Supplementary Material (ESI) for Chemical Communications

Supporting Information

1,2-Addition of Trialkylaluminium Reagents on *N*-Diphenylphosphinoyl-ketimines in the Absence of Any Additional Reagents

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General: ^{1}H-NMR spectra were recorded on a *Bruker* AM 400 (400 MHz) spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to $CHCl_3$ (7.26 ppm) as internal standard. All couplings constants are absolute values and *J* values are expressed in hertz (Hz). The description of signals include: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, ddd = doublet of dd, dt = doublet of triplets and tt = triplet of triplets. The spectra were analyzed according to first order. The signal abbreviations include: Ar-H = aromatic proton. – ^{13}C-NMR spectra were recorded on a *Bruker* AM 400 (100 MHz) spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to $CHCl_3$ (77.4 ppm) as internal standard. The signal structure was analyzed by DEPT and is described as follows: + = primary or tertiary C-atom (positive signal), – = secondary C-atom (negative signal), and q = quaternary C-atom (no signal). – MS (EI) (electron impact mass spectrometry): *Finnigan* MAT 90 (70 eV). The molecular fragments are quoted as the relation between mass and charge (*m/z*), the intensities as a percentaged value relative to the intensity of the base signal (100%). The abreviation [M^+] refers to the Molecul-Ion. – IR (infrared spectroscopy): FT-IR *Bruker* IFS 88. IR spectra of solids were recorded in KBr, and as thin films on KBr for oils and liquids. The deposit of the absorption band was given in wave numbers $\tilde{\nu}$ in cm^{-1}. The forms and intensities of the bands were characterized as follows: vs = very strong 0–10% T, s = strong 10–40% T, m = medium 40–70% T, w = weak 70–90% T, vw = very weak 90–100% T, br = broad. – Elemental analysis: *Elementar* Vario Microcube. Descriptions without nominated temperature were done at room temperature (rt), and the following abbreviations were used: *calcd.* (theoretical value), *found* (measured value). Information is given in masspercent. – Routine monitoring of reactions were performed using Silica gel coated aluminium plates (Merck, silica gel 60, F_{254}), which analysed under UV-light at 254 nm and/or dipped in a solution of molybdato phosphate (5% phosphor molybdic acid in ethanol, dipping solution) and potassium permanganate (0.45 g potassium permanganate and 2.35 g of sodium carbonate in 90 ml of water, dipping solution) and heated with a heatgun. Solvent mixtures are understood as volume/volume. Solid materials were powdered. Solvents, reagents and chemicals were purchased from Aldrich, Fluka, Janssen, and Merck. Tetrahydrofuran was distilled from sodium/benzophenone under argon prior use. Dichloromethane, ethyl acetate and diethyl ether were distilled from calcium hydride. All reactions involving moisture sensitive reactants were executed under an argon atmosphere using oven dried and/or flame dried glassware. All other solvents, reagents and chemicals were used as purchased unless stated otherwise.

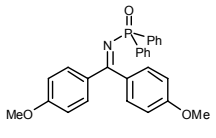
General procedure for the preparation of *N*-diphenylphosphinoylketimines.[1] To a stirred solution of the corresponding oxime (10 mmol) and triethylamine (20 mmol) in 20 mL of *n*-pentane/dichloromethane (1:1), diphenylchlorophosphine (10 mmol) was slowly added over 15 min at –78 °C. After the addition was completed, the temperature was gradually increased to room temperature within 1 h and the mixture was allowed so stir overnight. When the reaction was finished the mixture was filtered through Celite® and the filtrate was washed with water and brine. The residue was subjected to column chromatography (ethyl acetate/ dichloromethane, 1:10-1:5). The product was further repurified by recrystallisation from hexane/dichloromethane.

[1] S. Masumoto, H. Usuda, M. Suzuki, M. Kanai and M. Shibasaki, *J. Am. Chem. Soc.* **2003**, *125*, 5634.

General procedure for the addition of trialkylaluminium reagents to *N*-diphenylphosphinoylketimines. Under a dry argon atmosphere, the corresponding imine (0.5 mmol) was dissolved in 1.0 mL of dry toluene and stirred for 0.5 h at room temperature to give a homogenous solution. Then $AlEt_3$ or $AlMe_3$ (4.00 mmol), used as a 1 M solution in toluene or hexane, was added under argon and stirred for the indicated time. After all of the starting material was consumed, the mixture was quenched by addition of methanol and saturated solution of K-Na-tartrate. The aqueous layer was extracted with ethyl acetate (3 × 5 mL), dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure. The products were obtained in high purity without further purification.

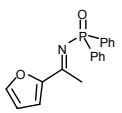
Characterization of compounds

N-(bis(4-methoxyphenyl)methylene)-P,P-diphenylphosphinic amide (**5**):



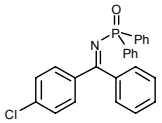
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.96-7.90 (m, 4 H, P(=O)-Ar$_o$-H), 7.56-7.54 (m, 4 H, CN-Ar$_o$-H), 7.44-7.36 (m, 6 H, P(=O)-Ar$_m$-H u. Ar$_p$-H), 6.89-6.87 (m, 4 H, CN-Ar$_m$-H), 3.85 (s, 6 H, 2 × OCH_3) ppm – ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 180.72 (+, d, CN, *J* = 7.7 Hz), 162.10 (C_q, 2 × *C*-OCH_3), 136.26 (C_q, *C*-CN), 134.96 (C_q, *C*-CN), 132.53 [C_q, *C*-P(=O)], 131.93 [(+, 2 × *C*2- u. *C*6-P(=O)-Ar], 131.60 u. 131.51 [(+, 2 × *C*4-P(=O)-Ar], 130.92 u. 130.90 [(+, 2 × *C*3- u.*C*5-P(=O)-Ar], 128.21 u. 128.08 [(+, 2 × *C*2- u. *C*6-Ar-CN], 113.09 [(+, 2 × *C*3- u. *C*5-Ar-CN], 55.33 (+, 2 × *C*H_3) ppm – IR (KBr): $\tilde{\nu}$ = 3388 (vw), 3057 (w), 3008 (w), 2954 (w), 2568 (vw), 1592 (m), 1510 (m), 1256 (m), 1209 (m), 1174 (m), 859 (m), 723 (m), 697 (m), 550 (m) cm^{-1} – MS (FAB, 3-NBA) *m/z* (%): 442 (100) [M^{+1}], 242 (17), 231 (8), 201 (56), 137 (6).

(E)-N-(1-(furan-2-yl)ethylidene)-P,P-diphenylphosphinic amide (**7**):



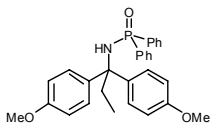
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.98-7.93(m, 4 H, P(=O)-Ar$_o$-H), 7.60 (t, 1 H, O-CH, *J* = 0.7 Hz), 7.46-7.38 (m, 6 H, P(=O)-Ar$_m$-H u. Ar$_p$-H), 7.22 (d, 1 H, O-C=C*H*-3, *J* = 3.5 Hz), 6.53 (dd, 1 H, O-C=C*H*-4, *J* = 3.5 Hz, *J* = 1.7 Hz), 2.79 (d, 3 H, CH_3, *J* = 2.0 Hz) ppm – ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 154.52 (C_q, *C*-CN), 154.23 (+, *C*N), 146.42 (+, *C*4-OAr), 135.38 u. 134.08 [C_q, 2 × *C*-P(=O)], 131.54 u. 131.45 [+, 2 × *C*3-P(=O)-Ar], 131.25 u. 131.22 [(+, 2 × *C*2- u. *C*6-P(=O)-Ar], 128.34 u. 128.22 [(+, 2 × *C*3- u.*C*5-P(=O)-Ar], 116.35 (+, *C*2-OAr), 112.50 (+, *C*3-OAr), 22.19 u. 22.06 (+, *C*H_3) ppm – IR (KBr): $\tilde{\nu}$ = 3700 (w), 3095 (s), 2923 (m), 2852 (m), 2760 (w), 2634 (w), 2465 (w), 2412 (m), 2292 (w), 1965 (m), 1916 (m), 1623 (s), 1566 (s), 1468 (s), 1439 (s), 1294 (s), 1234 (s), 1197 (s), 1110 (s), 786 (s), 560 (s), 531 (s) cm^{-1} – MS (70 eV, EI), *m/z* (%): 309 (100) [M^+], 308 (23), 201 (92), 185 (20), 125 (15), 77 (29), 43 (31).

(E)-N-((4-chlorophenyl)(phenyl)methylene)-P,P-diphenylphosphinic amide (**10**):



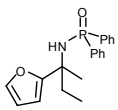
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.94-7.89 (m, 4 H, P(=O)-Ar$_o$-H), 7.57-7.55 (m, 2 H, P(=O)-Ar$_p$-H), 7.53-7.38 (m, 11 H, P(=O)-Ar$_m$-H, CN-Ar-H, Cl-Ar$_o$-H), 7.37-7.35 (m, 2 H, Cl-Ar$_m$-H) ppm – ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 180.43 (C_q, d, CN, *J* = 8.1 Hz), 138.35 (C_q, d, CN-*C*1-Ar, *J* = 17.0 Hz), 136.96 (C_q, d, CN-*C*1-Ar-Cl, *J* = 16.8 Hz), 135.35 (C_q, *C*-Cl), 134.05 [C_q, 2 × *C*-P(=O)], 131.60 u. 131.51 [+, 2 × *C*2- u. *C*6-P(=O)-Ar], 131.32 u. 131.29 [+, 2 × *C*4-P(=O)-Ar], 130.81 (+, *C*3- u. *C*5-Ar-Cl), 129.50 (+, *C*3- u. *C*5-CN-Ar), 128.38 (+, *C*4-CN-Ar), 128.25 [+, 2 × *C*3- u. *C*5-P(=O)-Ar], 128.16 (+, *C*2- u. *C*6-CN-Ar), 128.01 (+, *C*2- u. *C*6-Ar-Cl) ppm – IR (KBr): $\tilde{\nu}$ = 3055 (m), 1633 (m), 1591 (m), 1576 (m), 1487 (m), 1438 (m), 1398 (w) 1315 (m), 1278 (m), 1207 (m), 1121 (m), 1090 (m), 851 (m), 737 (m), 724 (m), 700 (m), 552 (m), 532 (m) cm^{-1} – MS (FAB, 3-NBA) *m/z* (%): 416 (100) [M^+], 216 (5), 201 (76), 183 (4), 155 (6), 137 (5).

N-(1,1-bis(4-methoxyphenyl)propyl)-P,P-diphenylphosphinic amide:



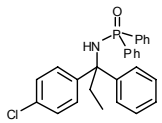
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.70-7.65 (m, 4 H, P(=O)-Ar$_o$-H), 7.39-7.34 (m, 2 H, P(=O)-Ar$_p$-H), 7.31-7.27 (m, 4 H, P(=O)-Ar$_m$-H), 7.20-7.18 (m, 4 H, 6.89-6.87 (m, 4 H, CH_3O-Ar$_o$-*H*), 6.67-6.65 (m, 4 H, CH_3O-Ar$_m$-*H*), 3.75 (s, 6 H, 2 × OCH_3), 2.60 (q, 2 H, CH_2, *J* = 7.3 Hz), 1.70 (bs, 1 H, NH), 0.73 (t, 3 H, CH_3, *J* = 7.2 Hz) ppm – ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 158.17 (C_q, *C*-OCH_3), 137.28 u. 137.22 (C_q, 2 × *C*1-Ar-OCH_3), 135.12 u. 133.84 [C_q, 2 × *C*-P(=O)], 131.60 u. 131.51 (+, 4 × *C*2- u. *C*6- Ar-OCH_3), 130.95 u. 130.93 [+, 4 × *C*2- u. *C*6-P(=O)-Ar], 129.39 [+, 2 × *C*4-P(=O)-Ar], 128.09 u. 127.97 [+, 2 × *C*3- u.*C*5-P(=O)-Ar], 112.87 (4 × *C*3- u. *C*5-Ar-OCH_3], 64.64 (C_q, *C*-NH), 55.14 (+, 2 × O*C*H_3), 33.79 u. 33.77 (–, *C*H_2), 9.11 (+, CH_2-*C*H_3) ppm – IR (KBr): $\tilde{\nu}$ = 3170 (m), 3056 (w), 2988 (w), 2934 (w), 2874 (w), 2835 (w), 1609 (m), 1510 (m), 1465 (m), 1437 (m), 1252 (m), 1182 (m), 1123 (m), 1106 (m), 1034 (m), 992 (m), 874 (w), 831 (m), 821 (m), 724 (m), 695 (m), 545 (m), 531 (m) cm^{-1} – MS (FAB, 3-NBA) *m/z* (%): 472 (6) [M^+], 442 (32), 364 (4), 283 (3), 255 (100), 242 (16), 218 (35), 201 (32), 148 (5), 122 (6), 92 (4).

N-(2-(furan-2-yl)butan-2-yl)-P,P-diphenylphosphinic amide:



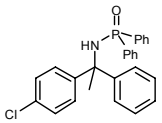
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.85-7.73 (m, 4 H, P(=O)-Ar$_o$-H), 7.47-7.32 (m, 6 H, P(=O)-Ar$_m$-H u. Ar$_p$-H), 7.23 (dd, 1 H, O-CH, *J* = 1.8 Hz, *J* = 0.8 Hz), 6.16 (dd, 1 H, O-C=C*H*-4, *J* = 3.2 Hz, *J* = 1.8 Hz), 6.05 (dd, 1 H, O-C=C*H*-3, *J* = 3.2 Hz, *J* = 0.8 Hz), 3.33 (bd, 1 H, NH, *J* = 7.2 Hz), 2.06-1.97 (m, 2 H, CH_2), 1.57 (s, 3 H, C-CH_3), 0.78 (t, 3 H, CH_2-C*H*$_3$) ppm – ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 157.23 u. 157.18 (C$_q$, *C*1-OAr), 140.17 (+, *C*4-OAr), 134.32 u. 133.04 [C$_q$, 2 × *C*-P(=O)], 130.98 u. 130.89 [+, 2 × *C*4-P(=O)-Ar], 130.53 u. 130.44 [(+, 2 × *C*2- u. *C*6-P(=O)-Ar], 127.41 u. 127.29 [+, 2 × *C*3- u. *C*5-P(=O)-Ar], 108.94 (+, *C*2-OAr), 104.83 (+, *C*3-OAr), 56.03 (C$_q$, d, *C*-NH, *J* = 2.4 Hz), 35.11 (–, d, *C*H$_2$, *J* = 4.2 Hz), 23.15 (+, d, C-*C*H$_3$, *J* = 3.8 Hz), 8.79 (+, CH_2-*C*H$_3$ ppm – IR (KBr): $\tilde{\nu}$ = 3196 (br), 3057 (m), 2977 (m), 2937 (m), 2879 (w), 1592 (w), 1503 (m), 1437 (m), 1375 (m), 1294 (m), 1234 (m), 1192 (m), 1123 (m), 1053 (m), 1011 (m), 962 (m), 923 (m), 868 (m), 800 (m), 748 (m), 724 (m), 697 (m), 566 (m), 540 (m) cm^{-1} – MS (70 eV, EI), *m/z* (%): 339 (6) [M$^+$], 311 (20), 310 (100), 201 (54), 77 (8).

N-(1-(4-chlorophenyl)-1-phenylpropyl)-P,P-diphenylphosphinic amide:



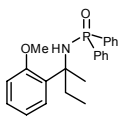
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.74-7.59 (m, 4 H, P(=O)-Ar$_o$-H), 7.43-7.15 (m, 13 H, NHC-Ar-H, P(=O)-Ar$_m$-H u. Ar$_p$-H, Cl-Ar$_o$-H), 7.04-7.01 (m, 2 H, Cl-Ar$_m$-H), 3.71 (bd, 1 H, NH, *J* = 5.1 Hz), 2.76-2.49 (m, 2 H, CH_2), 0.73 (t, 3 H, CH_3, *J* = 7.3 Hz) ppm – ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 145.01 (C$_q$, d, NHC-*C*1-Ar, *J* = 5.8 Hz), 143.14 (C$_q$, d, NHC-*C*1-Ar-Cl, *J* = 4.0 Hz), 134.87 (Cq, 2 ×*C*-P(=O)], 134.46 (+, NHC-*C*2- u. *C*6-Ar), 133.17 (C$_q$, *C*-Cl), 132.77 (+, *C*3- u. *C*5-Ar-Cl), 131.59 u. 131.50 [+, 4 × *C*2- u. *C*6-P(=O)-Ar], 131.43 u. 131.34 [+, 2 × *C*4-P(=O)-Ar], 131.28 (+, *C*2- u. *C*6-Ar-Cl), 131.02 (+, NHC-*C*3- u. *C*5-Ar), 130.10 (+, *C*2- u. *C*6-Ar-Cl), 127.57 u. 127.53 [+, 4 × *C*3- u. *C*5-P(=O)-Ar], 126.92 (+, NHC-*C*4-Ar), 66.07 (C$_q$, d, *C*-NH, *J* = 2.4 Hz), 33.34 (–, d, CH_2, *J* = 2.4 Hz), 8.99 (+, CH_3) ppm –IR (KBr): $\tilde{\nu}$ = 3149 (m), 3057 (m), 2960 (m), 2934 (w), 2875 (w), 1594 (w), 1490 (m), 1438 (m), 1398 (m), 1178 (s), 1124 (m), 1108 (m), 1090 (m), 1070 (m), 1025 (m), 1012 (m), 870 (m), 748 (m), 725 (m), 694 (s), 570 (m), 539 (s) cm^{-1}

N-(1-(4-chlorophenyl)-1-phenylethyl)-P,P-diphenylphosphinic amide:



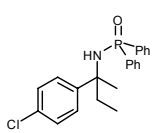
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.81-7.68 (m, 4 H, P(=O)-Ar$_m$-H), 7.49-7.30 (m, 10 H, 2 × P(=O)-Ar$_{o,p}$-H, Ar$_o$-H, Cl-Ar$_o$-H), 7.23-7.18 (m, 5 H, Cl-Ar$_m$-H, Ar$_p$-H, Ar$_m$-H), 1.97 (s, 3 H, CH_3) ppm – ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 147.19 (C$_q$, d, *C*1-Ar, *J* = 4.8 Hz), 145.72 (C$_q$, d, *C*1-Ar-Cl, *J* = 3.6 Hz), 140.08 u. 132.05 [C$_q$, 2 × *C*-P(=O)], 130.98 (C$_q$, *C*-Cl), 128.61 (+, *C*3- u. *C*5-Ar-Cl), 128.53 (+, *C*2- u. *C*6-Ar), 128.34 (+, d, 2 × *C*4-P(=O)-Ar, *J* = 3.9 Hz), 128.29 u. 128.10 (+, 2 × *C*2- u. *C*6-P(=O)-Ar), 127.08 (+, *C*3- u. *C*5-P(=O)-Ar), 126.58 (+, *C*2- u. *C*6-Ar-Cl), 126.26 (+, *C*3- u. *C*5-Ar), 62.85 (C$_q$, d, *C*-NH, *J* = 2.4 Hz), 29.04 (+, d, *C*H$_3$, *J* = 4.1 Hz) ppm – IR (KBr): $\tilde{\nu}$ = 3129 (br), 3054 (m), 2837 (w), 1592 (w), 1489 (m), 1436 (m), 1179 (m), 1123 (m), 1106 (m), 1014 (m), 970 (m), 850 (m), 827 (m), 695 (m), 561 m), 540 (m) cm^{-1} – MS (70 eV, EI), *m/z* (%): 431/433 (10/3) [M$^+$], 416/418 (18/6), 277/279 (36/11), 231 (76), 217 (12), 201 (45), 154/156 (57/18), 139/140 (100/33), 111/113 (63/22), 91 (62), 77 (73), 51 (31).

N-(2-(2-methoxyphenyl)butan-2-yl)-P,P-diphenylphosphinic amide:



^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.87-7.82 (m, 2 H, P(=O)-Ar$_m$-H), 7.68-7.63 (m, 2 H, P(=O)-Ar$_m$-H), 7.47-7.38 (m, 3 H, P(=O)-Ar$_p$-H, CH_3O-Ar-*H*$_6$), 7.28-7.26 (m, 2 H, P(=O)-Ar$_o$-H), 7.19-7.14 (m, 2 H, P(=O)-Ar$_o$-H), 7.08 (dd, 1 H, CH_3O-Ar-*H*$_5$, *J* = 7.7 Hz, *J* = 1.6 Hz), 6.95 (dd, 1 H, CH_3O-Ar-*H*$_3$, *J* = 8.2 Hz, *J* = 1.0 Hz), 6.88 (dt, 1 H, CH_3O-Ar-*H*$_4$, *J* = 7.5 Hz, *J* = 1.2 Hz), 5.01 (bd, 1 H, NH, *J* = 9.1 Hz), 3.83 (s, 3 H, OCH_3), 2.19-2.07 (m, 2 H, CH_2), 1.61 (s, 3 H, C-CH_3), 0.67 (t, 3 H, CH_2-C*H*$_3$, *J* = 7.5 Hz) ppm – ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 157.21 (C$_q$, *C*2-Ar-OCH_3), 134.30 (C$_q$, d, *C*1-Ar-OCH_3, *J* = 4.2 Hz), 131.94 u. 131.84 [C$_q$, 2 × *C*-P(=O)], 130.93 u. 130.91 [(+, 2 × *C*4-P(=O)-Ar], 130.53 u. 130.44 [(+, 2 × *C*2- u. *C*6-P(=O)-Ar], 128.02 u. 128.95 [+, 2 × *C*3- u. *C*5-P(=O)-Ar], 127.00 (+, *C*6-Ar-OCH_3), 125.32 (+, *C*4-Ar-OCH_3), 120.78 (+, *C*5-Ar-OCH_3), 111.49 (+, *C*3-Ar-OCH_3), 60.30 (C$_q$, *C*-NH), 55.19 (+, O*C*H$_3$), 36.89 (–, d, *C*H$_2$, *J* = 4.1 Hz), 23.38 (+, d, C-*C*H$_3$, *J* = 4.5 Hz), 9.38 (+, CH_2-*C*H$_3$) ppm – IR (KBr): $\tilde{\nu}$ = 3385 (m), 3056 (w), 2968 (w), 2836 (w), 2215 (vw), 1598 (w), 1437 (m), 1234 (m), 1120 (m), 1023 (m), 752 (m), 723 (m), 533 (m) cm^{-1} – MS (70 eV, EI), *m/z* (%): 380 (1) [M$^+$], 351 (20), 350 (100), 318 (2), 218 (2), 202 (7), 201 (47), 133 (4), 105 (3), 91 (3), 84 (6), 77 (7), 47 (3).

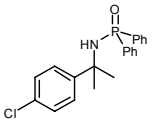
N-(2-(4-chlorophenyl)butan-2-yl)-P,P-diphenylphosphinic amide:



^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.75-7.64 (m, 4 H, P(=O)-Ar$_m$-H), 7.29-7.24 (m, 6 H, P(=O)-Ar$_o$-H, P(=O)-Ar$_p$-H), 7.23-7.18 (m, 2 H, Cl-Ar$_o$-H), 7.12-7.09 (m, 2 H, Cl-Ar$_m$-H), 3.14 (bs, 1 H, NH), 1.96-1.76 (ddq, 2 H, CH_2, *J* = 13.7 Hz, *J* = 7.3 Hz, *J* = 6.4 Hz), 1.44 (s, 3 H, C-CH_3), 0.55 (t, 3 H, CH_2-C*H*$_3$, *J* = 7.4 Hz) ppm – ^{13}C-NMR (100 MHz, $CDCl_3$):

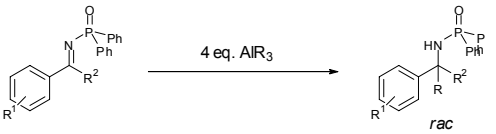
δ = 144.31 (C_q, d, *C*1-Ar-Cl, *J* = 4.9 Hz), 134.20 (C_q, d, *C*1-P(=O)-Ar, *J* = 40.1 Hz), 132.92 (C_q, *C*4-Ar-Cl), 131.39 (+, *C*3- u. *C*5-Ar-Cl), 130.80 (+, d, *C*4-P(=O)-Ar, *J* = 9.6 Hz), 130.51 (+, d, *C*2- u. *C*6-P(=O)-Ar, *J* = 9.4 Hz), 127.41 (+, d, *C*2- u. *C*6-Ar-Cl, *J* = 23.7 Hz), 126.86 (+, d, *C*3- u. *C*5-P(=O)-Ar, *J* = 74.3 Hz), 59.54 (C_q, d, *C*-NH, *J* = 2.8 Hz), 36.89 (–, d, *C*H_2, *J* = 4.0 Hz), 26.30 (+, d, C-*C*H_3, *J* = 3.9 Hz), 7.78 (+, CH_2-*C*H_3) ppm – IR (KBr): $\tilde{\nu}$ = 3147 (br), 3052 (m), 2974 (m), 1905 (w), 1637 (w), 1590 (w), 1437 (m), 1187 (m), 1122 (m), 963 (m), 724 (m), 695 (m), 533 (m) cm^{-1} – MS (70 eV, EI), *m/z* (%): 384/386 (0.20/0.05) [M^+], 368/370 (2/1), 354/356 (100/27), 216 (9), 201 (77), 124 (3), 77 (11).

N-(2-(4-chlorophenyl)propan-2-yl)-P,P-diphenylphosphinic amide:



^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.82-7.77 (m, 4 H, P(=O)-Ar$_m$-H), 7.46-7.44 (m, 2 H, Cl-Ar$_o$-H), 7.41-7.32 (m, 6 H, P(=O)-Ar$_o$-H, P(=O)-Ar$_p$-H), 7.21-7.19 (m, 2 H, Cl-Ar$_m$-H), 3.12 (bs, 1 H, NH), 1.57 (s, 6 H, 2 × CH_3) ppm – ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 147.53 (C_q, d, *C*1-Ar-Cl, *J* = 5.1 Hz), 134.54 (C_q, d, *C*1-P(=O)-Ar, *J* = 128.8 Hz), 132.58 (C_q, *C*4-Ar-Cl), 131.79 (+, *C*3- u. *C*5-Ar-Cl), 131.70 (+, *C*2- u. *C*6-P(=O)-Ar), 131.59 (+, d, *C*4-P(=O)-Ar, *J* = 2.7 Hz), 128.47 (+, d, *C*3- u. *C*5-P(=O)-Ar, *J* = 12.6 Hz), 128.34 (+, *C*2- u. *C*6-Ar-Cl), 57.32 (C_q, d, *C*$(CH_3)_2$, *J* = 2.7 Hz), 31.43 (+, 2 × *C*H_3, *J* = 3.8 Hz) ppm – IR (KBr): $\tilde{\nu}$ = 3133 (m), 2972 (m), 2856 (m), 1905 (w), 1591 (w), 1485 (m), 1437 (m), 1183 (m), 1108 (m), 1009 (m), 932 (m), 827 (m), 719 (m), 645 (w), 532 (m) cm^{-1} – MS (70 eV, EI), *m/z* (%): 369/371 (3/1) [M^+], 354/356 (33/9), 216 (4), 201 (100), 199 (11), 124 (3), 77 (1).

Performed Experiments



Scheme 1 1,2-addition of trialkyl aluminium reagents on *N*-diphenylphosphinoylketimines..

Table 1 Reaction conditions

Entry	R^1	R^2	Metal Organyl	Solvent	T [°C]	Time [h]	Yield [%]
1a	4-Cl-C_6H_4	CH_3	1 eq $AlEt_3$	toluene	25	0.5	/
1b	4-Cl-C_6H_4	CH_3	2 eq $AlEt_3$	toluene	25	0.5	36
1c	4-Cl-C_6H_4	CH_3	3 eq $AlEt_3$	toluene	25	0.5	74
1d	4-Cl-C_6H_4	CH_3	4 eq $AlEt_3$	toluene	25	0.5	88
1e	4-Cl-C_6H_4	CH_3	5 eq $AlEt_3$	toluene	25	0.5	98
2a	4-OMe-C_6H_4	CH_3	1 eq $AlEt_3$	toluene	25	20	/
2b	4-OMe-C_6H_4	CH_3	2 eq $AlEt_3$	toluene	25	20	80
2c	4-OMe-C_6H_4	CH_3	3 eq $AlEt_3$	toluene	25	20	99
3a	4-Cl-C_6H_4	CH_3	4 eq $AlEt_3$	toluene	0	1	65
3b	4-Cl-C_6H_4	CH_3	4 eq $AlEt_3$	toluene	-25	1	7
3c	4-Cl-C_6H_4	CH_3	4 eq $AlEt_3$	toluene	-78	1	/
4a	4-Cl-C_6H_4	CH_3	4 eq $AlEt_3$	toluene	-30	16	28
4b	4-Cl-C_6H_4	CH_3	3 eq $AlEt_3$	Et_2O	0	16	/
4c	4-Cl-C_6H_4	CH_3	4 eq $AlEt_3$	THF	-25	16	/
5a	4-Cl-C_6H_4	CH_3	4 eq $ZnEt_2$[a]	*n*-hexane	25	72	/
5b	4-NO_2-C_6H_4	CH_3	4 eq $ZnEt_2$[b]	toluene	25	16	/
6	4-NO_2-C_6H_4	CH_3	4 eq $AlEt_3$	toluene	25	16	/
7	2-OH-C_6H_4	CH_3	8 eq $AlEt_3$	toluene	25	16	/
8	2-NH_2-C_6H_4	CH_3	4 eq $AlEt_3$	*n*-hexane	25	4	/
9	2-OMe-C_6H_4	CH_3	4 eq $AlEt_3$	toluene	25	16	98
10	Furyl	CH_3	4 eq $AlEt_3$	toluene	25	16	99
11	4-Cl-C_6H_4	CH_3	4 eq $AlMe_3$	toluene	25	24	92
12	4-Cl-C_6H_4	CH_2CH_3	6 eq $AlMe_3$	toluene	25	20	63
13	4-Cl-C_6H_4	C_6H_5	4 eq $AlMe_3$	toluene	25	20	84
14	4-OMe-C_6H_4	4-OMe-C_6H_4	4 eq $AlEt_3$	toluene	25	16	87
15	4-Cl-C_6H_4	C_6H_5	4 eq $AlEt_3$	toluene	25	20	62

[a] Addition of 0.1 eq (R_p,*S*)-Paracyclophane-Ligand, [b] Addition of 1.0 eq *N*,*N*-Dimethylethanolamine.