

Cationic η^3 -benzyl nickel compounds with diphosphine ligands as catalyst precursors for ethylene oligomerization/polymerization: influence of the diphosphine bite angle [☆]

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Abstract

The oligomerization and/or polymerization of ethylene catalyzed by the cationic η^3 -benzyl complexes $[\text{Ni}(\eta^3\text{-CH}_2\text{C}_6\text{H}_4\text{-}p\text{-CF}_3)(\text{P-P})]^+ \text{BPh}_4^-$ ($\text{P-P} = \text{Pr}_2\text{P}(\text{CH}_2)_n\text{Pr}_2$, $n = 1\text{--}3$) have been studied. The activity of these single component catalysts depends on the length of the $(\text{CH}_2)_n$ bridge of the diphosphine ligand. Thus, the dippm derivative ($n = 1$) displays higher activity than compounds of the dippe ($n = 2$) or dippp ($n = 3$) ligands. The molecular weight of the products is also a function of n , and varies in the order dippm > dippe > dippp, with the former two catalysts giving rise to low molecular weight polyethylenes and the latter to oligomers.

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1. Introduction

During the past decades, considerable advances have been achieved in the design and application of late metal complexes as catalysts for olefin polymerization [1]. While most of these catalysts contain ligands based on hard-donor atoms (N–N, N–O) [2], or mixed hard-soft donors (P–O, P–N) [3], reports on diphosphine-based Ni polymerization catalysts are scarce despite the crucial role that the latter ligands play in homogeneous catalysis [4]. It has been demonstrated that in CO/olefin copolymerization, both the steric properties and the bite angle [5] of the associated diphosphine ligands exert a profound influence on the catalytic activity [4]. These

factors could also be used to modify the catalyst activity from olefin oligomerization to polymerization. Thus, Spencer prepared a series of agostic ethyl complexes of the type $[\text{M}(\text{Et})(\text{P-P})]^+$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$), and showed that the barrier for β -elimination (which is related to polymerization termination by chain-transfer processes) is influenced by the nature of the metal center and the length of the P–P ligand backbone [6]. More recently, Brookhart has reported that in the dimerization of ethylene catalyzed by the palladium complexes $[\text{PdMe}(\text{OEt}_2)(\text{P-P})]^+$, the structure of the catalyst resting state is a function of the length of the polymethylene bridge of the diphosphine [7]. In the present contribution, we report the synthesis of cationic complexes of the type $[\text{Ni}(\eta^3\text{-CH}_2\text{C}_6\text{H}_4\text{-}p\text{-CF}_3)(\text{P-P})]^+ \text{BPh}_4^-$ ($\text{P-P} = \text{bis}(\text{diisopropylphosphino})\text{methane}$ (dippm), **4**; 1,2-bis-(diisopropylphosphino)ethane (dippe), **5**, and 1,3-bis-(diisopropylphosphino)propane (dippp), **6**), along with their behaviour as moderately active single

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component catalysts for the polymerization or the oligomerization of ethylene. We describe some of the main features of this system, focusing on the influence of the diphosphine bite angle on the catalyst performance.

Allyl ligands have found important uses in Ni-catalyzed olefin oligomerization and polymerization reactions, due to their capability of modifying their coordination mode from η^3 to η^1 , providing in this way both a precursor M-alkyl unit and an empty site available for monomer coordination [8]. Although the well-known [9] pseudoallylic benzyl ligands display this feature to a higher degree than conventional allyl groups, it is only recently that Bazan [10a–10c] and others [10d] have taken advantage of this feature, and employed η^3 -benzylnickel complexes as catalyst precursors in olefin polymerization reactions. We have followed a similar approach, introducing an electron withdrawing group (CF_3) in the aromatic ring of the benzyl ligand in order to further destabilize its η^3 binding mode.

2. Results and discussion

The synthesis of the cationic complexes **4–6** has been carried out as outlined on Scheme 1. The oxidative addition of *p*-(trifluoromethyl)benzyl chloride to the Ni(cod)(P–P) complexes afford the corresponding neutral η^1 -benzyl derivatives **1–3** as dark orange–red crystals. The reaction is straightforward for the dippe and dipp complexes **2** and **3**, since the Ni(0) compounds can be generated in situ from Ni(cod)₂ and the appropriate diphosphine. However, very pure samples of Ni(dippm)(cod) and a careful control of the experimental conditions are required for the preparation of **1** (see Section 4). When THF solutions of **1–3** are treated with NaBPh₄, a rapid color change from dark orange to bright orange–yellow takes place, and the corresponding cationic compounds **4–6** are produced in good yields. These cationic derivatives are stable in the solid state for extended periods of time, a valuable property for catalytic applications. In contrast with the NMR spectra of the η^1 -benzyl precursors, which display broad features at room temperature, those of **4–6** exhibit sharp signals, that are in accord with the η^3 -coordination mode proposed for the benzyl ligand [9]. For example, the methylene ¹³C resonance is shifted by more than 10 ppm

toward low field as compared with that of the neutral precursor, and the corresponding ¹J_{CH} coupling constant increases to ca 155–160 Hz. Like other η^3 -benzyl complexes, the aromatic signals in the ¹H and the ¹³C{¹H} spectra of **4–6** suggest higher symmetry than expected, as a consequence of a fast suprafacial shift of the Ni(P–P) fragment between the two possible η^3 -benzyl coordination sites [9c,11].

The pseudoallylic coordination of the benzyl ligand has been confirmed by an X-ray diffraction study of compound **4**. Fig. 1 shows an ORTEP view of the cationic moiety of this compound. The main feature of this structure is the distortion of the square planar geometry of the Ni atom, illustrated by the small values of the P1–Ni–P2 (77.59(2)°) and C(1)–Ni–C(3) (71.13(9)°) angles,

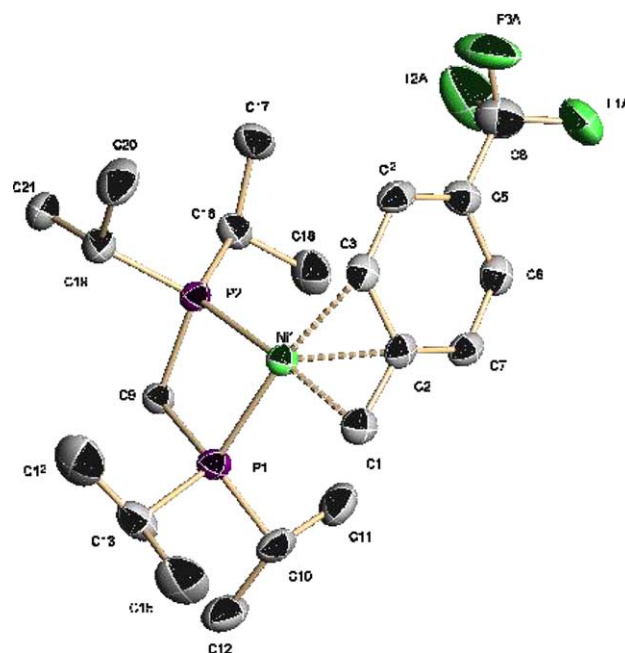
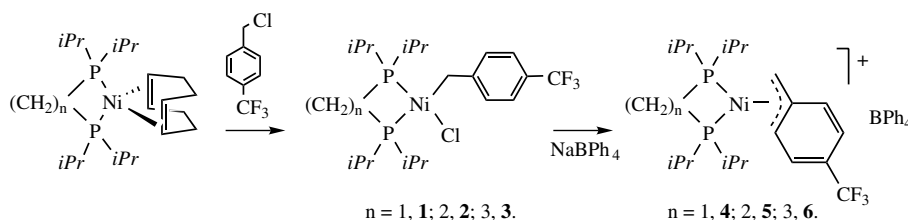


Fig. 1. View of the molecular structure of the cationic part of complex **4** together with the atomic numbering system. Selected bond distances (Å) and angles (°): Ni–C(1) 1.981(2), Ni–C(2) 2.044(2), Ni–C(3) 2.185(2), Ni–P(1) 2.1430(6), Ni–P(2) 2.2015(6), C(1)–C(2) 1.421(3), C(2)–C(3) 1.420(3), C(2)–C(7) 1.422(3); C(1)–Ni–C(3) 71.13(9), C(1)–Ni–P(1) 97.90(7), P(1)–Ni–P(2) 77.59(2), P(2)–Ni–C(3) 113.42(6), C(1)–C(2)–C(3) 117.6(2), Ni–C(3)–C(2) 65.11(11), P(1)–C(9)–P(2) 95.30(11). Angle between planes C(1)–C(2)–C(3) and Ni–P(1)–P(2)–C(1)–C(3): 72.45(1).



Scheme 1.

which are imposed by the η^3 -benzyl and dippm ligands. Notwithstanding this, bond distances within the pseudoallylic unit are comparable to those found in other structurally characterized pseudoallylic complexes of Ni [8c,9,10b,10d], and provide no evidence for a weakening of the metal-ligand π interaction. In fact, the interaction between the pseudoallyl ligand and the metal center appears to be more symmetrical than usual in this type of complex (e.g., the C(1)–C(2) and C(2)–C(3) bond distances are identical (1.421(3) and 1.420(3) Å), suggesting that η^3 -coordination could be somewhat more favoured in cationic benzylnickel compounds than in related neutral derivatives.

The catalytic activity of complexes **4–6** has been tested in CH_2Cl_2 and THF, at a constant ethylene pressure of 4 bar, in the absence of any cocatalyst. Table 1 summarizes the results of these reactions. As the catalysts display low to moderate activities, the experiments were conducted over long periods of time (24 h), with continuous monitoring of the ethylene consumption. Preliminary experiments showed that changes in the ethylene pressure within the 2–8 bar range have little impact on the activity of the three catalysts. The catalytic activity of **5** and **6** is at its maximum nearby 40 °C (entries 3–6), but catalyst **4** becomes rapidly deactivated at this temperature in CH_2Cl_2 .

In all cases, the consumption of ethylene was preceded by an induction period of up to 180 min. Similar induction periods have been observed in ethylene oligomerization reactions catalyzed by Ni complexes, and have been attributed to the slow rate of the first ethylene insertion reaction, leading to the active species [12]. This time interval is followed by a period of 18–20 h of ethylene consumption, which may show spells of inactivity, probably as a consequence of the slowness of the activation process, which seems to be comparable to the catalyst life time. Since the activation period and the life time of the catalyst are different in each experiment, instead of using absolute productivities, the catalytic activities should be better expressed in terms of the maximum activity achieved (calculated from the slope of the consumption curves) or as the average value extended over the time during which the catalyst remains active.

As can be seen in Table 1, the catalytic activities are strongly influenced by the size of the polymethylene spacer of the diphosphine ligands. Thus, the dippm complex **4** is significantly more active than the dippe and dipp derivatives, **5** and **6**, respectively. This result is not entirely unexpected, as ligands with small bite angles have been found to give high activities in other Ni-based oligomerization or polymerization systems [13]. The three catalysts retain a significant activity even in a potentially coordinating solvent such as THF.

The bite angle of the diphosphine also affects the molecular weight of the products. While the dippm

Table 1
Ethylene oligomerization and polymerization with catalysts **4–6**^a

Entry	Catalyst	Solvent	Temp (°C)	Polyethylene yield (mg) ^b	Oligomers yield (mg) ^c	M_n	M_w	PDI	Branches per 1000 carbons	Maximum TOF ^d	Catalyst life ^e (h)	Average TOF ^f
1	4	THF	25	690	170	3162/794			12	187	18.2	63.7
2	4	CH_2Cl_2	25	1610	0	10,126	18,455	1.82	5.9	230	13.9	165
3	4	THF	40	367	262	1359	2425	1.78	13.6	197	20.8	67.9
4	4	CH_2Cl_2	40	208	10	1734	3308	1.91	6.5	538	3.3	130
5	5	THF	40	107	10	1230	2057	1.93	9.1	20.4	21.1	11.1
6	5	CH_2Cl_2	40	210	0	1080	2161	2.00	4.5	66.2	19.8	19.6
7	6	THF	40	0	15	78				74.6	15.0	22.8
8	6	CH_2Cl_2	40	0	45	79				47.6	14.0	19.8

^a $P = 4$ bar. Catalyst concentration 1.2 mM.

^b Mg of the precipitated polymer, filtered from solution.

^c Mg of the soluble fraction of oligomers, obtained as the solution is evaporated to dryness.

^d The maximum activity observed in each polymerization experiment.

^e Time during which some activity is observed.

^f It is the activity extended to all the catalyst life (mol ethylene/(mol catalyst* h)).

derivative, **6**, only produces C₄–C₂₂ oligomers with a Schulz–Flory distribution curve characterized by $\alpha = 0.46$ (as determined by GC), compounds **4** and **5** catalyze the formation of low molecular weight polyethylenes, the higher molecular weight being produced by the latter catalyst. The ¹H NMR spectra of the oligomers or polymers display signals in the 4.8–5.9 ppm region, due to terminal or internal vinyl groups. The intensities of these signals allow M_n estimations that are consistent with the values obtained from GPC measurements. In addition, the ¹H and ¹³C NMR spectra of the polymers obtained with **3** and **4** reveal that these are slightly branched (5–15 Me groups/1000 C).

The polymers obtained in THF display somewhat larger number of branches and lower M_n than those produced in CH₂Cl₂. This effect might be due to THF coordination to Ni, since it is known that SHOP oligomerization catalysts can shift their activity to polymerization when strong ligands (e.g., PPh₃) are removed from the reaction medium. A second difference between the products obtained in CH₂Cl₂ and THF relates to the generation in the latter solvent of a significant fraction of soluble oligomers, especially in the case of **4**. As the polydispersity of the polyethylene insoluble fraction does not depend appreciably upon the solvent used ($M_w/M_n = 1.8$ – 2.0), the formation of soluble oligomers in THF suggests a bimodal molecular weight distribution of the product, even though the higher molecular weight fraction separates because of its lower solubility. The formation of oligomers increases at lower temperatures, and thus the GPC curve of the product obtained from **4** at 25 °C in THF displays two peaks with $M_n = 3162$ and 794, respectively, due to incomplete separation of the abundant low-molecular weight fraction. The bimodal molecular weight distribution suggests that in donor solvents the catalyst may operate through two competing mechanisms.

3. Conclusions

The cationic η^3 -benzylcomplexes [Ni(η^3 -CH₂C₆H₄-*p*-CF₃)(P–P)]⁺ BPh₄[–] **4–6** catalyze the oligomerization and/or polymerization of ethylene with moderate activity. The catalytic activity and the molecular weight of the products produced by these complexes are dependent on the bite angle of the diphosphine ligand attached to the metal center. Thus, the ligand dippp with the widest bite angle gives rise to oligomers, whereas the dippe and dippm complexes produce low molecular weight polymers. The activity of the dippm complex is significantly higher than those of the dippe and dippp ligands. The ethylene uptake curves reveal that the start of the catalytic process is preceded by an induction period that suggests the existence of a slow initiation process. Further studies to determine the mechanism of

the polymerization reaction and to improve the activity of the catalysts are currently under way.

4. Experimental

Microanalyses were performed by the Analytical Service of the Instituto de Investigaciones Químicas. The spectroscopic instruments used were Bruker Model Vector 22 for IR spectra, and Bruker DPX-300, DRX-400 and DRX-500 for NMR spectroscopy. The ¹³C resonance of the solvent was used as an internal standard, but chemical shifts are reported with respect to SiMe₄. The ¹³C{¹H} NMR assignments were helped in all cases with the use of gate-decoupling and two dimensional techniques. ³¹P{¹H} NMR shifts are referenced to external 85% H₃PO₄. All preparations and other operations were carried out under oxygen-free nitrogen by conventional Schlenck techniques. Solvents were dried and degassed before use. The phosphines PMe₃, Pr₂ⁱPCH₂CH₂Pr₂ⁱ (dippe) and Pr₂ⁱPCH₂CH₂CH₂PPri₂ⁱ (dippm) were prepared according to literature methods.

5. Ni(η^1 -CH₂C₆H₄-*p*-CF₃)Cl(dippm), **1**

(a) Synthesis of Ni(dippm)(cod): 0.26 ml (1 mmol) of dippm were added to a suspension of 275 mg (1 mmol) of Ni(cod)₂ in 30 ml of toluene, cooled at –80 °C. The mixture was stirred at room temperature for 1 h and the solvent was evaporated under reduced pressure. The residue was extracted with 30 ml of Et₂O and filtered. After concentration and cooling to –20 °C, pale yellow crystals of the complex Ni(dippm)(cod) were obtained. Yield: 43%. Anal. Calc. for C₂₁H₄₂P₂Ni: C, 60.8; H, 10.2. Found: C, 60.7; H, 10.2. ¹H NMR (C₆D₆, 20 °C) δ 1.04 (m, 24H, CH₃), 1.82 (t, 2H, ²J_{HP} = 6.8 Hz, CH₂–P), 2.36 (m, 4H, CH), 1.77 (m, 4H, CHH), 2.56 (m, 4H, CHH) 4.85 (s, 4H, =CH); ³¹P{¹H} NMR (C₆D₆, 20 °C) δ 17.2 (s); ¹³C{¹H} NMR (C₆D₆, 20 °C) δ 18.7 (s, CH₃), 18.9 (s, CH₃), 25.9 (t, ¹J_{CP} = 14 Hz, CH₂), 26.3 (t, ¹J_{CP} = 6 Hz, CH), 32.1 (t, ³J_{CP} = 4 Hz, CH₂), 77.5 (t, ²J_{CP} = 3 Hz, =CH).

(b) Synthesis of **1**: To a solution of 207 mg (0.50 mol) of Ni(dippm)(cod) in 5 ml of toluene at –80 °C, 75 μ l (0.50 mmol) of *p*-trifluoromethylbenzyl chloride were added. The mixture was stirred for 24 h at room temperature and the solvent was evaporated to dryness. The residue was extracted with Et₂O, filtered and the solution concentrated under reduced pressure and cooled to –20 °C. Complex **1** was collected in \approx 60% yield as an orange powder, although the samples were always contaminated with minor amounts (less than 5%) of unknown impurities that could not be removed by recrystallization. ¹H NMR (C₆D₆, 20 °C) δ 0.91 (dd,

12H, $^3J_{\text{HP}} = 20.1$ Hz, $^3J_{\text{HH}} = 6.6$ Hz, CH₃), 1.10 (dd, 12H, $^3J_{\text{HP}} = 15.8$ Hz, $^3J_{\text{HH}} = 7.1$ Hz, CH₃), 1.24 (t, 2H, $^2J_{\text{HP}} = 8.4$ Hz, CH₂), 1.72 (m, 4H, CH), 2.70 (s, 2H, CH₂), 7.41 (d, 2H, $^3J_{\text{HH}} = 8.1$ Hz, C_{ar}H), 7.76 (d, 2H, $^3J_{\text{HH}} = 8.0$ Hz, C_{ar}H); $^{31}\text{P}\{^1\text{H}\}$ NMR (C₆D₆, 20 °C) δ -11.3 (bs), 8.7 (bs); $^{13}\text{C}\{^1\text{H}\}$ NMR (C₆D₆, 20 °C) δ 16.4 (t, $^1J_{\text{CP}} = 18$ Hz, CH₂), 17.8 (s, CH₃), 18.8 (s, CH₃), 19.6 (m, CH₂), 24.2 (d, $^1J_{\text{CP}} = 9$ Hz, CH), 24.3 (d, $^1J_{\text{CP}} = 9$ Hz, CH), 123.4 (q, $^2J_{\text{CF}} = 32$ Hz, C_{ar}-CF₃), 124.6 (s, C_{ar}H), 126.1 (q, $^1J_{\text{CF}} = 271$ Hz, CF₃), 128.4 (s, C_{ar}H), 154.3 (s, C_{ar}).

6. Ni(η^1 -CH₂C₆H₄-*p*-CF₃)Cl(P^{^A}P) (P^{^A}P = dippe, 2; dippp, 3)

To a suspension of Ni(cod)₂ (275 mg, 1 mmol) in toluene (50 ml) cooled at -78 °C, the appropriate dipphosphine (dippe: 0.31 ml, 1 mmol or dippp: 0.29 ml, 1 mmol) was added, and the mixture was stirred for 15 min at room temperature. *p*-Trifluoromethylbenzyl chloride (0.15 ml, 1 mmol) was then added, and the mixture stirred overnight. The solvent was pumped off and the residue extracted with Et₂O. The volume was reduced under vacuum and the concentrated solution is kept at -20 °C until crystallization.

2: Dark orange crystals, 63% yield. Anal. Calc. for C₂₂H₃₈ClF₃P₂Ni: C, 51.2; H, 7.4. Found: C, 50.8; H, 7.1. ^1H NMR (C₆D₆, 20 °C) δ 1.14 (dd, 6H, $^3J_{\text{HP}} = 12.5$ Hz, $^3J_{\text{HH}} = 7.0$ Hz, CH₃), 1.31 (m, 18H, CH₃), 1.40 (m, 2H, CH₂), 1.69 (m, 2H, CH₂), 2.24 (m, 2H, CH), 2.33 (m, 2H, CH), 2.40 (t, 2H, $^3J_{\text{HP}} = 6.7$ Hz, CH₂), 7.28 (d, 2H, $^3J_{\text{HH}} = 8.1$ Hz, C_{ar}H), 7.52 (d, 2H, $^3J_{\text{HH}} = 8.0$ Hz, C_{ar}H); $^{31}\text{P}\{^1\text{H}\}$ NMR (C₆D₆, 20 °C) AX spin system, $\delta_{\text{A}} = 74.6$, $\delta_{\text{X}} = 84.8$, $J_{\text{AX}} = 16$ Hz; $^{13}\text{C}\{^1\text{H}\}$ NMR (C₆D₆, 20 °C) δ 17.8 (dd, $^1J_{\text{CP}} = 19$ Hz, $^2J_{\text{CP}} = 11$ Hz, CH₂), 18.6 (s, CH₃), 18.7 (s, CH₃), 20.0 (d, $^2J_{\text{CP}} = 3$ Hz, CH₃), 20.5 (s, CH₃), 23.1 (t, $J_{\text{CP}} = 24$ Hz, CH₂), 24.7 (d, $^1J_{\text{CP}} = 18$ Hz, CH), 26.0 (d, $^1J_{\text{CP}} = 25$ Hz, CH), 20.1 (dd, $^2J_{\text{CP}} = 65$, 26 Hz, CH₂), 123.6 (q, $^2J_{\text{CF}} = 32$ Hz, C_{ar}-CF₃), 124.2 (d, $J_{\text{CP}} = 3$ Hz, C_{ar}H), 125.8 (q, $^1J_{\text{CF}} = 271$ Hz, CF₃), 128.9 (d, $J_{\text{CP}} = 2$ Hz, C_{ar}H), 153.9 (s, C_{ar}).

3: Purple crystals, 60% yield. Anal. Calc. for C₂₃H₄₀ClF₃P₂Ni: C, 52.2; H, 7.6. Found: C, 51.9; H, 7.2. ^1H NMR (CD₂Cl₂, 20 °C) δ 0.54 (m, 3H, CH₃), 0.72 (m, 3H, CH₃), 1.00 (m, 16H, CH₃ and CH₂), 1.15 (m, 8H, CH₃ and CH₂), 1.18 (m, 2H, CH), 2.10 (m, 2H, CH), 2.78 (d, 2H, $^3J_{\text{HP}} = 2.8$ Hz, CH₂), 7.44 (d, 2H, $^3J_{\text{HH}} = 8.2$ Hz, C_{ar}H), 7.85 (d, 2H, $^3J_{\text{HH}} = 8.1$ Hz, C_{ar}H); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD₂Cl₂, 20 °C) AX spin system, $\delta_{\text{A}} = 16.6$, $\delta_{\text{X}} = 25.8$, $J_{\text{AX}} = 41$ Hz; $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂, 20 °C) δ 16.6 (m, CH₂), 17.5 (s, CH₃), 17.7 (m, CH₂), 17.8 (s, CH₃), 19.3 (s, CH₃), 19.9 (s, CH₃), 21.1 (s, CH₂), 23.9 (d, $^1J_{\text{CP}} = 21$ Hz, CH), 25.5 (d, $^1J_{\text{CP}} = 25$ Hz, CH), 23.1 (dd, $^2J_{\text{CP}} = 63$, 27 Hz, CH₂), 124.0 (q, $^2J_{\text{CF}} = 32$ Hz, C_{ar}-CF₃), 124.4 (d, $J_{\text{CP}} = 3$ Hz, C_{ar}H),

126.1 (q, $^1J_{\text{CF}} = 271$ Hz, CF₃), 130.2 (s, C_{ar}H), 151.0 (s, C_{ar}).

7. Synthesis of complex [Ni(η^3 -CH₂C₆H₄-*p*-CF₃)(P^{^A}P)]⁺[BPh₄]⁻ (P^{^A}P = dippp, 4; dippe, 5; dippp, 6)

To a cooled (-78 °C) solution of Ni(η^3 -CH₂C₆H₄-*p*-CF₃)(Cl)(P^{^A}P) (1 mmol) in 80 ml of anhydrous THF was added NaBPh₄ (340 mg, 1 mmol). After stirring at room temperature for 1 h the solvent was removed in vacuo. The resulting yellow solid was extracted with dichloromethane and this solution was centrifuged to remove the NaCl, taken to dryness and the solid recrystallized.

4: Orange crystals, recrystallized from dichloromethane. 72% yield. Anal. Calc. for C₄₅H₅₆BF₃P₂Ni: C, 68.8; H, 7.2. Found: C, 68.5; H, 7.3. ^1H NMR (CD₂Cl₂, 20 °C) δ 1.01 (dd, 6H, $^3J_{\text{HP}} = 17.4$ Hz, $^3J_{\text{HH}} = 7.4$ Hz, CH₃), 1.10 (dd, 6H, $^3J_{\text{HP}} = 16.7$ Hz, $^3J_{\text{HH}} = 7.1$ Hz, CH₃), 1.27 (dd, 6H, $^3J_{\text{HP}} = 18.0$ Hz, $^3J_{\text{HH}} = 7.2$ Hz, CH₃), 1.28 (dd, 6H, $^3J_{\text{HP}} = 17.1$ Hz, $^3J_{\text{HH}} = 7.0$ Hz, CH₃), 2.00 (m, 2H, CH), 2.32 (m, 2H, CH), 2.50 (dd, 2H, $^2J_{\text{HP}} = 5.9$, 5.3 Hz, CH₂), 2.55 (t, 2H, $^2J_{\text{HP}} = 9.6$ Hz, CH₂-P), 6.25 (d, 2H, $^3J_{\text{HH}} = 7.3$ Hz, C_{ar}H), 7.83 (d, 2H, $^3J_{\text{HH}} = 7.9$ Hz, C_{ar}H); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD₂Cl₂, 20 °C) AX spin system, $\delta_{\text{A}} = 3.8$, $\delta_{\text{X}} = 20.3$, $J_{\text{AX}} = 43$ Hz; $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂, 20 °C) δ 18.9 (s, CH₃), 19.0 (s, CH₃), 20.9 (t, $^1J_{\text{CP}} = 21$ Hz, CH₂), 24.9 (d, $^1J_{\text{CP}} = 13$ Hz, CH), 26.7 (d, $^1J_{\text{CP}} = 18$ Hz, CH), 37.3 (bd, $^2J_{\text{CP}} = 20$ Hz, CH₂), 111.4 (d, $J_{\text{CP}} = 7$ Hz, C_{ar}H), 119.7 (s, C_{ar}), 128.6 (q, $^1J_{\text{CF}} = 32$ Hz, C_{ar}-CF₃), 133.1 (s, C_{ar}H), 124.1 (q, $^1J_{\text{CF}} = 273$ Hz, CF₃).

5: Orange crystals, recrystallized from CH₂Cl₂/Et₂O. 82% yield. Anal. Calc. for C₄₆H₅₈BF₃P₂Ni: C, 69.1; H, 7.3. Found: C, 68.7; H, 7.4. ^1H NMR (CD₂Cl₂, 20 °C) δ 0.83 (dd, 6H, $^3J_{\text{HP}} = 17.2$ Hz, $^3J_{\text{HH}} = 7.2$ Hz, CH₃), 1.09 (dd, 6H, $^3J_{\text{HP}} = 14.2$ Hz, $^3J_{\text{HH}} = 7.0$ Hz, CH₃), 1.17 (dd, 6H, $^3J_{\text{HP}} = 15.4$ Hz, $^3J_{\text{HH}} = 7.0$ Hz, CH₃), 1.51 (dd, 6H, $^3J_{\text{HP}} = 17.1$ Hz, $^3J_{\text{HH}} = 7.2$ Hz, CH₃), 1.61 (m, 2H, CH₂), 1.90 (m, 4H, CH₂ and CH), 2.34 (m, 2H, CH), 2.70 (t, 2H, $^3J_{\text{HP}} = 4.2$ Hz, CH₂), 6.23 (d, 2H, $^3J_{\text{HH}} = 7.7$ Hz, C_{ar}H), 7.86 (d, 2H, $^3J_{\text{HH}} = 7.9$ Hz, C_{ar}H); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD₂Cl₂, 20 °C) δ 84.8 (s), 77.2 (s); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂, 20 °C) δ 18.6 (s, CH₃), 18.9 (s, CH₃), 19.5 (d, $^2J_{\text{CP}} = 4$ Hz, CH₃), 19.5 (m, CH₂), 19.7 (s, CH₃), 22.9 (dd, $^1J_{\text{CP}} = 26$ Hz, $^2J_{\text{CP}} = 13$ Hz, CH₂), 24.7 (d, $^1J_{\text{CP}} = 23$ Hz, CH), 27.7 (d, $^1J_{\text{CP}} = 27$ Hz, CH), 40.4 (dd, $^2J_{\text{CP}} = 209$ Hz, CH₂), 110.8 (s, C_{ar}H), 119.8 (s, C_{ar}), 124.0 (q, $^1J_{\text{CF}} = 272$ Hz, CF₃), 129.0 (q, $^2J_{\text{CF}} = 40$ Hz, C_{ar}-CF₃), 133.0 (s, C_{ar}H).

6: Orange crystals, recrystallized from acetone. Yield 52%. Anal. Calc. for C₄₇H₆₀BF₃P₂Ni: C, 69.4; H, 7.4. Found: C, 69.4; H, 7.4. ^1H NMR (CD₂Cl₂, 20 °C) δ 0.77 (dd, 6H, $^3J_{\text{HP}} = 17.1$ Hz, $^3J_{\text{HH}} = 7.3$ Hz, CH₃), 1.04 (dd, 6H, $^3J_{\text{HP}} = 13.4$ Hz, $^3J_{\text{HH}} = 6.9$ Hz, CH₃), 1.15 (dd, 6H,

$^3J_{\text{HP}} = 16.4$ Hz, $^3J_{\text{HH}} = 7.2$ Hz, CH_3), 1.15 (dd, 6H, $^3J_{\text{HP}} = 15.2$ Hz, $^3J_{\text{HH}} = 7.0$ Hz, CH_3), 1.30 (m, 2H, $\text{CH}_2\text{-P}$), 1.44 (m, 2H, $\text{CH}_2\text{-P}$), 1.63 (m, 2H, CH), 1.75 (m, 2H, CH_2), 2.16 (m, 2H, CH), 2.70 (t, 2H, $^3J_{\text{HP}} = 4.3$ Hz, CH_2), 6.20 (d, 2H, $^3J_{\text{HH}} = 7.6$ Hz, $\text{C}_{\text{ar}}\text{H}$), 7.75 (d, 2H, $^3J_{\text{HH}} = 7.9$ Hz, $\text{C}_{\text{ar}}\text{H}$); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 20 °C) AX spin system, $\delta_{\text{A}} = 15.9$, $\delta_{\text{X}} = 35.2$, $J_{\text{AX}} = 30$ Hz; $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 20 °C) δ 16.3 (dd, $^1J_{\text{CP}} = 23$ Hz, $^3J_{\text{CP}} = 3$ Hz, $\text{CH}_2\text{-P}$), 17.9 (dd, $^1J_{\text{CP}} = 21$ Hz, $^3J_{\text{CP}} = 6$ Hz, $\text{CH}_2\text{-P}$), 18.2 (s, CH_3), 18.8 (s, CH_3), 20.3 (s, CH_3), 20.5 (d, $^2J_{\text{CP}} = 5$ Hz, CH_3), 21.3 (s, CH_2), 25.5 (d, $^1J_{\text{CP}} = 24$ Hz, CH), 29.5 (d, $^1J_{\text{CP}} = 28$ Hz, CH), 40.6 (dd, $^2J_{\text{CP}} = 19$, 10 Hz CH_2), 112.1 (d, $J_{\text{CF}} = 4$ Hz, $\text{C}_{\text{ar}}\text{H}$), 119.5 (s, C_{ar}), 124.3 (q, $^1J_{\text{CF}} = 273$ Hz, CF_3), 129.7 (q, $^2J_{\text{CF}} = 31$ Hz, $\text{C}_{\text{ar}}\text{-CF}_3$), 132.6 (d, $J_{\text{CF}} = 3$ Hz, $\text{C}_{\text{ar}}\text{H}$).

Crystal data for 4: $\text{C}_{45}\text{H}_{56}\text{BF}_3\text{P}_2\text{Ni}$, $M_{\text{r}} = 785.36$, red prism ($0.44 \times 0.37 \times 0.34$ mm) crystallized from CH_2Cl_2 , orthorhombic, space group $P 21 21 21$ (no. 19), $a = 9.5884(5)$ Å, $b = 19.5775(10)$ Å, $c = 22.3413(12)$ Å, $V = 4193.8(4)$ Å³, $Z = 4$, $D_{\text{x}} = 1.244$ Mg/m³, λ (Mo $\text{K}\alpha$) = 0.71073 Å, $\mu = 0.58$ mm⁻¹, $T = 100(2)$ K.

X-ray diffraction data were collected on a Bruker SMART diffractometer equipped with a APEX CCD detector, graphite monochromated Mo $\text{K}\alpha$ radiation, and a Kryoflex low-temperature device. Four sets of frames covering a hemisphere of the reciprocal space were recorded (606, 435, 230 y 100 frames to $\varphi = 0^\circ, 90^\circ, 180^\circ$ and 0° respectively, ω -scans, $\Delta\omega = 0.3^\circ$, time per frame 10 s). Data reduction up to $\theta = 30^\circ$ by program SAINT, corrections for absorption with program SADABS, 27707 reflections measured, 9862 independent, $R_{\text{int}} = 0.0352^{15a}$. Structure solution with direct methods and program SHELXS97, structure refinement on F^2 using program SHELXL97 [14b].

The asymmetric unit of the structure is formed by one mononuclear cationic complex of the π -benzyl Nickel(II) and one anionic molecule of tetraphenylborate. The trifluoromethyl group in the cationic complex π -benzyl Nickel(II) was observed disordered in two positions and the occupancy factors for these two disordered moieties were refined with complementary occupancy factors 0.713/0.287.

All non-hydrogen atoms were refined with anisotropic displacement parameters but some geometric restraints (DFIX command) were necessary for the fluorine–carbon bonds. All the hydrogen atoms were included in the refinement from observed positions and refined, first with free isotropic displacement parameters, and later with free positional and thermal parameters; except for the methyl hydrogens that were included from calculated positions and refined riding on the atoms, which they are bonded with isotropic thermal parameters. Final refinement with 9862 data, nine restraints, and 657 parameters gave $R_1 = 0.0470$, $wR_2 = 0.0670$ (all data), and $R_1 = 0.0380$, $wR_2 = 0.0649$ [$I > 2\sigma(I)$], ($S = 0.928$). Absolute structure parameter, Flack

Table 2
Crystal data and structure refinement for 4

Identification code	Ear1as
Empirical formula	$\text{C}_{45}\text{H}_{56}\text{BF}_3\text{NiP}_2$
Formula weight	785.36
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P 21 21 21$
Unit cell dimensions	
a (Å)	= 9.5884(5)
b (Å)	= 19.5775(10)
c (Å)	= 22.3413(12)
α	= 90°
β	= 90°
γ	= 90°
Volume	4193.8(4) Å ³
Z	4
Density (calculated) (Mg/m ³)	1.244
Absorption coefficient	0.582 mm ⁻¹
$F(000)$	1664
Crystal size	0.44 × 0.37 × 0.34 mm ³
Theta range for data collection	1.38–28.64°
Index ranges	–12 ≤ h ≤ 12, –21 ≤ k ≤ 25, –20 ≤ l ≤ 30
Reflections collected	27,707
Independent reflections	9862 [$R_{\text{int}} = 0.0352$]
Completeness to theta = 28.64	94.5%
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	0.8275 and 0.7838
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9862/9/657
Goodness-of-fit on F^2	0.928
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0380$, $wR_2 = 0.0648$
R indices (all data)	$R_1 = 0.0470$, $wR_2 = 0.0669$
Absolute structure parameter	–0.004(8)
Largest different peak and hole	0.591 and –0.257 e Å ⁻³

parameter $x = -0.004(8)$. The highest residual peak, 0.589 e Å⁻³, and deepest hole, –0.256 e Å⁻³, were located close to the heavier atom Ni and have no chemical sense (Table 2).

8. Polymerization of ethylene by complexes 4–6

General procedure for the polymerization of ethylene of complexes 4–6: A solution of 25 μmol of the corresponding complex (4, 5 or 6) in 2 ml of THF (entries 1, 3, 5 and 7) or dichloromethane (entries 2, 4, 6 and 8) was prepared and stored under a nitrogen atmosphere. This solution was added to a pressure reactor that contained 18 ml of the same solvent under an ethylene pressure of 4 bars and maintained at the work temperature. The solution was stirred for 24 h, during which time the ethylene consumption was monitored continuously. Polymerization was terminated by shutting off the ethylene supply. The supernatant liquid was analyzed by GC and the insoluble polymer formed was filtered off,

dried and weighed. The solvent was then evaporated and the residue was transferred to a vial, and weighed.

9. Supporting information available

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 228266 for Compound **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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