2}), 132.55 (dd, $^2J_{C,P}$ = 9.8, $^3J_{C,P}$ = 6.0 Hz, *ortho*-CH_{ArPPh2}, 4 C), 144.76 (d, $^3J_{C,P}$ = 5.0 Hz, C_{quat}, CSO_2), 146.06 (s, C_{quat}, C-*n*Bu) ppm. MS (FAB^+): *m/z* calcd. for $C_{34}H_{34}O_2NP_2S$ $[M + H]^+$ 594.2725; found 594.2732. $C_{34}H_{34}O_2NP_2S$ calcd. C 68.78, H 7.64, N 2.36; found C 68.76, H 7.73, N 2.38.

Synthesis of Complexes

Synthesis of Complex 6: 4-Bromo-*N*-(1,1,2,2-tetraphenyldiphosphanylidene)benzenesulfonamide (200 mg, 0.331 mmol, 1.01 equiv.) and nickel(II) bromide dimethoxyethane adduct

(101 mg, 0.327 mmol, 1 equiv.) were suspended in toluene (3 mL). The mixture was stirred at 60 °C until complete consumption of nickel(II) bromide dimethoxyethane adduct. A solid formed and the liquid was removed by using a syringe. The precipitate was washed with pentane (3 × 5 mL) and dried under reduced pressure to yield a reddish brown solid (isolated yield: 215 mg, 80%). Crystals suitable for diffraction were obtained by slow diffusion of pentane into a dichloromethane/toluene solution of the product. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.16 (m, 8 H, PPh_2), 7.76 (t, J = 7.3 Hz, 4 H, *para*-ArH), 7.59 (m, 8 H, PPh_2), 7.06 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, $ArSO_2$), 6.18 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, $ArSO_2$) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ = 65.52 ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 125.46 (t, $^1J_{C,P}$ = 26.5 Hz, 4 C, C_{quat}, *ipso*-C_{PPh2}), 125.63 (C_{quat}, C-Br), 128.81 (CH_{ArSO2}, 2 C), 129.50 (8 C, *meta*-CH_{Ar}), 132.50 (CH_{ArSO2}, 2 C), 134.20 (4 C, *para*-CH_{Ar}), 135.11 (8 C, *ortho*-CH_{Ar}), 137.8 (C_{quat}, C-SO_2) ppm. MS (FAB^+): *m*/*z* calcd. for $C_{30}H_{24}NO_2P_2Br_2SNi$ [M – HBr]$^+$ 741.8701; found 741.8702.

Synthesis of Complex 7: 4-Butyl-*N*-(1,1,2,2-tetraphenyldiphosphanylidene)benzenesulfonamide (200 mg, 0.344 mmol, 1 equiv.) and nickel(II) bromide dimethoxyethane adduct (106 mg, 0.344 mmol, 1 equiv.) were suspended in benzene (2 mL). The mixture was stirred at 65 °C until complete consumption of nickel(II) bromide dimethoxyethane adduct (1 h). A solid formed and the liquid was removed by using a syringe. The precipitate was washed with pentane (3 × 5 mL) and dried under reduced pressure to yield a brown solid (isolated yield: 188 mg, 68%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.91–5.91 (m, 24 H, ArH), 2.72–2.24 (m, 2 H, $CH_3CH_2CH_2CH_2CAr$), 1.51 (m, 2 H, $CH_3CH_2CH_2CH_2CAr$), 1.31 (m, 2 H, $CH_3CH_2CH_2CH_2CAr$), 0.95 (m, 3 H, $CH_3CH_2CH_2CH_2CAr$) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ = 64.07 ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 13.94 (CH_3), 22.59 (CH_2CH_3), 33.38 ($CH_2CH_2CH_3$), 35.69 ($ArCH_2$), 125.58 (t, $^1J_{C,P}$ = 26.7 Hz, C_{quat}, *ipso*-C_{PPh2}), 127.44 ($CH_{Ar–SO2}$, 2 C), 129.24 ($CH_{Ar–SO2}$, 2 C), 129.31 (t, $^3J_{C,P}$ = 6.1 Hz, 8 C, *meta*-CH_{PPh2}), 133.98 (br. s., 4 C, *para*-CH), 135.05 (t, $^2J_{C,P}$ = 6.0 Hz, *ortho*-CH_{PPh2}), 135.94 (C_{quat}, C-*n*Bu), 150.76 (C_{quat}, C-SO_2) ppm. $C_{34}H_{33}Br_2NNiO_2P_2S$ calcd. C 51.04, H 4.16, N 1.75; found C 51.22, H 4.23, N 1.69.

Synthesis of Complex 8: 4-Bromo-*N*-(1,1,2,2-tetraisopropyldiphosphanylidene)benzenesulfonamide (200 mg, 0.427 mmol, 1.01 equiv.) and nickel(II) bromide dimethoxyethane adduct (130 mg, 0.422 mmol, 1 equiv.) were suspended in toluene (3 mL). The mixture was stirred at 60 °C until complete consumption of nickel(II) bromide dimethoxyethane adduct. A solid formed and the liquid was removed by using a syringe. The precipitate was washed with pentane (3 × 5 mL) and dried under reduced pressure to yield a reddish solid (isolated yield: 174 mg, 57%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.97–7.57 (m, 4 H, Ar-SO_2), 2.82 (sept, $^3J_{H,H}$ = 7.0 Hz, 4 H, CH_3CHCH_3), 1.97–1.02 (m, 24 H, CH_3CHCH_3) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ = 111.26 ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 19.82 (d, $^2J_{C,P}$ = 84.82 Hz, 8 C, $CH_{3\ iPr}$), 31.29 (m, 4 C, CH_{iPr}), 125.27 (C_{quat}, C-Br), 129.73 ($CH_{Ar–SO2}$, 2 C), 133.84 ($CH_{Ar–SO2}$, 2 C), 138.41 (C_{quat}, C-SO_2) ppm. $C_{18}H_{32}Br_3NNiO_2P_2S$ calcd C 31.48, H 4.70, N 2.04; found C 31.46, H 4.87, N 1.91.

Synthesis of Complex 9: 4-Butyl-*N*-(1,1-diisopropyl-2,2-diphenyldiphosphanylidene)benzenesulfonamide (400 mg, 0.786 mmol, 1 equiv.) and nickel(II) bromide dimethoxyethane adduct (266 mg, 0.864 mmol, 1.1 equiv.) were dissolved in dichloromethane (20 mL) and stirred for 5 min at room temp. The red solution was passed through a glass filter and the filtrate was evaporated to dryness. The solid was washed with pentane (3 × 10 mL) and dried under reduced pressure to afford a red powder (isolated yield: 350 mg, 61%). Crystals suitable for diffraction were obtained by slow diffusion of pentane into a dichloromethane/toluene solution of the product. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.77–6.21 (m, 14 H, Ar), 3.29 (m, 4 H, CH_3CHCH_3 and CH_2Ar), 2.43 (m, 2 H, CH_2CH_2Ar), 1.66–1.00 (m, 14 H, CH_3CHCH_3 and $CH_3CH_2CH_2CH_2Ar$), 0.78 (t, $^3J_{H,H}$ = 7.8 Hz, 3 H, $CH_3CH_2CH_2CH_2Ar$) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ = 117.10 (d, $^2J_{P,P}$ = 119.6 Hz), 61.16 (d, $^2J_{P,P}$ = 121.4 Hz) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 13.78 (CH_3 *n*Bu), 18.15 (d, $^2J_{C,P}$ = 3.0 Hz, 2 C, $CH_{3\ iPr}$), 18.46 (d, $^2J_{C,P}$ = 2.0 Hz, 2 C, $CH_{3\ iPr}$), 22.33 (CH_2CH_3), 29.62 (d, $^2J_{C,P}$ = 16.8 Hz, 2 C, CH_{iPr}), 33.23 ($CH_2CH_2CH_3$), 35.66 ($ArCH_2$), 126.57 (d, $^1J_{C,P}$ = 53.2 Hz, 2 C, *ipso*-$C_{quat\ PPh2}$), 127.93 ($CH_{Ar–SO2}$, 2 C), 133.68 (d, $^4J_{C,P}$ = 3.0 Hz, 2 C, *para*-CH_{PPh2}), 135.46 (d, $^2J_{C,P}$ = 12.6 Hz, 4 C, *ortho*-CH_{PPh2}), 136.05 (C_{quat}, C-*n*Bu), 151.64 (C_{quat}, C-SO_2) ppm. $C_{28}H_{37}Br_2NNiO_2P_2S$ calcd C 45.94, H 5.09, N 1.91; found C 45.89, H 4.96, N 1.86.

Synthesis of Complex 10: 4-Butyl-*N*-(1,1-dicyclohexyl-2,2-diphenyldiphosphanylidene)benzenesulfonamide (98 mg, 0.165 mmol, 1.02 equiv.) and nickel(II) bromide dimethoxyethane adduct (50 mg, 0.162 mmol, 1 equiv.) were dissolved in dichloromethane and stirred for 2 h at room temp. The red solution was passed through a glass filter and the filtrate was evaporated to dryness. The solid was washed with pentane (3 × 5 mL) and dried under reduced pressure to afford a red powder (isolated yield: 73 mg, 54%). Crystals suitable for diffraction were obtained by slow diffusion of pentane into a dichloromethane/toluene solution of the product. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ = 108.15 (d, $^2J_{P,P}$ = 118.6 Hz), 60.28 (d, $^2J_{P,P}$ = 119.2 Hz) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 13.93 (CH_3), 22.64 (CH_2CH_3), 25.94 (2 C, $CH_{2\ Cy}$), 26.87 (d, $J_{C,P}$ = 12.5 Hz, 2 C, $CH_{2\ Cy}$), 27.22 (d, $J_{C,P}$ = 13.4 Hz, 2 C, $CH_{2\ Cy}$), 28.57 (2 C, $CH_{2\ Cy}$), 28.88 (d, $J_{C,P}$ = 4.0 Hz, 2 C, $CH_{2\ Cy}$), 33.43 ($CH_2CH_2CH_3$), 35.87 ($ArCH_2$), 38.77 (d, $J_{C,P}$ = 15.2 Hz, 2 C, CH_{Cy}), 126.96 (d, $^1J_{C,P}$ = 53.9 Hz, 2 C, *ipso*-$C_{quat\ PPh2}$), 128.15 ($CH_{Ar–SO2}$, 2 C), 128.92 (d, $^3J_{C,P}$ = 12.5 Hz, 4 C, *meta*-CH_{PPh2}), 129.94 ($CH_{Ar–SO2}$, 2 C), 133.78 (d, $^4J_{C,P}$ = 2.9 Hz, 2 C, *para*-CH), 135.68 (d, $^2J_{C,P}$ = 12.5 Hz, 4 C, *ortho*-CH), 136.61 (C_{quat}, C-*n*Bu), 151.74 (C_{quat}, C-SO_2) ppm. MS (FAB^+): *m*/*z* calcd. for $C_{34}H_{45}Br_2NO_2P_2SNi$ $[M]^+$ 811.0354; found 811.0337. $C_{34}H_{45}Br_2NO_2P_2SNi$calcd C 50.28, H 5.58, N 1.72; found C 47.23, H 5.90, N 1.64.

Synthesis of [1,2-Bis(diphenylphosphanyl)ethane]nickel(II) Dichloride : To a suspension of nickel(II) chloride dimethoxyethane adduct (325 mg, 1.48 mmol, 1 equiv.) in dichloromethane (50 mL) was added a solution of 1,2-bis(diphenylphosphanyl)ethane (653 mg, 1.64 mmol, 1.1 equiv.) dissolved in dichloromethane (20 mL). The mixture was stirred overnight at room temp. to give a red precipitate. The solvents were evaporated under reduced pressure and the powder was washed with pentane (3 × 20 mL) and dried under vacuum to give a dark-red solid (isolated yield: 444 mg, 54%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.15 (t, $^3J_{P,P}$ = 18 Hz, 4 H, CH_2), 7.50–7.63 (m, 12 H, ArH), 7.90–8.02 (m, 8 H, ArH) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ = 57.55 (s) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 28.17 (t, $^1J_{C,P}$ = 25 Hz, 2 C, CH_2), 128.90 (t, $^1J_{C,P}$ = 25 Hz, 4 C, $C_{quat\ PPh2}$), 129.37 (t, $^3J_{C,P}$ = 5.4 Hz, 8 C, *meta*-CH_{PPh2}), 132.25 (s, 4 C, *para*-CH_{PPh2}), 134.05 (t, $^2J_{C,P}$ = 4.7 Hz, 8 C, *ortho*-CH_{PPh2}) ppm.

Synthesis of [1,2-Bis(diisopropylphosphanyl)ethane]nickel(II) Dibromide : To a suspension of nickel(II) bromide dimethoxyethane adduct (324 mg, 1.05 mmol, 1 equiv.) in dichloromethane (20 mL)

was added commercial 1,2-bis(diisopropylphosphanyl)ethane (300 mg, 1 mmol, 1.1 equiv.). The insoluble mixture was stirred for 16 h, then the solvent was evaporated under vacuum. The resulting powder was washed with pentane (4× 10 mL) to remove excess ligand and DME. The resulting powder was dried under vacuum. Isolate yield: 360 mg, 75%. The physical and spectroscopic data of the product were consistent with reported values.[22] ^{1}H NMR (300 MHz, CD_2Cl_2) overlapping signals of CH_2 and *i*Pr. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ = 95.37 (s) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 18.89 (s, CH_3), 20.90 (s, CH_3), 21.68 (t, $^1J_{C,P}$ = 19.3 Hz, CH_2), 28.08 (t, $^1J_{C,P}$ = 13.4 Hz, $CH_{i\mathrm{Pr}}$) ppm. $C_{14}H_{32}Br_2NiP_2$ calcd C 34.97, H 6.71; found C 34.87, H 6.78.

Crystal Structures: CCDC-980069 (for **1**), -980681 (for **4**), -980070 (for **6**), -980071 (for **9**), and -980072 (for **10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Procedure for the Oligomerisation of Ethylene/MAO: A 250 mL reactor was dried under vacuum at 100 °C for 2 h and then pressurised at 5 bar ethylene. The reactor was cooled to room temperature and the ethylene was evacuated, leaving a slight overpressure inside the reactor. Toluene (43 mL) was injected into the reactor and either heated to 45 °C or cooled to 10 °C (for tests at 30 °C) whilst stirring. When the temperature inside the reactor had stabilised, stirring was stopped and a toluene solution of catalyst (10 μmol, 5 mL) was injected, followed by MAO (10% in toluene, 2 mL, 300 equiv.). The reactor was then filled with 30 bar ethylene (ca. 8.3 g) and magnetic stirring was started (t = 0). The reaction ran for 1 h or shorter for very active systems at the desired temperature. The reaction was stopped by closing the ethylene supply and cooling the reactor to 25 °C with moderate stirring. The gas phase was evacuated, quantified (flowmeter) and collected in a 30 L plastic drum by water displacement (stirring the liquid phase was necessary). The drum was shaken with residual water to homogenise the gas phase and it was injected in GC. The reactor was opened, the liquid phase was transferred by pipette to a glass bottle and neutralised with 20% aqueous H_2SO_4. The toluene phase was injected into the GC and analysed.

Supporting Information (see footnote on the first page of this article): Details on single-crystal X-ray crystallography, ^{1}H, ^{13}C and ^{31}P NMR spectra, and elemental analyses of all compounds.

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