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Novel phosphine ligands bearing 3(5)-pyrazolyl and 4-(2-amino)pyrimidinyl groups: Synthesis and coordination chemistry

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Abstract

Novel triphenyl phosphine ligands bearing pyrazole or 2-aminopyrimidine groups in the *ortho* or *meta* position of one or three of the phenyl rings were obtained starting from the corresponding acyl derivatives $Ph_2P(o\text{-}C_6H_4\text{-}COCH_3)$, $Ph_2P(m\text{-}C_6H_4\text{-}COCH_3)$, or $P(m\text{-}C_6H_4\text{-}COCH_3)_3$. Conversion of the acyl groups into 3-dimethylamino-2-propen-1-onyl units was achieved by reaction with $HC(OMe)_2NMe_2$ which underwent ring closing with hydrazine or guanidine to yield the desired heterocycles. Two palladium complexes were synthesized using the coordinatively labile precursor $(PhCN)_2PdCl_2$, one of them could be characterized by X-ray structure analysis.

Keywords: Phosphine ligands; Pyrazoles; Pyrimidines; Palladium

1. Introduction

Controlled modifications of already known ligand systems have greatly changed the face of homogeneous catalysis in the last decades. The modifications not only resulted in improved catalytic performances (i.e. higher conversion and selectivity), but also enlarge the scope of homogeneous catalysis. For example, more and more metal-based catalytic organic processes could be realized under aqueous conditions, or contrarily in non-polar organic solvents, both of which were not generally considered as suitable reaction media until a few years ago.

For some time, our group has been interested in the reinvestigation of phosphine ligands. Our strategy is to implement new functionalities in this known ligand system, which may allow to realize some of the principles of metallo-proteins in homogeneous catalysis (i.e. some weak chemical interactions, which are still difficult to be completely quantified by modern analytical methods such as NMR or X-ray). Recently, we have reported some phosphine ligands bearing additional donor sites in the backbone for the binding of Lewis acids. It has been proved that this binding of Lewis acids to phosphine ligands is not only detectable in terms of spectroscopy features but also relevant for catalysis [1].

In the present paper, we describe a facile and efficient access to yet unknown phosphine ligands bearing 3(5)-pyrazolyl- or 4-(2-amino)pyrimidinyl groups [2] and derived complexes with palladium. These ligands may be of potential interest for catalytic reactions. For example, the mono functionalized derivatives are structurally closely related to diphenyl(2-(2-pyridyl)phenyl) phosphine, which has been used as ligand in different catalytic transformations [3]. Additionally, multiple functionalization of PPh_3 with pyrazole or pyrimidine groups, which is as simple as mono functionalization, opens up a new access to water soluble ligands, due to the basic (pyrazole, pyrimidine) and protic (pyrazole) properties of the heterocycles or by further derivatization. Such ligands may also find application in aqueous-phase organometallic catalysis [4].

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2. Results and discussion

Pyrazoles or pyrimidines can be obtained by ring closing condensation of β-diketones with either hydrazine or precursor compounds bearing a NH=C(R)–NH_2 unit. Only a few arylphosphines with β-diketone side chains have been described up to now, probably due to synthetic difficulties [5]. We have been working on the synthesis of arylpyrazoles and developed a different access to such compounds a few years ago. Here, 1-aryl-3-dimethylamino-2-propen-1-ones are used as "masked" aromatic β-ketones, showing an analogous reactivity in ring closing reactions with hydrazine [6]. These compounds can easily be prepared by the condensation of aromatic acyl derivatives with *N*,*N*-dimethylformamide dimethyl acetale. For the application of this route in phosphine chemistry, an acetyl group attached to at least one of the phenyl rings of PPh_3 is required. Such compounds have already been reported several times in the literature [7].

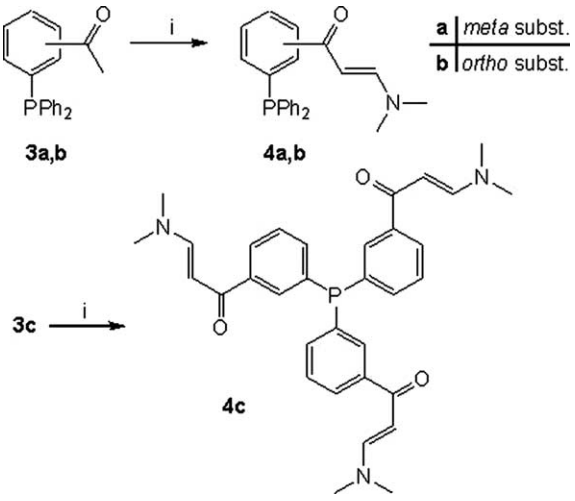
(3-Acetylphenyl)diphenyl phosphine (**3a**) and (2-acetylphenyl)diphenyl phosphine (**3b**) were obtained in good yields by a modified published procedure [7b] starting from (3-bromophenyl)methyl ketone and (2-bromophenyl)-methyl ketone, respectively (Scheme 1). **3a** is a highly viscous colorless oil exhibiting a ^{31}P NMR resonance at −3.84 ppm, while **3b** is a lemon yellow solid with a ^{31}P NMR resonance at −1.49 ppm.

The color of **3b** is not due to impurities, since the compound can be recrystallized without changing its yellow color. Schiemenz et al. [7b] already reported this color and the intense deep orange color of the difunctionalized derivative $PhP(o\text{-}C_6H_4\text{-}COCH_3)_2$ but gave no explanation for it. We are at the moment investigating this phenomenon by means of spectroscopy and quantum chemical calculations.

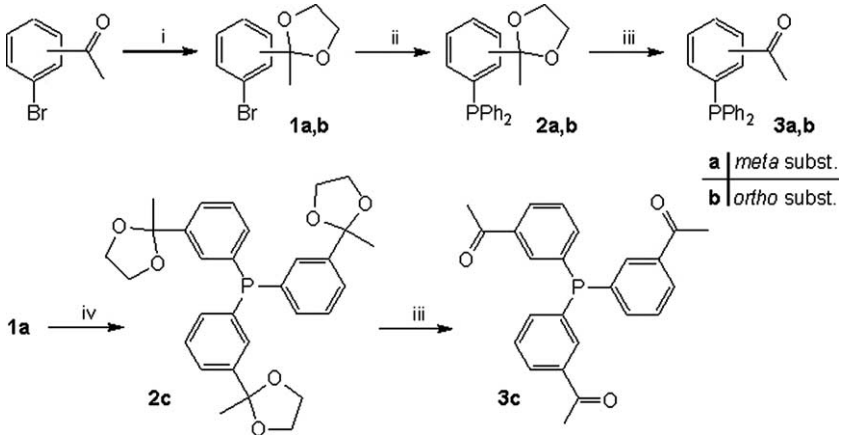
Tri(3-acetylphenyl) phosphine (**3c**), the trisubstituted analogue of **3a**, was synthesized following the same strategy as for **3a**,**b** (Scheme 1), except the fact that after the formation of the Grignard reagent, phosphorus trichloride was used instead of chlorodiphenyl phosphine. The crude product, a yellow oil, was not purified but used directly for the following C–C coupling reaction.

Heating a 1:2 mixture of the acetyl phosphines **3a**,**b** and *N*,*N*-dimethylformamide dimethyl acetale for 2 h yielded almost quantitatively the corresponding *meta* and *ortho* substituted 1-aryl-3-dimethylamino-2-propen-1-ones **4a**,**b** (Scheme 2). Reacting **3c** under the same conditions with 6 equivalents of the acetale, led to the trisubstituted derivative **4c** in 60% yield.

Compounds **4a**–**c** are intensively orange–yellow to orange–red colored, a characteristic feature for these donor/acceptor substituted olefins [6] The structure of the α, β-unsaturated ketones can clearly be assigned by means of NMR spectroscopy (^1H NMR: two doublets at ∼7.7 and ∼5.5 ppm with $^3J_{HH}$ coupling constants of ∼12 Hz for =C*H*N$(CH_3)_2$ and CO*CH*=; ^{13}C NMR: $\delta \sim 190$ ppm for C=O, and ∼155 and ∼95 ppm for =*C*HN$(CH_3)_2$ and CO*C*H=). Compared to the corresponding acetyl phosphines **3a**–**c**, the ^{31}P NMR resonances of **4a**–**c** are slightly shifted to higher field ($\delta = -6.36$, −8.76 and −3.89 ppm for **4a**–**c**).

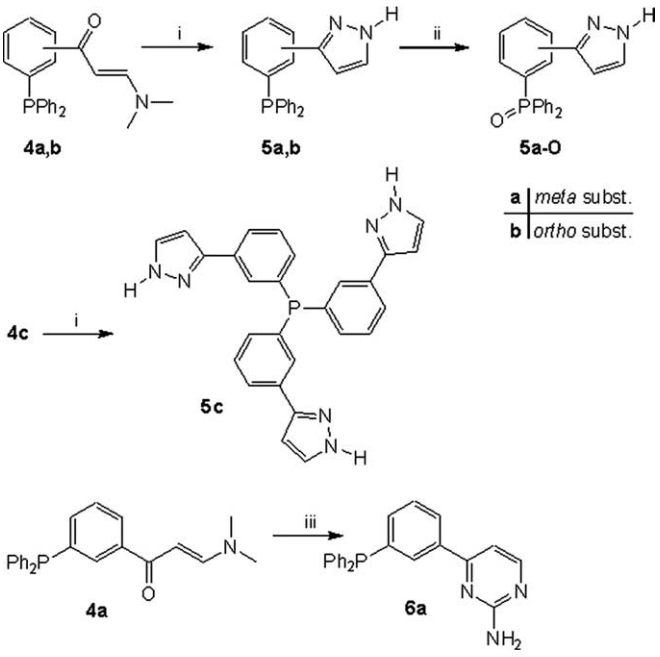


Scheme 2. (i) $HC(OMe)_2(NMe_2)$, reflux.



Scheme 1. (i) Ts-OH, $HOCH_2CH_2OH$, toluene, reflux; (ii) Mg, thf, $ClPPh_2$; (iii) H_2O/thf, Ts-OH, reflux; (iv) Mg, thf, PCl_3.

The ring closure of **4a**–**c** with excess of hydrazine monohydrate was carried out under reflux conditions in EtOH solution. After removal of the solvent and recrystallization, the pyrazoles **5a**–**c** were obtained as colorless to light yellow solids in yields of 64–94% (Scheme 3). ^{13}C NMR spectra show characteristic chemical shifts at ~150, ~140–135 and ~105 ppm for the carbon atoms C-3_{pz}, C-5_{pz} and C-4_{pz}. The pyrazolyl rings also exhibit characteristic resonances in the ^{1}H NMR spectra: **5c**, e.g. shows a doublet at 6.65 ppm with a coupling constant $^{3}J_{HH}$ of 2.2 Hz, which is clearly separated from the aromatic resonances and typical for 4_{pz}-H of 3-aryl substituted pyrazoles.



Scheme 3. (i) EtOH, $N_2H_4 \cdot H_2O$, reflux; (ii) H_2O_2, toluene; (iii) $[(NH_2)_3C]_2CO_3$, EtOH/H_2O, KOH, reflux.

Reaction of **4a** with an excess of guanidinium carbonate in EtOH/aqueous KOH at reflux temperature for several hours, resulted in the formation of a 4-(2-amino)pyrimidinyl ring in the *meta* position of one of the phenyl rings of the PPh_3 unit (Scheme 3). In ^{1}H NMR spectrum of ligand **6a**, two doublets at 8.26 and 6.99 ppm with a coupling constant $^{3}J_{HH}$ of 5.2 Hz originate from the protons at 6_{pm} and 5_{pm} positions. In DMSO-d_6, the two protons of the amino group are found at a chemical shift of 6.68 ppm. The ^{13}C NMR signals at 164.7, 163.9, 160.1 and 106.7 ppm can be assigned to the four carbon atoms of the pyrimidine ring.

The introduction of the 3(5)-pyrazolyl and 4-(2-amino)pyrimindyl rings only slightly influences the electronic situation of the phosphorus center. The ^{31}P NMR resonances of **5a**–**c** and **6a** are observed between −4.44 and −10.46 ppm, which is almost the same as for compounds **4a**–**c**.

Oxidation at the phosphorous center is performed quantitatively by hydrogen peroxide. The phosphine oxide **5a-O** was synthesized exemplary, its solid state structure was determined by single crystal X-ray structure analysis. **5a-O** crystallizes from ethanol as colorless prisms in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell. As expected, hydrogen bonding dominates the solid state structure: the proton of the N–H function of the pyrazole undergoes intermolecular hydrogen bonding to the phosphine oxide (bond distances [Å]: N2–H2 0.89(2), H2···O 1.84(2), N2···O 2.707(2); bond angle [°]: 164(2)). This results in the formation of planar zig-zag chains

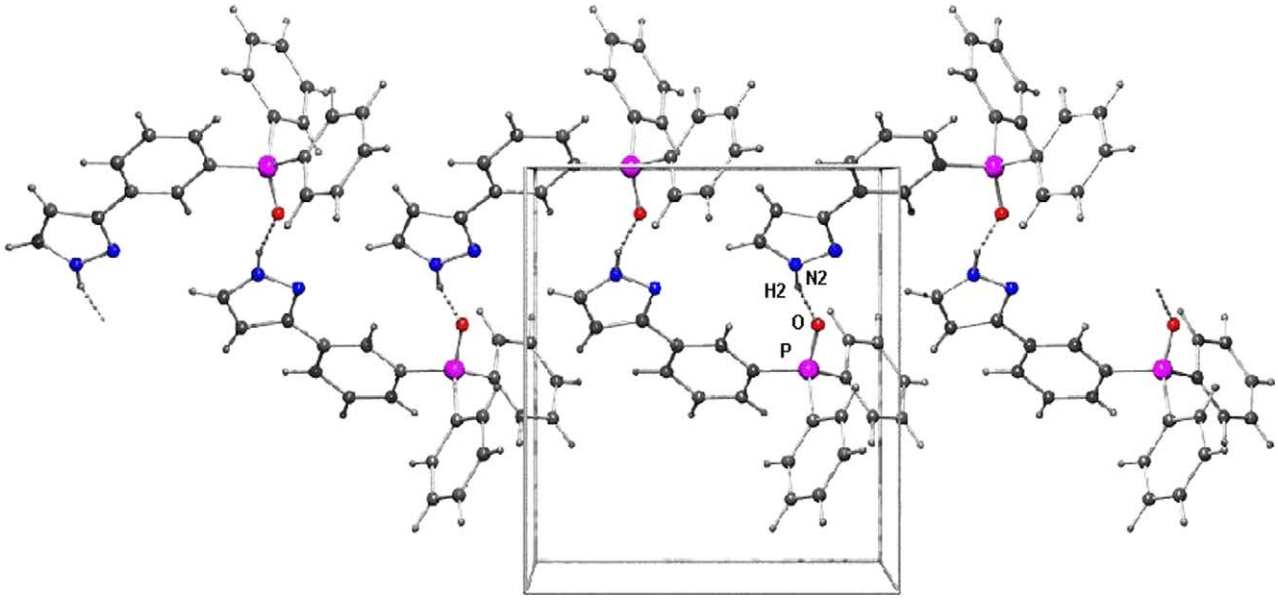


Fig. 1. PLUTON [9] plot of the solid state structure of **5a-O** showing the hydrogen bound chains running parallel to the *a*-axis. Selected bond lengths [Å], angles [°] and torsion angles [°]: P–O 1.494(1), P–C11 1.802(2), P–C21 1.799(2), P–C31 1.801(2), N2–H2 0.89(2), H2···O 1.84(2), N2···O 2.707(2); N2–H2···O 164(2); C12–C13–C17–N1 16.8(2).

(Fig. 1) parallel to the *a*-axis of the unit cell. These chains are oriented perpendicular to each other, interconnected by additional (weaker) hydrogen bonds between proton H251 at one of the phenyl rings and the phosphine oxide (bond distances [Å]: C25–H251 0.97(2), H251···O 2.55(2), N2···O 3.460(2); bond angle [°]: 157(2)), leading to a three dimensional network of hydrogen interactions. The phenyl rings at the phosphorous center are oriented in the typical paddle wheel mode. The pyrazole ring is almost coplanar to the phenyl ring (torsion angle [°]: 16.8(2)). To our knowledge, this is the first solid state structure showing a hydrogen bound polymer with a phosphine oxide and a nitrogen containing heterocycle [8].

Reaction of two equivalents of **5a** with $(PhCN)_2PdCl_2$ gave complex **7a** (Scheme 4). Elemental analysis advised that in **7a** ligand **5a** coordinates monodentate via the phosphorous atom (comparable to PPh_3) to the Pd^{2+} center. Due to ^{31}P NMR data, the two phosphine ligands are coordinated in *cis*-configuration. In contrast to the behavior of the *meta*-substituted ligand **5a**, its *ortho*-substituted congener **5b** always reacts in a 1:1 ratio with $(PhCN)_2PdCl_2$. Even with large excesses of **5b** only the chelate complex **7b** can be isolated (Scheme 4).

The different coordination of the ligands **5a** and **5b** to the $PdCl_2$ moiety is clearly expressed by the ^1H and ^{31}P NMR data of the resulting complexes **7a** and **7b**. In the ^1H NMR of **7a**, the resonance of the N–H proton (12.97 ppm) is observed at almost the same chemical shift as in the free ligand **5a** (12.92 ppm), while the N–H proton in **5b** (12.94 ppm) is deshielded by the coordination of the pyrazole ring in **7b** (13.23 ppm). The same effect is found for the proton in the 4-position of the pyrazole ring: **5a**, 6.62; **7a**, 6.62; **5b**, 6.30; **7b**, 7.13 ppm. The N–H stretching frequencies of **5a** and **7a** are observed at almost the same energies (3215 and 3218 cm^{-1}), indicating an negligible influence of the Pd–P coordination on the situation of the pyrazole ring. However P–Pd–N coordination in **7b** and additional hydrogen bonding (see structure discussion below) clearly weakens the N–H bond (**5b**: 3186, **7b**: 3227 cm^{-1}). As expected, the ^{31}P resonances of **7a** (25.43) and **7b** (26.96 ppm) are shifted towards lower field compared to the free ligands **5a** and **5b**.

Yellow crystals of **7b** suitable for X-ray diffraction studies were obtained from slowly cooling a hot saturated solution in MeOH (Fig. 2). Fig. 2 shows the structure in the solid state. **7b** crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell, forming dimers via intermolecular hydrogen bonding between the N–H proton of one molecule and one of the chloro ligands of a neighboring complex (N2–H2 0.78(4), H2···Cl2 2.55(4), N2···Cl2 3.219(3) Å, N2–H2···Cl2 145(3)°). Additionally, an intramolecular hydrogen bond is found (N2–H2 0.78(4), H2···Cl1 2.78(3), N2···Cl1 3.162(3) Å, N2–H2···Cl1 113(3)°). The dimers are linked by (weak) hydrogen bonds between H331 and Cl1 leading to double chains

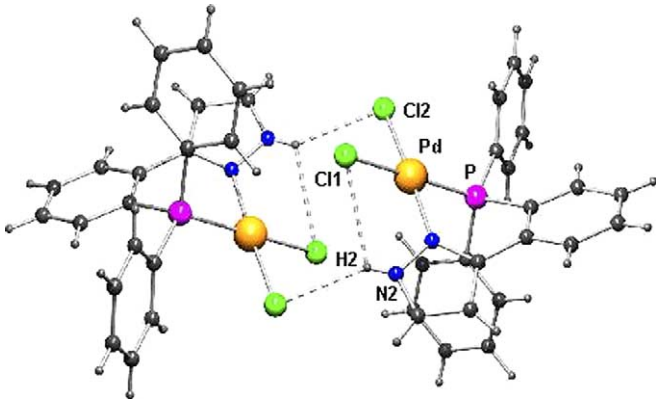
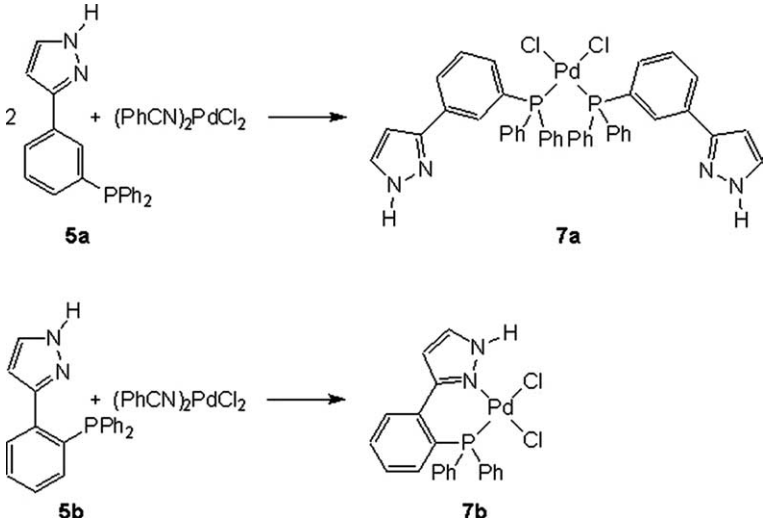


Fig. 2. PLUTON [9] plot of the solid state structure of **7b**. Selected bond lengths [Å], angles [°] and torsion angles [°]: Pd–Cl1 2.3714(8), Pd–Cl2 2.2897(7), Pd–P 2.2257(8), Pd–N1 2.018(3), N2–H2 0.78(4), H2···Cl2 2.55(4), N2···Cl2 3.219(3), H2···Cl1 2.78(3), N2···Cl1 3.162(3); Cl1–Pd–Cl2 90.90(3), Cl1–Pd–P 172.28(3), Cl1–Pd–N1 89.49(7), Cl2–Pd–P 95.28(3), Cl2–Pd–N1 176.16(7), P–Pd–N1 84.65(7), N2–H2···Cl2 145(3), N2–H2···Cl1 113(3); Pd–P–C11–C12 43.1(3), P–C11–C12–C3 0.8(4), N1–C3–C12–C11 –28.5(5), Pd–N1–C3–C12 –0.5(4), N1–Pd–P–C11 –48.2(1).



Scheme 4.

running parallel to the crystallographic *c*-axis (not shown in Fig. 2; C33–H331 0.98(5), H331···Cl1 2.81(5), C33···Cl1 3.579(4) Å, C33–H331···Cl1 136(3)°). Due to the small bite angle of the chelate system, the phenylene backbone is bent from the plane defined by Pd, N1 and P. Additionally, this plane is not coplanar to the plane defined by Pd, Cl1 and Cl2, probably due to the intermolecular hydrogen bonds. Only a few palladium complexes with chelating P,N-ligands wherein the nitrogen donor atom is part of a heterocycle and Pd, N, and P are included in a six membered ring system have been described up to now [10]. However, the geometry of the coordination site of **7b** is generally comparable with the solid state structures of those compounds.

3. Conclusion

A simple and efficient synthesis of novel phosphine ligands with 3(5)-pyrazolyl- and 4-(2-amino)pyrimidinyl-side functions could be presented and their effectiveness in coordination to palladium could be shown. The NH and NH_2 functions of the ligands allow to introduce further functionalities for substrate recognition, chirality transfer as well as the adoption of the ligands and derived metal complexes to different reaction media, especially to the aqueous phase. These investigations are on the way at the moment.

4. Experimental

General remarks. The synthesis of compounds containing phosphorus was carried out under an inert gas atmosphere of argon or nitrogen and with dried solvents. $PdCl_2(PhCN)_2$ (Strem 46-0400) was obtained commercially. All other starting materials were obtained from Aldrich and used without further purification. Elemental analyses were carried out at the Institute of Chemistry (TU Chemnitz) or the Department of Chemistry (TU Kaiserslautern). Infrared spectra were recorded with a Perkin–Elmer FT-IR 1000 spectrometer. NMR spectra were recorded with a Bruker Avance 400 or 250 spectrometer. The NMR resonances were assigned according to Scheme 5.

4.1. [3-(3-Dimethylamino-1-oxoprop-2-en-yl)phenyl]diphenylphosphine (*4a*)

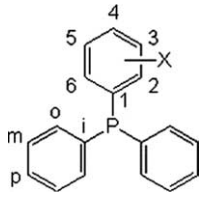
A mixture of 9.9 g (32.6 mmol) of **3a** and 7.7 g (64.7 mmol) of *N*,*N*-dimethylformamide dimethyl acetale was refluxed for 2 h. After evaporation under high vacuum, the residue was crystallized from EtOH to give an orange–red solid in almost quantitative yield. Anal. Calc. for $C_{23}H_{22}NOP$: C, 76.86; H, 6.17; N, 3.90. Found: C, 76.30; H, 6.02; N, 3.79%. IR (KBr, cm^{-1}): 2914m, 1644vs, 1586m, 1574w, 1556m, 1538m, 1477w, 1434s, 1420s, 1353m, 1300w, 1284m, 1264w, 1236m, 1205w, 1118w, 1103w, 1087m, 1066m, 1024w, 995w, 976m, 909m, 766s, 744s, 696vs, 650m, 541w, 528m, 509m, 495m, 488m, 430w, 410w. ^{1}H NMR (250.1 MHz, 25 °C, $CDCl_3$): δ 7.87 (tt, $^3J_{HH} = 8.8$ Hz, $^4J_{HH} = 1.9$ Hz, 2H, *p*-H), 7.73 (d, 1H, $^3J_{HH} = 12.3$ Hz, =C*H*N(CH_3)$_2$), 7.42–7.26 (m, 12H, ar-H), 5.56 (d, 1H, COCH=), 3.07, 2.83 (2 s, 6H, N(CH_3)$_2$). ^{13}C{^{1}H} NMR (62.9 MHz, 25 °C, $CDCl_3$): δ 188.6 (C=O), 154.7 (=*C*HN-(CH_3)$_2$), 141.0 (d, $^3J_{PC} = 7.2$ Hz, C-3), 137.5 (d, $^1J_{PC} = 12.0$ Hz, C-1), 137.4 (d, $^1J_{PC} = 10.6$ Hz, C-i), 136.4 (d, $^2J_{PC} = 16.3$ Hz, C-2), 134.2 (d, $^2J_{PC} = 19.7$ Hz, C-o), 133.4 (d, $^2J_{PC} = 23.0$ Hz, C-6), 129.2 (s, C-p), 129.0 (d, $^3J_{PC} = 6.7$ Hz, C-m), 128.9 (d, $^3J_{PC} = 5.8$ Hz, C-5), 128.4 (s, C-4), 92.6 (CO*C*H=), 45.5, 37.6 (N(CH_3)$_2$). ^{31}P{^{1}H} NMR (101.2 MHz, 25 °C, $CDCl_3$): δ −6.36. MS, *m*/*z* (%): 359 (88) $[M]^+$.

4.2. [2-(3-Dimethylamino-1-oxoprop-2-en-yl)phenyl]diphenylphosphine (*4b*)

Compound **4b** was synthesized similarly to **4a** as a red–brown solid in quantitative yield. It crystallizes with half an equivalent of the solvent. Anal. Calc. for $C_{23}H_{22}NOP \cdot (C_2H_5OH)_{0.5}$: C, 75.39; H, 6.54; N, 3.66. Found: C, 76.71; H, 6.73; N, 3.68%. IR (KBr, cm^{-1}): 3047w, 2905w, 1637vs, 1575vs, 1552s, 1477w, 1430s, 1422s, 1356m, 1292w, 1274m, 1237m, 1200w, 1114w, 1078m, 1034m, 975w, 897m, 813w, 758m, 742m, 694s, 653w, 545w, 505m, 485w. ^{1}H NMR (400.1 MHz, 25 °C, $CDCl_3$): δ 7.66–7.63 (m, 1H, 3-H), 7.38 (td, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.2$ Hz, 1H, 5-H or 4-H), 7.31–7.27 (m, 12H, ar-H, =C*H*N(CH_3)$_2$), 7.07–7.04 (m, 1H, 6-H), 5.42 (d, $^3J_{HH} = 12.5$ Hz, 1H, COCH=), 2.96, 2.71 (2 s, 6H, N(CH_3)$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, 25 °C, $CDCl_3$): δ 192.0 (C=O), 155.0 (=*C*HN(CH_3)$_2$), 148.1 (d, $^2J_{PC} = 27.0$ Hz, C-2), 139.3 (d, $^1J_{PC} = 12.1$ Hz, C-i), 136.5 (d, $^2J_{PC} = 19.5$ Hz, C-6), 135.0 (s, C-1), 134.2 (d, $^2J_{PC} = 19.8$ Hz, C-o), 129.6 (s, C-5), 128.7 (s, C-4), 128.6 (d, $^3J_{PC} = 6.7$ Hz, C-m), 128.5 (s, C-p), 127.9 (d, $^3J_{PC} = 5.4$ Hz, C-3), 97.1 (CO*C*H=), 45.2, 37.3 (N(CH_3)$_2$). ^{31}P{^{1}H} NMR (162.0 MHz, 25 °C, $CDCl_3$): δ −8.76. MS, *m*/*z* (%): 359 (95) $[M]^+$.

4.3. Tri[3-(3-dimethylamino-1-oxoprop-2-en-yl)phenyl]phosphine (*4c*)

According to the procedure given above for **4a** and **4b**, **4c** was prepared and crystallized from MeOH as a deep orange–yellow microcrystalline solid with one equivalent of the solvent in 60% yield. Anal. Calc. for $C_{33}H_{36}N_3O_3P \cdot (CH_3OH)$: C, 69.73; H, 6.88; N, 7.17. Found: C, 69.87; H, 6.77; N, 7.04%. IR (KBr, cm^{-1}): 2909w, 2803w, 1718w, 1642vs, 1587s, 1575s, 1551vs, 1434s, 1420s, 1355s, 1306w, 1285m, 1267m, 1238s, 1204w, 1096m, 1065m,



Scheme 5. Numbering of the phosphines.

979w, 909m, 764m, 726w, 689w, 653w, 587w, 553w, 534w, 477w. ^{1}H NMR (400.1 MHz, 25 °C, $CDCl_3$): δ 7.91, 7.85 (2 d, 6H, $^3J_{HH} = 7.5$ Hz, $^3J_{HH} = 8.5$ Hz, 4-H, 6-H), 7.79 (d, 3H, $^3J_{HH} = 12.2$ Hz, =C*H*N(CH_3)$_2$), 7.44–7.35 (m, 6H, 2-H, 5-H), 5.55 (d, 3H, COCH=), 3.12, 2.85 (2 s, 18H, N(CH_3)$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, 25 °C, $CDCl_3$): δ 188.2 (C=O), 155.0 (=*C*HN(CH_3)$_2$), 141.0 (d, $^3J_{PC} = 7.4$ Hz, C-3), 137.1 (d, $^1J_{PC} = 12.0$ Hz, C-1), 136.4 (d, $^2J_{PC} = 17.6$ Hz, C-6), 133.3 (d, $^2J_{PC} = 23.1$ Hz, C-2), 129.0 (d, $^3J_{PC} = 6.5$ Hz, C-5), 128.6 (s, C-4), 92.7 (CO*C*H=), 45.4, 37.8 (N(CH_3)$_2$). ^{31}P{^{1}H} NMR (162.0 MHz, 25 °C, $CDCl_3$): δ −3.89. ESI MS, *m/z* (%): 570.2133 (18) $[M + O + H]^+$, 527.1793 (100) $[M + H]^+$.

4.4. [3-(3-Pyrazolyl)phenyl]diphenylphosphine (**5a**)

3.5 g (9.7 mmol) of **4a** and 2.5 g (50.0 mmol) of hydrazine monohydrate were refluxed in EtOH for 3 h. After cooling to r.t., the solvent was removed in vacuum. The remaining yellow oil was crystallized from MeOH to give a light yellow crystalline solid. Yield: 3.0 g, 94%. Anal. Calc. for $C_{21}H_{17}N_2P$: C, 76.82; H, 5.22; N, 8.53. Found: C, 75.77; H, 5.27; N, 8.39%. IR (KBr, cm^{-1}): 3215m, 1596w, 1582w, 1524w, 1476m, 1449m, 1432s, 1398m, 1326w, 1305w, 1178m, 1130w, 1096m, 1081m, 1051m, 1026m, 996m, 952m, 923w, 896w, 842w, 808m, 777s, 742s, 693s, 658m, 600w, 575w, 562m, 542m, 519m, 490s, 467w, 454w, 431w, 416w. ^{1}H NMR (400.1 MHz, 25 °C, DMSO-d_6): δ 12.92 (br, 1H, N–H), 7.82–7.26 (m, 14H, ar-H, 5_{pz}-H), 7.12 (t, 1H, $^3J_{HH} = 7.2$ Hz, 5-H), 6.62 (d, 1H, $^3J_{HH} = 1.5$ Hz, 4_{pz}-H). ^{13}C{^{1}H} NMR (100.6 MHz, 25 °C, DMSO-d_6): δ 150.3 (C-3_{pz}), 138.0 (C-5_{pz}), 137.5 (d, $^1J_{PC} = 11.3$ Hz, C-i), 134.2 (d, $^2J_{PC} = 19.5$ Hz, C-o), 132.9 (d, $^3J_{PC} = 1.8$ Hz, C-3), 132.9 (d, $^2J_{PC} = 17.3$ Hz, C-6), 132.4 (d, $^1J_{PC} = 9.6$ Hz, C-1), 130.8 (d, $^2J_{PC} = 22.6$ Hz, C-2), 130.0 (d, $^3J_{PC} = 6.5$ Hz, C-5), 130.0 (s, C-p), 129.6 (d, $^3J_{PC} = 6.9$ Hz, C-m), 126.8 (s, C-4), 102.8 (C-4_{pz}). ^{31}P{^{1}H} NMR (162.0 MHz, 25 °C, DMSO-d_6): δ-5.30. ESI MS, *m/z* (%): 345.1157 (53) $[M + O + H]^+$, 329.1224 (100) $[M + H]^+$.

4.5. [2-(3-Pyrazolyl)phenyl]diphenylphosphine (**5b**)

Compound **5b** was prepared following the same procedure as for **5a** as a colorless crystalline solid. Yield: 2.0 g, 64%. Anal. Calc. for $C_{21}H_{17}N_2P$: C, 76.82; H, 5.22; N, 8.53. Found: C, 76.44; H, 5.18; N, 8.53%. IR (KBr, cm^{-1}): 3186s, 3050w, 1583w, 1524m, 1490m, 1477m, 1456m, 1433s, 1417m, 1354m, 1306w, 1291w, 1173m, 1122m, 1080m, 1055m, 1036m, 1025m, 998w, 974w, 948m, 928w, 871w, 847w, 806m, 756s, 747s, 695s, 610m, 532w, 516m, 499m, 486m, 464w, 438w, 418w. ^{1}H NMR (400.1 MHz, 25 °C, DMSO-d_6): δ 12.94 (br, 1H, N–H), 7.66-7.62 (m, 2H, 3-H, 5_{pz}-H), 7.44 (t, $^3J_{HH} = 7.4$ Hz, 1H, 4-H), 7.36–7.34 (m, 6H, m, *p*-H), 7.27 (t, 1H, 5-H), 7.19–7.15 (m, 4H, *o*-H), 6.92–6.90 (m, 1H, 6-H), 6.30 (br, 1H, 4_{pz}-H).^{13}C{^{1}H} NMR (100.6 MHz, 25 °C, DMSO-d_6): δ 150.8 (C-3_{pz}), 140.2 (C-5_{pz}), 138.8 (br, C-i), 135.9 (d, $^2J_{PC} = 18.8$ Hz, C-2), 134.8 (s, C-1), 134.2 (d, $^2J_{PC} = 19.9$ Hz, C-o), 132.1 (d, $^2J_{PC} = 9.2$ Hz, C-6), 130.5 (d, $^3J_{PC} = 4.8$ Hz, C-5), 129.7 (s, C-4), 129.4 (d, $^3J_{PC} = 6.5$ Hz, C-m), 129.4 (s, C-p), 128.5 (s, C-3), 106.5 (C-4_{pz}). ^{31}P{^{1}H} NMR (162.0 MHz, 25 °C, DMSO-d_6): δ −10.46. ESI MS, *m/z* (%): 345.1184 (10) $[M + O + H]^+$, 329.1217 (100) $[M + H]^+$.

4.6. Tri[3-(3-pyrazolyl)phenyl]phosphine (**5c**)

Following the same method as for **5a** and **5b**, **5c** was obtained as a light yellow crystalline solid in the yield of 83%, which crystallizes with one equiv. of water. Anal. Calc. for $C_{27}H_{21}N_6P \cdot (H_2O)$: C, 67.78; H, 4.84; N, 17.56. Found: C, 67.83; H, 5.37; N, 17.81%. IR (KBr, cm^{-1}): 3170s, 3055w, 2966m, 2921m, 1594m, 1572w, 1533w, 1454m, 1398m, 1349m, 1293w, 1172w, 1095m, 1081w, 1047m, 996w, 963w, 931m, 795s, 764s, 694s, 662w, 612w, 580w, 516w, 503w, 475w. ^{1}H NMR (400.1 MHz, 25 °C, DMSO-d_6): δ 12.94 (br, 3H, N–H), 7.88-7.80 (m, 6H, ar-H), 7.71 (d, 3H, $^3J_{HH} = 2.4$ Hz, 5_{pz}-H), 7.51–7.44 (m, 3H, ar-H), 7.23–7.18 (m, 3H, ar-H), 6.65 (d, 3H, 4_{pz}-H). C{^{1}H} NMR (100.6 MHz, 25 °C, DMSO-d_6): δ 148.7 (C-3_{pz}), 138.0 (d, $^1J_{PC} = 12.0$ Hz, C-1), 134.2 (d, $^3J_{PC} = 6.5$ Hz, C-3), 133.0 (d, $^2J_{PC} = 16.6$ Hz, C-6), 130.9 (d, $^2J_{PC} = 24.0$ Hz, C-2), 130.0 (d, $^3J_{PC} = 6.5$ Hz, C-5), 126.8 (s, C-4), 102.8 (C-4_{pz}), C-5_{pz} not observed. ^{31}P{^{1}H} NMR (162.0 MHz, 25 °C, DMSO-d_6): δ −4.44. ESI MS, *m/z* (%): 477.1405 (43) $[M + O + H]^+$, 461.1491 (100) $[M + H]^+$.

4.7. [3-(4-(2-Amino)pyrimidinyl)phenyl]diphenylphosphine (**6a**)

2.9 g (8.1 mmol) of **4a** and 1.5 g (8.5 mmol) of guanidinium carbonate were suspended in 20 mL of EtOH. After the addition of 0.95 g of KOH in 4 mL of H_2O, the mixture was heated to reflux for 2 h. After the removal of the solvent in vacuum, the residue was dissolved in diluted HCl, and followed by neutralization with 25% of ammonia. A light yellow solid was precipitated during the neutralization, which was further washed with small amounts of EtOH and ether. Yield: 2.4 g, 83%. Anal. Calc. for $C_{22}H_{18}N_3P \cdot (C_2H_5OH)_{0.25}$: C, 73.66; H, 5.36; N, 11.43. Found: C, 74.08; H, 5.42; N, 11.07%. IR (KBr, cm^{-1}): 3496m, 3396w, 3274m, 3134m, 1624s, 1569s, 1549s, 1465s, 1433s, 1340m, 1281m, 1274m, 1218m, 1126w, 1093m, 1026w, 997w, 920w, 817m, 791m, 745s, 696m, 630m, 541w, 518m, 495m, 461w, 432w, 418w. ^{1}H NMR (250.1 MHz, 25 °C, DMSO-d_6): δ 8.26 (d, 1H, $^3J_{HH} = 5.2$ Hz, 6_{pm}-H), 8.14–8.02 (m, 2H, ar-H), 7.53–7.17 (m, 12H, ar-H), 6.99 (d, 1H, 5_{pm}-H), 6.68 (br, 2H, NH_2). ^{13}C{^{1}H} NMR (62.9 MHz, 25 °C, DMSO-d_6): δ 164.7 (C-2_{pm}), 163.9 (C-4_{pm}), 160.1 (C-6_{pm}), 138.2 (d, $^2J_{PC} = 18.2$ Hz, C-6), 138.2 (d, $^3J_{PC} = 2.8$ Hz, C-3), 137.2 (d, $^1J_{PC} = 11.2$ Hz, C-i), 135.6 (d, $^1J_{PC} = 11.7$ Hz, C-1), 134.2 (d, $^2J_{PC} = 19.6$ Hz, C-o), 132.7 (d, $^2J_{PC} = 28.7$ Hz, C-2), 130.1 (d, $^3J_{PC} = 4.3$ Hz, C-5), 130.0 (s, C-p), 129.7 (d, $^3J_{PC} = 6.8$ Hz, C-m), 128.3 (s, C-4), 106.7 (C-5_{pm}). ^{31}P{^{1}H}

NMR (101.2 MHz, 25 °C, DMSO-d_6): δ −7.60. ESI MS, *m/z* (%): 372.1231 (15) $[M + O + H]^+$, 356.1297 (100) $[M + H]^+$.

4.8. cis-Dichlorobis{[3-(3-pyrazolyl)phenyl]diphenylphosphine} palladium(II) (7a) and Dichloro{[2-(3-pyrazolyl)phenyl] diphenylphosphine} palladium(II) (7b)

250 mg (0.65 mmol) of di(benzonitrile)dichloropalladium(II) were added to solutions of compound **5a** (427 mg, 1.30 mmol) or **5b** (214 mg, 0.65 mmol) in 20 mL of toluene. The mixtures were refluxed for 4 h. The products, which precipitated as yellow microcrystalline solids were slightly contaminated with traces of elemental palladium. Thus, they were recrystallized from hot saturated MeOH solutions.

7a. Yield: 385 mg, 71%. Anal. Calc. for $C_{42}H_{34}N_4Cl_2P_2Pd \cdot (CH_3OH)$: C, 59.63; H, 4.42; N, 6.47. Found: C, 59.51; H, 4.29; N, 6.41%. IR (KBr, cm^{-1}): 3218m, 3135w, 3051w, 1530w, 1481m, 1464w, 1450w, 1435s, 1390m, 1352w, 1334w, 1313w, 1282w, 1179m, 1158w, 1124w, 1095s, 1083w, 1046m, 1028w, 997w, 960w, 904w, 808m, 789m, 770w, 747m, 708m, 690s, 660w, 612w, 565m, 512s, 506s, 488m, 458w, 448w, 432w. ^{1}H NMR (400.1 MHz, 25 °C, DMSO-d_6): δ 12.97 (br, 2H, N–H), 8.23–7.80 (m, 6H, ar-H, 5_{pz}-H), 7.68–7.23 (m, 24H, ar-H), 6.62 (br, 2H, 4_{pz}-H). $^{31}P\{^1H\}$ NMR (162.0 MHz, 25 °C, DMSO-d_6): δ 25.43.

7b. Yield: 240 mg, 73%. Anal. Calc. for $C_{21}H_{17}N_2PCl_2Pd$: C, 49.88; H, 3.39; N, 5.54. Found: C, 49.70; H, 3.54; N, 5.38%. IR (KBr, cm^{-1}): 3227s, 1586w, 1567w, 1526w, 1496w, 1480m, 1463m, 1434s, 1424m, 1377m, 1332w, 1302w, 1284w, 1261w, 1195m, 1184m, 1172w, 1157w, 1132m, 1101s, 1078m, 1057w, 1026w, 999w, 972w, 922w, 879w, 844w, 784m, 764s, 752m, 744m, 732m, 714m, 694s, 678w, 656w, 617w, 598m, 546s, 527m, 518s, 506s, 470m, 452w, 435m. ^{1}H NMR (400.1 MHz, 25 °C, DMSO-d_6): δ 13.23 (br, 1H, N–H), 8.15–8.12 (m, 1H, 3-H), 7.99 (br, 1H, 5_{pz}-H), 7.82 (t, $^3J_{HH} = 7.4$ Hz, 1H, 4-H), 7.65–7.45 (m, 11H, ar-H), 7.13 (br, 1H, 4_{pz}-H), 6.99–6.95 (m, 1H, 6-H). $^{31}P\{^1H\}$ NMR (162.0 MHz, 25 °C, DMSO-d_6): δ 26.96.

4.9. X-ray crystal structure determination of compounds 5a-O and 7b (data in parentheses)

Crystal data and details of the structure determination are presented in Table 1. Suitable single crystals for the X-ray diffraction studies were grown as mentioned above. A clear colorless prism (**7b**: yellow plate) was stored under perfluorinated ether, transferred in a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection were carried out on an area detecting system (NONIUS, MACH3, κ-CCD) at the window of a rotating anode (NONIUS, FR951) and graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The unit cell parameters were obtained by full-matrix least-squares refinement of 1839 (**7b**: 3751) reflections. Data collection were performed at 123 (**7b**: 123) K (OXFORD CRYOSYSTEMS) within a θ-range of $2.29° < \theta < 25.34°$ (**7b**: $1.92° < \theta < 25.35°$). Measured each with nine data sets in rotation scan modus with $\Delta\varphi/\Delta\omega = 1.0°$ (**7b**: 1.5°). A total number of 40,474 (**7b**: 46,996) intensities were integrated. Raw data were corrected for Lorentz polarization and, arising from the scaling procedure, for latent decay and absorption effects. After merging

Table 1
Summary of the crystal data and details of data collection and refinement for compounds **5a-O** and **7b**

	5a-O	**7b**
Empirical formula	$C_{21}H_{17}N_2OP$	$C_{21}H_{17}Cl_2N_2PPd$
Formula mass	344.34	505.66
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$ (no. 19) [14]	$P2_1/n$ (no. 14) [14]
a (Å)	10.6486(1)	9.1883(1)
b (Å)	11.4396(1)	21.2540(2)
c (Å)	14.2171(1)	10.3636(1)
β (°)	90	101.1593(5)
V (Å^3)	1731.87(3)	1985.62(3)
Z	4	4
$\rho_{calc.}$ (g cm^{-3})	1.321	1.691
μ (mm^{-1})	0.169	1.293
T (K)	123	123
F (000)	720	1008
Crystal size (mm)	$0.33 \times 0.36 \times 0.71$	$0.05 \times 0.20 \times 0.28$
θ-range (°)	2.3/25.3	1.9/25.4
Index ranges	*h*: ±12/*k*: ±13/*l*: ±17	*h*: ±11/*k*: ±25/*l*: ± 12
Reflections collected	40,474	3635
Independent reflections ($I_0 > 2\sigma(I_0)$/all data/R_{int})	3002/3163/0.038	3295/3635/0.049
Data/restraints/parameters	3163/0/294	3635/0/312
R_1 ($I_0 > 2\sigma(I_0)$/all data)	0.0265/0.0291	0.0281/0.0330
wR_2 ($I_0 > 2\sigma(I_0)$/all data)	0.0664/0.0681	0.0657/0.0677
Goodness-of-fit	1.04	1.06
$\Delta\rho_{max/min}$ (e Å^{-3})	−0.27/0.14	−0.38/2.43

[$R_{int} = 0.038$ (**7b**: 0.049)] a sum of 3163 (**7b**: 3635) (all data) and 3002 (**7b**: 3295) [$I_o > 2\sigma(I_c)$], respectively, remained and all data were used. The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found and refined with individual isotropic displacement parameters. Full-matrix least-squares refinements with 294 (**7b**: 312) parameters were carried out by minimising $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err <0.001 (**7b**: 0.001). **5a-O**: The final residual electron density maps showed no remarkable features. **7b**: The high positive residual electron density is probably caused by a deficient absorption correction procedure. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms have been taken from *International Tables for Crystallography*. All calculations were performed on an Intel Pentium II PC, with the STRUX-V system, including the programs PLATON [11] SIR92 [12], and SHELXL-97 [13]. **5a-O**: The correct enantiomer is proved by Flack's Parameter $\varepsilon = -0.00(8)$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-284453 (**5a-O)** and CCDC-284454 (**7b)**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.08.032.

References

[1] Y. Sun, M. Ahmed, R. Jackstell, M. Beller, W.R. Thiel, Organometallics 23 (2004) 5260–5267.
[2] Y. Sun, A. Hienzsch, W.R. Thiel, DE 140900212, Technische Universität Chemnitz.
[3] (a) J.M. Takacs, S.D. Schröder, J. Han, M. Gifford, X. Jiang, T. Saleh, S. Vayalakkada, A.H. Yap, Org. Lett. 5 (2003) 3595–3598;
(b) A. Gsponer, G. Consiglio, Helv. Chim. Acta 86 (2003) 2170–2172;
(c) G. Consiglio, A. Gsponer, Polym. Mater. Sci. Eng. 87 (2002) 78–79.
[4] B. Cornils, W.A. Herrmann (Eds.), Aqueous-Phase Organometallic Catalysis, Wiley-VCH, Weinheim, Germany, 1998.
[5] (a) T.B. Rauchfuss, S.R. Wilson, D.A. Wrobleski, J. Am. Chem. Soc. 103 (1981) 6769–6770;
(b) D.A. Wrobleski, T.B. Rauchfuss, J. Am. Chem. Soc. 104 (1982) 2314–2316;
(c) D.A. Wrobleski, C.S. Day, B.A. Goodman, T.B. Rauchfuss, J. Am. Chem. Soc. 106 (1984) 5464–5472;
(d) D.A. Wrobleski, S.R. Wilson, T.B. Rauchfuss, Inorg. Chem. 21 (1982) 2114–2115;
(e) D.A. Wrobleski, T.B. Rauchfuss, A.L. Rheingold, K.A. Lewis, Inorg. Chem. 23 (1984) 3124–3129.
[6] (a) A.-K. Pleier, H. Glas, M. Grosche, P. Sirsch, W.R. Thiel, Synthesis (2001) 55–62;
(b) A.-K. Pleier, E. Herdtweck, S.A. Mason, W.R. Thiel, Eur. J. Org. Chem. (2003) 499–506.
[7] (a) G.P. Schiemenz, H.J. Kaack, Liebigs Ann. Chem. 9 (1973) 1494–1504;
(b) G.P. Schiemenz, H.J. Kaack, Liebigs Ann. Chem. 9 (1973) 1480–1493;
(c) G.P. Schiemenz, Chem. Ber. 99 (1966) 504–513;
(d) G.P. Schiemenz, Chem. Ber. 99 (1966) 514–519;
(e) L.B. Schenkel, J.A. Ellman, Org. Lett. 5 (2003) 545–548;
(f) M.H. Johansson, C. Andersson, A.J. Oskarsson, Mol. Struct. 606 (2002) 51–59;
(g) C. Liek, P. Machnitzki, T. Nickel, S. Schenk, M. Tepper, O. Stelzer, Z. Naturforsch., B: Chemical Sci. 54 (1999) 1532–1542;
(h) B.T. Rasley, M. Rapta, R.J. Kulawiec, Organometallics 15 (1996) 2852–2854;
(i) S.J. Coote, G.J. Dawson, C.G. Frost, J.M.J. Williams, Synlett (1993) 509–510;
(j) Y. Wang, C.W. Lai, F.Y. Kwong, W. Jia, K.S. Chan, Tetrahedron 60 (2004) 9433–9439;
(k) T.B. Grindley, K.F. Johnson, H. Kaack, A.R. Katritzky, G.P. Schiemenz, R.D. Topsom, Aust. J. Chem. 28 (1975) 327–333;
(l) F.Y. Kwong, C.W. Lai, M. Yu, K.S. Chan, Tetrahedron 60 (2004) 5635–5645;
(m) F.Y. Kwong, C.W. Lai, M. Yu, Y. Tian, K.S. Chan, Tetrahedron 59 (2003) 10295–10305;
(n) E. Le Gall, M. Troupel, J.-Y. Nedelec, Tetrahedron 59 (2003) 7497–7500;
(o) D. Van Allen, D.J. Venkataraman, J. Org. Chem. 68 (2003) 4590–4593;
(p) F.Y. Kwong, C.W. Lai, Y. Tian, K.S. Chan, Tetrahedron Lett. 41 (2000) 10285–10289;
(q) F.Y. Kwong, K.S. Chan, Chem. Commun. (2000) 1069–1070;
(r) S.E. Tunney, J.K. Stille, J. Org. Chem. 52 (1987) 748–753.
[8] Search on CSD version 5.26 (November 2004). There is one example showing a hydrogen bound dimer (diphenyl(2-(2,3-dihydro-1,3-benzothiazol-2-yl)phenyl)phosphineoxide): A. Castineiras, M.C. Gomez, P. Sevillano, J. Mol. Struct. 554 (2000) 301–306.
[9] A.L. Spek, PLUTON, A Program for Plotting Molecular and Crystal Structures, University of Utrecht, The Netherlands, 1995.
[10] (a) D. Masui, M. Ohnuki, M. Yamaguchi, T. Yamagishi, Acta Crystallogr. Sect., C: Cryst. Struct. Commun. 59 (2003) m487–m490;
(b) A.J. Blacker, M.L. Clarke, M.S. Loft, M.F. Mahon, M.E. Humphries, J.M. Williams, J. Chem. Eur. J. 6 (2000) 353–360;
(c) J.P. Cahill, F.M. Bohnen, R. Goddard, C.P. Krüger, J. Guiry, Tetrahedron: Asymm. 9 (1998) 3831–3839;
(d) Z. Zhu, T. Kajino, M. Kojima, K. Nakajima, Inorg. Chim. Acta 355 (2003) 197–204;
(e) N.W. Alcock, J.M. Brown, M. Pearson, S. Woodward, Tetrahedron: Asymm. 3 (1992) 17–20;
(f) L. Xiao, W. Weissensteiner, K. Mereiter, M. Widhalm, J. Org. Chem. 67 (2002) 2014–2206;
(g) F.Y. Kwong, A.S.C. Chan, K.S. Chan, Tetrahedron 56 (2000) 8893–8899;
(h) H. Nakano, Y. Okuyama, Y. Suzuki, R. Fujita, C. Kabuto, Chem. Commun. (2002) 1146–1147.
[11] A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2000.
[12] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Cryst. 27 (1994) 435–436.
[13] G.M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen, Germany, 1998.
[14] International Tables for Crystallography, vol. A, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992.