Highly efficient P-N nickel(II) complexes for the dimerisation of ethylene

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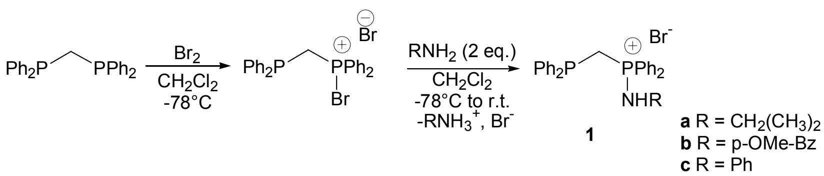
Table of contents

Experimental Section

General: All experiments were performed under an atmosphere of dry nitrogen or argon using standard schlenk and glove box techniques. Solvents were freshly distilled under argon from Na/benzophenone (THF, diethylether, petroleum ether), from P_2O_5 (dichloromethane**,** NEt_3). Bis(diphenylphosphino)methane (DPPM), bis(diphenylphosphino ethane (DPPE), 2,2-dimethylpropylamine, p-methoxybenzylamine, aniline, di(isopropyl)chlorophosphine, iopropylamine, methanol, and MAO solution (10% wt in toluene) were purchased from Aldrich and used without further purification. Ethylene (99.5% pure) was purchased from Air Liquide and *n*-heptane (analytical grade) was purchased from Carlo Erba. $NiBr_2$(DME)[1], ligands **1b,c**[2] and nickel complex **4b**[2] were prepared according to literature procedure. Nuclear magnetic resonance spectra were recorded on Bruker Avance 300 spectrometer operating at 300 MHz for ^{1}H, 75.5 MHz for ^{13}C and 121.5 MHz for ^{31}P. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P are relative to a 85% H_3PO_4 external reference. Coupling constant are expressed in hertz. The following abbreviations are used: b, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; v, virtual. Elemental analyses were performed by the "Service d'analyse du CNRS", at Gif sur Yvette, France**.** Electronic ionization mass spectra (EI-MS) were recorded with a JEOL GCmate instrument.

Synthesis and characterization of ligands 1

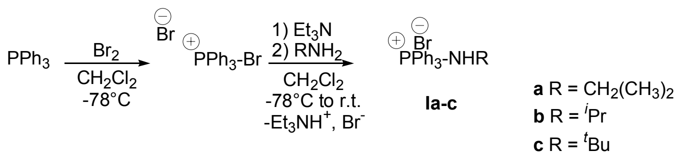


Bromine (80 µL, 1.56 mmol) was added dropwise to a solution of dppm (0.600 g, 1.56 mmol) in CH_2Cl_2 (40 mL) at -78°C. The reaction mixture was stirred for 20 minutes. ^{31}P {^{1}H} (CH_2Cl_2) δ_P –23.2 (d, J_{PP} = 83 Hz), 58.6 (d, J_{PP} = 83 Hz) .

The 2,2-dimethylpropylamine (0.365 mL, 3.12 mmol) was added to the solution of DPPMBr at –78°C. The cold bath was removed and the reaction mixture was stirred for 1h at room temperature. The solution was washed twice with water (20 mL), the organic layer was dried over $MgSO_4$ and the solvent was removed under vacuum to deliver a white solid, which was washed with diethyl ether.

1a (0.584, 74%). $^{31}P\{^1H\}$ ($CDCl_3$) δ_P –30.7 (d, $^2J_{PP}$ = 78.5 Hz), 42.9 (d, $^2J_{PP}$ = 78.5 Hz). ^1H ($CDCl_3$) δ_H 0.76 (9H, s, CH_3), 2.48 (2H, dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 8.0 Hz, $CH_2C(CH_3)_3$), 4.30 (2H, d, $^2J_{PH}$ = 17.0 Hz, PCH_2P), 7.00 (1H, d, $^3J_{HH}$ = 7.0 Hz, N*H*), 7.21 (4H, m, *p*-H (PPh_2)), 7.35 (4H, td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HP}$ = 3.0 Hz, *m*-H (PPh_2)), 7.49 (4H, td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HP}$ = 3.0 Hz, *m*-H (PPh_2)), 7.60 (4H,t, $^3J_{HH}$ = 7.5 Hz, *p*-H (PPh_2)), 7.78 (4H, dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ = 12.5 Hz, *o*-H (PPh_2)). $^{13}C\{^1H\}$ ($CDCl_3$) δ_C 22.7 (J_{CP} not measurable, PCH_2P), 27.3 (s, CH_3), 32.4 (d, $^3J_{CP}$ = 8.0 Hz, $CH_2C(CH_3)_3$), 53.7 (d, $^2J_{CP}$ = 4.5 Hz, $CH_2C(CH_3)_3$), 119.5 (d, ^2J = 98 Hz, $C^{IV}(PPh_2)$), 128.8 (d, $^3J_{CP}$ = 8.0 Hz, *m*-CH (Ph_2P)), 129.4 (d, $^3J_{CP}$ = 13.0 Hz, *m*-CH (Ph_2P)) ,129.6 (s, *p*-CH (Ph_2P)), 133.0 (d, $^2J_{CP}$ = 21 Hz, *o*-CH (Ph_2P)), 133.7 (dd, $^2J_{CP}$ = 10.5 Hz, $^4J_{CP}$ = 3.0 Hz, *o*-CH (Ph_2P)), 134.4 (d, $^4J_{CP}$ = 3.0 Hz, *p*-CH (Ph_2P)), 135.2 (J_{CP} not measurable, $C^{IV}(PPh_2)$). Anal. Calc. for $C_{29}H_{32}BrNP_2$: C, 64.93; H, 6.01 ; N , 2.61. Found : C, 65.06 ; H, 6.22 ; N , 2.47.

Synthesis and characterization of phosphine-aminophosphonium I



Bromine (1.96 mL, 38.13 mmol) was added to a solution of triphenylphosphine (10g, 38.13 mmol) in CH_2Cl_2 (200 mL) at –78°C. While warming to room temperature the solution turned yellow, stirring was pursued 1h. Then, the reaction mixture was cooled to –78°C and Et_3N (5.31 mL, 38.13 mmol) followed by the amine (38.13 mmol) were added. After stirring 2h at room temperature, the solution was washed twice with water (100 mL), the organic layer was dried over $MgSO_4$ and the solution was concentrated under vacuum. After reducing the solvent volume to 50 mL, THF (50 mL) was added, the product precipitated. After removing the CH_2Cl_2, the phosphine-aminophosphonium **Ia-c** was isolated by filtration as a white solid.

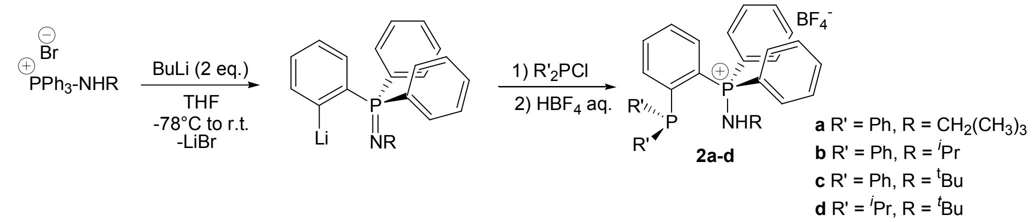
Ia : Yield 92% (7.5 g). $^{31}P\{^1H\}$ ($CDCl_3$) δ 39.2 (s, P). ^1H ($CDCl_3$) δ 0.74 (9H, s, CH_3), 2.82 (2H, dd, $^3J_{HH}$= 8.0 Hz ,$^3J_{HP}$= 10.0 Hz, NCH_2), 7.62 (6H, td, $^3J_{HH}$= 7.5 Hz, $^4J_{HP}$= 4.5 Hz, *m*-H (Ph_3P)), 7.71 (3H, t, $^3J_{HH}$= 7.5, *p*-H (Ph_3P)), 7.86 (6H, dd, $^3J_{HH}$=

7.5 Hz, $^3J_{HP}$= 8.5 Hz, *o*-H (Ph_3P)),NH not seen. ^{13}C {^1H} ($CDCl_3$) δ 27.3 (s, CH_3), 32.7 (d, $^3J_{CP}$= 6.5 Hz, $C(CH_3)_3$), 56.6 (d, $^2J_{CP}$= 1.0 Hz, CH_2), 121.5 (d, $^1J_{CP}$= 102.5 Hz, C^{IV}-(Ph_3P)), 129.9 (d, $^2J_{CP}$= 13.1 Hz, *o*-CH (Ph_3P)), 134.1 (d, $^3J_{CP}$= 10.8 Hz, *m*-CH (Ph_3P)), 134.7 (t, $^4J_{CP}$=2.8 Hz, *p*-CH (Ph_3P)).

Ib : Yield 80% (6.1 g). ^{31}P {^1H} ($CDCl_3$) δ 36.6 (s, P). ^1H ($CDCl_3$) δ 1.35 (6H, d, $^3J_{HH}$= 6.0 Hz, Me), 3.16 (1H, hept d, $^3J_{HH}$= 6.0 Hz,$^3J_{HP}$= 3.0 Hz, CH), 7.20 (1H, b d, $^2J_{HP}$= 10.0 Hz, NH), 7.60 (6H, td, $^3J_{HH}$= 7.5 Hz, $^4J_{HP}$= 3.0 Hz, m-H (Ph_3P)), 7.72 (3H, v t, $^3J_{HH}$= 7.5 Hz, p-H (Ph_3P)), 7.83 (6H, dd, $^3J_{HH}$= 7.5 Hz, $^3J_{HP}$= 6.0 Hz, o-H (Ph_3P)). ^{13}C {^1H} ($CDCl_3$) δ 24.8 (t, $^3J_{CP}$= 13.0 Hz, Me), 47.0 (d, $^2J_{CP}$= 2.0 Hz, CH), 121.8 (d, $^1J_{CP}$= 102.0 Hz, C^{IV}-(Ph_3P)), 129.7 (d, $^3J_{CP}$= 13.0 Hz, m-CH (Ph_3P)), 133.6 (t, $^2J_{CP}$= 11.0 Hz, o-CH (Ph_3P)), 134.6 (t, $^4J_{CP}$=3.0 Hz, p-CH (Ph_3P)).

Ic : Yield 76% (6.0 g). ^{31}P {^1H} ($CDCl_3$) δ 34.2 (s, P). ^1H ($CDCl_3$) δ 1.27 (9H, s, tBu), 7.14 (1H, d, $^2J_{HP}$= 6.5 Hz, NH), 7.58 (6H, td, $^3J_{HH}$= 7.5 Hz,$^4J_{HP}$= 3.5 Hz, *m*-H (Ph_3P)), 7.67 (3H, td, $^3J_{HH}$= 7.6 Hz, $^5J_{HP}$= 2.0 Hz, *p*-H (Ph_3P)), 7.90 (6H, dd, $^3J_{HH}$= 7.0 Hz,$^3J_{HP}$= 1.5 Hz, *o*-H (Ph_3P)). ^{13}C {^1H} ($CDCl_3$) δ 32.2 (d, $^3J_{CP}$= 4.5 Hz, tBu), 56.6 (d, $^2J_{CP}$= 4.5 Hz, C^{IV}), 123.1 (d, $^1J_{CP}$= 102.0 Hz, C^{IV}-(Ph_3P)), 129.6 (d, $^2J_{CP}$= 13.0 Hz, *o*-CH (Ph_3P)), 133.9 (d, $^3J_{CP}$= 11.0 Hz, *m*-CH (Ph_3P)), 134.5 (t, $^4J_{CP}$=3.0 Hz, *p*-CH (Ph_3P)).

Synthesis and characterization of ligands 2



BuLi (3 ;90 mL, 5.84 mmol) was added to a suspension of compound **I** (2.92 mmol) in Et_2O (100 mL) cooled at –78°C. The cold bath was then removed and stirring was pursued 30' at room temperature leading to a clear yellow solution. The formation of the anion was ascertained by NMR ^{31}P. Then, the reaction mixture was cooled to –78°C, the chlorophosphine (2.92 mmol) was added and a white precipitate appeared. After stirring 2h at room temperature, diethyl ether was removed under vaccum, CH_2Cl_2 (50 ml) was added, the solution was washed with a aqueous solution of tetrafluoroboric acid (1 M, 30mL) and twice with a saturated aqueous solution of $NaBF_4$ (20 mL). the organic layer was dried over $MgSO_4$ and the solution was concentrated under vacuum, the obtained white solid was washed with diethyl ether (20 mL).

2a (1.41, 78%). $^{31}P\{^1H\}$ ($CDCl_3$) δ_P –15.8 (d, $^2J_{PP}$ = 24.5 Hz), 41.3 (d, $^2J_{PP}$ = 24.5 Hz). ^1H ($CDCl_3$) δ_H 0.76 (9H, s, CH_3), 2.78 (2H, dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 7.5 Hz, $CH_2C(CH_3)_3$), 4.90 (1H, vt, $^3J_{HH}$ = 7.0 Hz, N*H*), 6.80 (4H, dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ = 8 Hz, *o*-H (PPh_2)), 7.20 (4H, vt, $^3J_{HH}$ = 7.5 Hz, *m*-H (PPh_2)), 7.30 (2H, t, $^3J_{HH}$ = 7.5 Hz, *p*-PPh_2), 7.49 (6H,m, PPh_2 et H-(ArPP)), 7.62 (2H, vt, $^3J_{HH}$ = 8.0 Hz, *p*-H (PPh_2)), 7.76 (4H, dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ = 7.5 Hz, *o*-H (PPh_2)), 7.82 (1H, m, H-(ArPP)), 8.16 (1H, dd, $^3J_{HH}$ = 7.5 Hz, J_{HP} = 8.0 Hz, H-(ArPP)). $^{13}C\{^1H\}$ ($CDCl_3$) δ_C 26.9 (s, CH_3), 32.4 (s, $C(CH_3)_3$), 54.7 (s, $CH_2C(CH_3)_3$), 121.0 (d, $^2J_{CP}$ = 109.0 Hz, C^{IV}(PPh_2)), 128.7 (d, $^3J_{PC}$ = 7.0 Hz, *m*-CH (Ph_2P)), 129.2 (d, $^2J_{CP}$ = 13.0 Hz, CH-(ArPP)), 129.4 (s, *p*-CH (Ph_2P)) ,129.7 (d, $^2J_{CP}$ = 13.5 Hz, *o*-CH (Ph_2P)), 131.6 (dd, $^2J_{CP}$ = 12.5 Hz, $^3J_{CP}$ = 10.5, CH-(ArPP)), 132.9(d, $^3J_{CP}$ = 7.5 Hz, *m*-CH (Ph_2P)), 133.8 (dd, $^2J_{CP}$ = 10.5 Hz, $^3J_{CP}$ = 3.0 Hz, *o*-CH (Ph_2P)), 134.9 (d, $^4J_{CP}$ = 2.5 Hz, *p*-CH (Ph_2P)), 135.2 (J_{CP} not measurable, C^{IV}(PPh_2)), 136.7 (dd, $^3J_{CP}$ = 9.5 Hz, $^2J_{CP}$ = 10.0 Hz, CH-(ArPP)). Anal. Calc. for $C_{35}H_{36}BF_4NP_2$: C, 67.87; H, 5,86 ; N , 2.26. Found : C, 68.12 ; H, 5.77 ; N , 1.97.

2b (1.24, 72%). $^{31}P\{^1H\}$ (CH_2Cl_2) δ -15.2 (d, $^3J_{PP}$= 25.5 Hz, $P^{(III)}$), 36.7 (d, $^3J_{PP}$= 25.5 Hz, $P^{(V)}$). ^1H ($CDCl_3$) δ 1.34 (6H, d, $^3J_{HH}$= 6.50 Hz, Me), 3.07 (1H, b s, C*H*), 6.76 (4H, v t, $^3J_{HH}$= 7.5 Hz, m-H (Ph_2P)), 7.16 (4H, v t, $^3J_{HH}$= 7.5 Hz, m-H (Ph_2P)), 7.28 (2H, m, p-H (Ph_2P)), 7.40 (4H, dd, $^3J_{HH}$= 7.5 Hz et $^3J_{HP}$= 11.0 Hz, o-H (Ph_2P)), 7.52 (2H, v t, $^3J_{HH}$= 7.5 Hz, p-H (Ph_2P)), 7.68 (1H, v t, $^3J_{HH}$= 8.0 Hz, H-(ArPP)), 7.83 (1H, m, H-(ArPP), 7.97 (dd, 4H, $^3J_{HH}$= 7.5 Hz et $^3J_{HP}$= 13.0 Hz, o-H (Ph_2P)), 8.40 (1H, mt, $^3J_{HH}$= 8.0 Hz, H-(ArPP)), 8.64 (1H, m, H-(ArPP)), NH not seen. $^{13}C\{^1H\}$ ($CDCl_3$) δ 25.5 (s, Me), 47.5 (s, CH), 123.9 (d, $^1J_{CP}$= 103.0 Hz, C^{IV}), 128.9 (d, $^3J_{CP}$= 6.5 Hz, m-CH-(Ph_2P)), 129.4 (v s, p-CH-(Ph_2P)), 129.6 (d, $^3J_{CP}$=5.5 Hz, m-CH-(Ph_2P)), 130.1 (v t, J_{CP}= 10.0 Hz, CH-(ArPP)), 131.5 (d, J_{CP}= 12.5 Hz, CH-(ArPP)), 133.3 (d, $^2J_{CP}$= 18.5 Hz, o-CH-(Ph_2P)), 134.0 (d, $^2J_{CP}$= 15.5 Hz, o-CH-(Ph_2P)), 134.1 (v s, C^{IV}), 134.6 (v s, p-CH-(Ph_2P)), 135.2 (v s, C^{IV}), 137.4 (d, J_{CP}=12.0 Hz, CH-(ArPP)), 139.0 (d,

J_{CP}= 13.5 Hz, CH-(ArPP)), 141.6 (v s, C^{IV}). Anal. Calc. for $C_{33}H_{32}BF_4NP_2$: C, 67.02; H, 5.45 ; N , 2.37. Found : C, 66.86 ; H, 5.39 ; N , 2.48.

2c (1.49, 84%). $^{31}P\{^1H\}$ ($CDCl_3$) δ -16.7 (d, $^3J_{PP}$ = 23.5 Hz , $P^{(III)}$), 34.9 (d, $^3J_{PP}$ = 23.5 Hz , $P^{(V)}$). ^1H ($CDCl_3$) δ 1.14 (9H, s, tBu), 4.60 (1H, b d, $^2J_{HP}$= 6.5 Hz, NH), 6.70 (4H, dd, $^3J_{HH}$= 7.5 Hz, $^4J_{HP}$= 8.0 Hz, m-H (Ph_2P)), 7.13 (4H, td, $^3J_{HH}$= 7.5 Hz, $^5J_{HP}$= 1.5 Hz, p-Ph_2P), 7.35 (1H, b d, $^3J_{HH}$= 7.5 Hz, H-(ArPP)), 7.42 (4H, td, $^3J_{HH}$= 7.5 Hz, $^4J_{HP}$= 3.5 Hz, m-H (Ph_2P)), 7.53 (4H, dd, $^3J_{HH}$= 7.5 Hz, $^3J_{HP}$= 15.0 Hz, o-H (Ph_2P)), 7.66 (2H, t, $^3J_{HH}$= 7.5 Hz, H-(ArPP)), 7.79 (4H, dd, $^3J_{HH}$= 7.5 Hz, $^3J_{HP}$= 12.0 Hz, H-(ArPP)). $^{13}C\{^1H\}$ ($CDCl_3$) δ_C 32.3 (d, $^3J_{CP}$= 4.0 Hz, CH_3), 57.1 (d, $^2J_{CP}$ = 5.0 Hz, $C(CH_3)_3$), 123.2 (d, $^1J_{CP}$= 104.0 Hz, $^1J_{CP}$= 2.5 Hz, $C^{IV}(Ph_2P)$, 129.1 (d, $^3J_{CP}$= 7.0 Hz, m-CH-(Ph_2P)), 129.2 (s, p-CH-(Ph_2P))d, , 130.0 (d, $^2J_{CP}$= 13.5 Hz, o-CH-(Ph_2P)), 130.3 (dd, $^3J_{CP}$= 5.5 Hz, $^2J_{CP}$= 13.0 Hz, CH-(ArPP)), 131.4 (d, $^3J_{CP}$= 13.0 Hz, CH-(ArPP)), 133.3 0 (d, $^2J_{CP}$= 19.0 Hz, o-CH-(Ph_2P)), 134.3 (d, $^3J_{CP}$= 11.0 Hz, m-CH-(Ph_2P)), 135.0 (d, $^4J_{CP}$= 3.0 Hz, p-CH-(Ph_2P)), 139.3 (b d, $^2J_{CP}$= 12.0 Hz, CH-(ArPP)), 141.6 (dd, $^3J_{CP}$= 14.0 , Hz, $^1J_{CP}$= 20.0, C^{IV}-CH-(Ph_2P)), C^{IV} of ArPP not seen. Anal. Calc. for $C_{34}H_{34}BF_4NP$: C, 67.45; H, 5.66 ; N , 2.31. Found : C, 67.61 ; H, 5.45 ; N , 2.23.

2d (1.18, 75%). $^{31}P\{^1H\}$ ($CDCl_3$) δ -1.8 (d, $^3J_{PP}$ = 18.5 Hz , $P^{(III)}$), 39.3 (d, $^3J_{PP}$ = 18.5 Hz , $P^{(V)}$). ^1H ($CDCl_3$) δ 0.63 (6H, dd, $^3J_{HH}$= 7.0 Hz et $^3J_{HP}$= 14.5 Hz, $CH(CH_3)_2$), 1.00 (6H, dd, $^3J_{HH}$= 7.0 Hz et $^3J_{HP}$= 14.1 Hz, $CH(CH_3)_2$), 1.27 (9H, s, tBu), 1.72 (2H, hept, $^3J_{HH}$= 7.0 Hz, $CH(CH_3)_2$), 5.94 (1H, b d, $^2J_{HP}$= 12.0 Hz, NH), 7.73-7.90 (m, 14H, H-(ArPP) and H-(PPh_2)). $^{13}C\{^1H\}$ ($CDCl_3$) δ 18.5 (d, $^2J_{CP}$= 16 Hz, $CH(CH_3)_2$), 19.4 (d, $^2J_{CP}$= 12 Hz, $CH(CH_3)_2$), 24.8 (d, $^1J_{CP}$= 11 Hz, $CH(CH_3)_2$), 31.4 (d, $^3J_{CP}$= 4 Hz, $C(CH_3)_3$), 56.2 (d, $^2J_{CP}$= 5 Hz, $C(CH_3)_3$), 122.7 (d, $^1J_{CP}$= 101 Hz, C^{IV}-(Ph_2P)), 127.9 (d, J_{CP}= 11 Hz, CH-(ArPP)), 128.6 (d, $^3J_{CP}$=13.5 Hz, m-CH-(Ph_2P)), 129.4 (d, J_{CP}= 14 Hz, CH-(ArPP)), 130.8 (d, J_{CP}= 10 Hz, CH-(ArPP)), 132.7 (d, $^4J_{CP}$= 3 Hz, p-CH-(Ph_2P)), 133.5 (td, $^2J_{CP}$= 13.5 Hz, $^5J_{CP}$= 3 Hz, o-CH-(Ph_2P)), 134.2 (d, J_{CP}= 13 Hz, CH-($C_6H_4P_2$)). C^{IV}-(ArPP) not observed. Anal. Calc. for $C_{28}H_{38}BF_4NP_2$: C, 62.58; H, 7.13 ; N , 2.61. Found : C, 62.39 ; H, 7.22 ; N , 2.41.

Synthesis and characterization of ligands 3

3 was synthesized similarly to **1** using dppe (1g, 2.50 mmol) instead of dppm.

(0.84, 65%). $^{31}P\{^1H\}$ ($CDCl_3$) δ -12.0 (d, $^3J_{PP}$ = 46.0 Hz , $P^{(III)}$), 38.9 (d, $^3J_{PP}$ = 46.0 Hz , $P^{(V)}$). ^1H ($CDCl_3$) δ 6.86 (1H, t, $^3J_{HH}$= 6.5 Hz, H-NPh)7.08 (2H, d, $^3J_{HH}$= 6.5 Hz, H-NPh), 7.30-7.42 (8H, m, H-(Ph_2P)), 7.47 (3H, m, NH and H-NPh), 7.60 (4H, dd, $^3J_{HH}$= 7.5 Hz, J_{PH}= 3.0 Hz, H-(Ph_2P)), 7.70 (2H, t, $^2J_{HH}$= 7.5.0 Hz, H-(Ph_2P)), 7.79 (4H, dd, $^3J_{HH}$= 7.5 Hz, $^3J_{HH}$= 13.5 Hz, H-(Ph_2P)). $^{13}C\{^1H\}$ ($CDCl_3$) δ 19,7 (J not measurable, CH_2P), 23.6 (J not measurable, CH_2P), 119.0 (d, $^1J_{CP}$= 40.0 Hz, C^{IV}-(Ph_2P)), 127.8 (d, J_{CP}= 8.0 Hz, CH-(Ph_2P)), 128,0 (s, CH-(NPh)), 128.6 (s, CH-(NPh)), 129.1 (d, J_{CP}= 13.0 Hz, CH-(Ph_2P)), 129.5 (d, $^1J_{CP}$= 51.0 Hz, C^{IV}-(Ph_2P)), 129.9 (d, J_{CP}=5.0 Hz, CH-(Ph_2P))**,** 131.2 (s, CH-(NPh)), 132.0 (d, J_{CP}= 5.0 Hz, CH-(Ph_2P)), 132.2 (d, J_{CP}= 3.0 Hz, CH-(Ph_2P), 134.0 (dd, J_{CP}= 13.5 Hz, J_{CP}= 3.0 Hz , CH-(Ph_2P)), 140.0 (J not measurable C^{IV}-(NPh)). Anal. Calc. for $C_{32}H_{30}BrNP_2$: C, 67.38; H, 5.30 ; N , 2.46. Found : C, 67.39 ; H, 5.13 ; N , 2.41.

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