Synthesis and Characterization of Phosphinecarboxamide and Phosphinecarbothioamide, and Their Complexation with Palladium(II) Complex †

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Abstract: Reactions of isocyanates/isothiocyanates with primary and secondary phosphines without solvent at room temperature afforded phosphinecarboxamide/phosphinecarbothioamide, respectively, in excellent yields. Furthermore, palladium complex Pd(COD)Cl₂ was allowed to react with Ph₂PC(O)NHPh (1a) to afford [Pd(Ph₂PC(O)NHPh-kP,S)₂Cl₂] (3). On the other hand, the reaction of Pd(COD)Cl₂ with 1 eq. of Ph₂PC(S)NHPh (2a) afforded [PdCl₂(Ph₂PC(S)NHPh-kP,S)] (4). In the case of a 1:2 molar ratio, [PdCl₂(Ph₂PC(S)NHPh-kP,S)[Ph₂PC(S)NHPh-kP,S]]Cl (5) was formed. The newly obtained compounds were fully characterized using multielement NMR measurements and elemental analyses. In addition, the molecular structures of Ph₂PC(O)NH(CH₂)₂Cl (1j), Ph₂PC(S)NHPh(4-Cl) (2c), and 3–5 were determined using single-crystal X-ray diffraction.

Keywords: hydrophosphination; phosphinecarboxamide; phosphinecarbothioamide; palladium(II) complex; hydrogen bond; cis/trans isomerization; crystal structure

1. Introduction

Phosphinecarboxamides R₂PC(O)NR'₂ and phosphinecarbothioamides R₂PC(S)NR'₂ are phosphorus-analogs of urea and thiourea, and these are interesting compounds in coordination chemistry because of the variety of coordination modes. These compounds are known to act as a P-coordinated monodentate ligand (type I) [1–7], a P,S-coordinated bidentate ligand forming a four-membered chelate ring (type II for phosphinecarbothioamide) [8–13], and a bridging ligand for two metal centers (type III and type IV for phosphinecarbothioamide) [7,14] (Figure 1).

![Figure 1. Typical coordination modes for phosphinecarboxamide and phosphinecarbothioamide.](https://example.com/figure1.png)
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were used, the desired products were not yielded. The double hydrophosphination of 1,3-
withdrawing group such as F, Cl, Br, and CF3 at the position on the phenyl ring were readily converted (within 40 min) into the corresponding phenylisocyanates and that of 1-naphthylisocyanate took longer (1k, 1l). The reaction of para-methoxyphenylisocyanate and that of 1-naphthylisocyanate took longer (1f, 1g). Iso-

cyanates with aliphatic substituent were also adaptable to this reaction (1i and 1j). When 2-
chlorophenylisocyante, sterically bulky cyclohexylisocyanate, and 1-adamantylisocyanate were used, the desired products were not yielded. The double hydrophosphination of 1,3- and 1,4-diisocyanatobenzene were found to yield the desired products, 1k and 1l, in 85% and 92% yields, respectively. In addition, the triple hydrophosphination product 1m could be obtained in 64% yield.

2. Results and Discussion

2.1. Synthesis of Phosphinecarboxamide and Phosphinecarbothioamide

We examined the substrate scope and limitation for the hydrophosphination of isocyanates and diphenylphosphine (Scheme 2). Phenylisocyanates with an electron-withdrawing group such as F, Cl, Br, and CF3 at the para position and Cl at the meta position on the phenyl ring were readily converted (within 40 min) into the corresponding phosphinecarboxamides in excellent yields (1b, 1c, 1d, 1e, 1h). The reaction of para-methoxyphenylisocyanate and that of 1-naphthylisocyanate took longer (1f, 1g). Iso-

cyanates with aliphatic substituent were also adaptable to this reaction (1i and 1j). When 2-
chlorophenylisocyanate, sterically bulky cyclohexylisocyanate, and 1-adamantylisocyanate were used, the desired products were not yielded. The double hydrophosphination of 1,3-
and 1,4-diisocyanatobenzene were found to yield the desired products, 1k and 1l, in 85% and 92% yields, respectively. In addition, the triple hydrophosphination product 1m could be obtained in 64% yield.

Scheme 1. Hydrophosphination reaction of phenylisocyanate with diphenylphosphine.
Scheme 2. Scope and limitation for hydrophosphination of isocyanates with diphenylphosphine \( \text{Ph}_2\text{PH} \) a,b. a Phosphine compound: isocyanate = 1:1 molar ratio. b Isolated yield. c 80 °C, 2 equiv. of \( \text{Ph}_2\text{PH} \) was used (vs. isocyanate). d 80 °C, 3 equiv. of \( \text{Ph}_2\text{PH} \) was used (vs. isocyanate).

The results of the scope and limitation for the hydrophosphination of phenylisocyanate with phosphine compounds are summarized in Scheme 3. Diphenylphosphine analogs with electron-donating or -withdrawing groups such as Me, OMe, and F at the para position of the phenyl rings, and dialkylphosphines such as \( \text{Ph}_2\text{PH} \) and \( \text{Pr}_2\text{PH} \) were also adaptable to this reaction. In the case of primary phosphine \( \text{PhPH}_2 \), single hydrophosphination product \( 1s \) was obtained in 71%, but a long reaction time (3 days) was required because of the small amount of hexane existing in commercially available \( \text{PhPH}_2 \) (see Section 3.1).

Scheme 3. Hydrophosphination of phenylisocyanate with secondary phosphines \( \text{R}_2\text{PH} \) and primary phosphine \( \text{PhPH}_2 \) a,b. a Phosphine compound: isocyanate = 1:1 molar ratio. b Isolated yield.
We reported the hydrophosphination of phenylisothiocyanate with diphenylphosphine to give the corresponding phosphinecarbothioamide 2a in a previous study [27]. Very recently, the hydrophosphination of isothiocyanates using a catalyst-free method was reported by Zhu and Wang’s group [30]. For comparison, we also examined the synthesis of phosphinecarbothioamide without catalyst and solvent. Scheme 4 summarizes the results showing good functional group tolerance. Several isothiocyanates could be employed in the reaction, in which R is the phenyl ring with withdrawing groups such as F, Cl, Br, and CF$_3$ at the para position (2a, 2b, 2c, 2d, 2e). These reactions were completed within 30 min. Using 4-methoxyphenylisothiocyanate, 1-naphthylisothiocyanate and 3-chlorophenylisocyanate, a long reaction time was required (2f, 2g, 2h). Surprisingly, the hydrophosphination reaction of 2-chlorophenylisothiocyanate took place. This result is in contrast with the hydrophosphination of 2-chlorophenylisocyanate. Isothiocyanate with an aliphatic substituent was also adaptable to this reaction (2i). 1-Adamathylisothiocyanate did not react. These tendencies are similar to those observed for the corresponding isocyanates except for 2-chlorophenylisocyanate. The hydrophosphination of phenylisothiocyanate with (4-methylphenyl)$_2$PH also proceeded well (2k).

![Scheme 4](image)

Scheme 4. Scope and limitation for the hydrophosphination of isothiocyanates with diarylphosphine.

The molecular structures of 1i and 2c were determined using a single-crystal X-ray diffraction study. Two independent molecules of 1i were crystallized in the unsymmetric unit. The ORTEP drawings are shown in Figure 2a) for 1i (P1 molecule) and b) for 2c, along with selected bond lengths and angles. The bond distances of P1–C3 (1.870(2) Å) and C3–N1 (1.328(3) Å) for 1i were similar to those of P1–C7 (1.8541(17) Å) and N1–C7 (1.336(2) Å) for 2c. The phosphinecarboxamide and phosphinecarbothioamide moieties displayed a pyramidalized geometry at the P atom (sum of angle around P1 = 330.8° for 1i and 306.5° for 2c), indicating that the π-electron conjugation of the C=O and C=S did not extend to the P. In contrast, the planar carboxamide and carbothioamide moieties (sum of angle around N1 = 359.9° for 1i and 360.0° for 2c) were observed, showing the delocalization of π-electron density between the carbonyl (thiocarbonyl) and amide groups. These were consistent with the previously reported phosphinecarboxamide [31].
It is noteworthy that gram-scale practical reactions were successfully performed: phosphinecarboxamide 1a and phosphinecarbothioamide 2a were isolated in 90% and 99% yields, respectively (Scheme 5).

\[ \text{Ph}_2PH + E\equiv\text{C}=\text{N}^+\text{Ph} \xrightarrow{\text{neat, r.t.}} \text{Ph}_2P\equiv\text{N}^+\text{Ph} \]

Scheme 5. Gram-scale synthesis of phosphinecarboxamide and phosphinecarbothioamide.

2.2. Synthesis of Palladium(II) Complexes with Phosphinecarboxamide and Phosphinecarbothioamide

The reaction of Pd(COD)Cl$_2$ with 1a at a 1:2 molar ratio produced the related bis(phosphinecarboxamide)palladium complex [Pd(Ph$_2$P(O)NPh-κP)$_2$Cl$_2$] (3) in 97% yield. Complex 3 was obtained even when Pd(COD)Cl$_2$ was treated with 1 equiv. of 1a (NMR yield: 48%) (Scheme 6). The NH proton signal of 1a was not observed in CDCl$_3$ because of the overlapped phenyl protons, but it was observed at δ 7.13 ppm in C$_6$D$_6$ [20]. In the $^1$H NMR spectrum of 3 in CDCl$_3$, the NH proton was observed at δ 10.56 ppm. This chemical shift indicates that the NH of 3 is involved in hydrogen bonding. The $^{31}$P NMR spectrum of 3 showed two singlets (δ 25.5 ppm and 32.5 ppm in ca. 8:1 ratio) at 20 °C. The ratio of the two singlets depended on the temperature (ca. 16:1 at 50 °C and ca. 4:1 at −50 °C) (see Supplementary Materials, Figure S1). We think that this Pd complex adopts a planar geometry and performs cis/trans isomerization; the signal of δ 25.5 ppm was assigned to trans-3 and that of δ 32.5 ppm to cis-3. The thermal cis/trans isomerization of bis(phosphine)palladium(II) complex is well known [32,33]. In our system, the thermodynamic parameters Δ$H^\circ$ (1.3 × 10$^4$ J mol$^{-1}$) and Δ$S^\circ$ (6.2 × 10$^1$ JK$^{-1}$ mol$^{-1}$) of 3 were obtained using van’t Hoff plots (see Supplementary Materials, Figure S2). These values were similar to those in the previous report [32,33].
Since single crystals were obtained from the reaction solution of Scheme 6, an X-ray structure analysis was performed, and the ORTEP drawing was obtained, as depicted in Figure 3, with the atomic numbering scheme. The complex (trans-3) was confirmed to adopt a typical square-planar configuration; the palladium center had two Cl atoms and two P-coordinated Ph2PC(O)NHPPh (1a), which were trans-positioned with respect to each other. This molecule had two N–H···Cl intramolecular hydrogen bonds (Cl1···H2n (2.28(4) Å), Cl2···H1n (2.22(6) Å)). The hydrogen bonds in addition to the bulkiness of 1a were considered to be the reason for the trans geometry. This is the first example of a planar complex in which two phosphinecarboxamide ligands are coordinated to the trans position. The Pd–P bond distances (2.3574(9), 2.3707(9) Å) were longer than those of previously reported for cis-[PdCl2((±)-pbap)]2 (pbap = 3-phenyl-1,3-dihydrobenzo [1,3]azaphosphol-2-one) (2.2420(7), 2.2282(7) Å) [2]. The sum of the angles around N1 and N2 atoms were ca. 360°. These angles were similar to those previously reported [31]. This observation indicates that the delocalization of π-electron density between the carbonyl and amide groups was maintained even after complex formation.

The reaction of Pd(COD)Cl2 with Ph₂PC(S)NHPPh (2a) at a 1:1 molar ratio produced [PdCl₂|Ph₂PC(S)NHPPh-κP,S] ([4] (57% yield) (Scheme 7 (upper)). In this complex, 2a acted as a P,S-chelating bidentate ligand. The 31P[1H] NMR spectrum of 4 showed a singlet at δ ~41.3 ppm. On the other hand, the reaction of Pd(COD)Cl₂ with 2a at a 1:2 molar ratio produced [PdCl|Ph₂PC(S)NHPPh-κP,S]|Ph₂PC(S)NHPPh-κP]Cl ([5] in 77% yield (Scheme 7 (lower)). Although the NH proton signal of 2a was observed at δ 8.64 ppm in CDCl₃, the corresponding signals of 4 and 5 in CDCl₃ were observed at δ 13.31 ppm and 13.00 ppm, respectively. These large downfield shifts of the NH proton show the hydrogen...
bonding between the NH proton and the Cl atom in solution. The $^{31}$P NMR spectra of 5 at various temperatures (20, −10, and −40 °C) are displayed in Figure 4. Coupled two doublets with $^2J$(PP) = 453.4 Hz were observed at $\delta$ = 54.2 ppm, 37.8 ppm and those with $^2J$(PP) = 26.2 Hz were observed at $\delta$ = 41.9 ppm, 37.3 ppm at 20 °C. We assigned the signals with the largest coupling constant to the trans complex and those with the smallest coupling constant to the cis complex. The ratio of the cis complex increased when the measurement temperature was lowered (ca. 1.8:1 at 20 °C, 2.6:1 at −10 °C, and ca. 4.1:1 at −40 °C), and this ratio changed reversibly with the temperature. This behavior has not been reported in previous complexes having phosphinecarbothioamide. Thermodynamic parameters $\Delta H^\circ$ (8.6 × 10$^3$ J mol$^{-1}$) and $\Delta S^\circ$ (2.5 × 10$^1$ JK$^{-1}$ mol$^{-1}$) of 5 were obtained using van’t Hoff plots and were similar to the values found for 3 (see Supplementary Materials, Figure S3).

The structures of 4 and 5 were studied via an X-ray crystal structure analysis. Two independent molecules of 5 crystallized in the unit cell. As these were basically the same, only one molecule (Pd1) is shown in Figure 5a). Complex 4 had a typical square-planar environment; palladium had two Cl atoms situated mutually in cis position and $P,S$-coordinated bidentate ligand 2a. The bond lengths of Pd–P (2.2064(7), 2.1887(7) Å), Pd–S (2.2954(8), 2.2928(8) Å), and Pd–Cl (2.3299(7), 2.3986(7) Å) were similar to those of the previously reported [PdCl$_2$(Ph$_2$PC(S)NMMe$_2$)$_2$] complex (2.209(1) Å for Pd–P bond, 2.290(1) Å for Pd–S bond, and 2.329(1), 2.376(1) Å for Pd–Cl bond) [11]. Intermolecular hydrogen bonds between the H1n atoms for the Pd1 molecule and the Cl4 atom were observed (2.18(3) Å for H1n···Cl2 and 2.29(3) Å for H2n···Cl2) (Figure 6) [25].

Figure 4. $^{31}$P NMR spectra (162 MHz, CD$_2$Cl$_2$, ppm) of 5 at 20 °C (a), −10 °C (b), and −40 °C (c).

The structures of 4 and 5 also showed inter-molecular hydrogen bonds (2.18(3) Å for H1n···Cl2 and 2.29(3) Å for H2n···Cl2) (Figure 6) [25]. Compound 5 consisted of a cationic palladium complex and a Cl$^-$ counter anion (Figure 5b). In the cationic Pd complex, the Pd atom is coordinated to the phosphorus atom of 2a as a monodentate ligand, a bidentate $P,S$-bonded 2a, and a Cl atom, acquiring a square-planar configuration. The two phosphorus atoms were cis with respect to each other. This is the first example of a
transition-metal complex with both monodentate and bidentate phosphinecarbothioamide ligands. Complex 5 also showed inter-molecular hydrogen bonds (2.18(3) Å for H1n···Cl2 and 2.29(3) Å for H2n···Cl2) (Figure 6) [25].

Figure 5. ORTEP drawings of (a) 4·0.5(CH$_3$)$_2$CO and (b) cis-5·CH$_2$Cl$_2$ with thermal ellipsoids at 30% probability. The crystal solvent and hydrogen atoms (except for NH protons) are omitted for simplicity. Selected bond lengths (Å) and angles (°): Pd1–P1 2.2064(7), Pd1–S1 2.2954(8), Pd1–Cl1 2.3299(7), Pd1–Cl2 2.3534(7), S1–C1 1.704(2), C1–N1 1.302(3), N1–H1n 0.83(2), P1–Pd1–S1 96.05(3), P1–Pd1–Cl1 171.48(2), S1–Pd1–Cl1 171.16(2), S1–Pd1–Cl2 96.35(3), Cl1–Pd1–Cl2 92.14(3) for 4; Pd1–P1 2.2324(7), Pd1–P2 2.2886(7), S1–Pd1–Cl1 171.48(2), S1–Pd1–Cl2 96.35(3), Cl1–Pd1–Cl2 92.14(3) for 5.

Figure 6. Inter-molecular hydrogen bonds (hash line) for trans-5.

3. Materials and Methods

3.1. General Considerations

The synthesis of phosphinecarboxamide and phosphinecarbothioamide was carried out using standard Schlenk techniques in a dry nitrogen atmosphere. The synthesis of complexes 3–5 was carried out in air. Iron complex CpFe(CO)$_2$(Me) [34] and palladium complex PdCl$_2$(COD) [35] were prepared according to the literature method. The other chemicals were commercially available. Phenylphosphine PhPH$_2$ (10% hexane solution) was used after distillation (however, a little amount of hexane could not be removed). Solvents were purified employing a two-column solid-state purification system or were distilled from appropriate drying agents under N$_2$. Spectroscopic data of the products obtained in this work, 1a–1g, 2a–2d, 2f, and 2k, agreed with those in the literatures [16,17]. Spectroscopic data of the products 1i–1s were preliminarily reported in [27]. NMR spectra ($^1$H, $^{13}$C, and $^{31}$P) were recorded at ambient temperature with a JNM ECS-400 spectrometer.
1H and 13C NMR data were referred to residual peaks of solvent as an internal standard. Peak positions of 31P NMR spectra were referenced to external 85% H3PO4 (δ = 140 ppm). Elemental analysis data were obtained with a Perkin–Elmer 2400 CHN elemental analyzer.

3.2. Synthesis

3.2.1. General Procedure for Synthesis of Phosphinecarboxamide and Phosphinecarbothioamide

The mixture of the phosphine compound (0.7 mmol) and isocyanate/isothiocyanate (0.7 mmol) was stirred at room temperature in a Schlenk tube. After the reaction was complete, all volatile materials were removed under reduced pressure. The residual powder was dried in vacuo to give the corresponding phosphinecarboxamide/phosphinecarbothioamide.

\( m\text{-ClC}_2\text{H}_4\text{NHC(O)PPH}_2 \) (1h): Ph2PH (0.7 mmol, 122 µL) was treated with 3-chlorophenylisocyanate (0.7 mmol, 85 µL) using a general procedure to give the product 1h (236 mg, 99%) as a white powder. 1H NMR (400 MHz, CDCl3, ppm) δ 7.06–7.07 (m, 1H), 7.16–7.21 (m, 1H), 7.30 (br, 1H), 7.45–7.46 (m, 7H), 7.51–7.53 (m, 1H), 7.57–7.61 (m, 4H), 7.80 (br, 1H, NH). 13C NMR (100.4 MHz, CDCl3, ppm) δ 117.6, 119.7, 124.9, 129.3 (d, J_C-P = 7.47 Hz), 130.1, 130.4, 132.8 (d, J_C-P = 10.8 Hz), 134.5 (d, J_C-P = 19.1 Hz), 134.8, 138.6, 176.6 (d, J_C-P = 16.6 Hz, C=O). 31P[1H] NMR (161.70 MHz, CDCl3, ppm) δ −0.76 (s). Elemental analysis (%) calcd for C20H15F3N: C, 67.69; H, 3.88; N, 3.60. Found: C, 67.69; H, 3.88; N, 3.53.

\( p\text{-CF}_3\text{C}_6\text{H}_4\text{NHC(S)PPH}_2 \) (2e): The mixture of Ph2PH (0.7 mmol, 122 µL) was treated with 4-trifluoromethylphenylisothiocyanate (0.7 mmol, 142 mg) using a general procedure to give the product 2e (270 mg, 99%) as a yellow powder. 1H NMR (400 MHz, CDCl3, ppm) δ 7.45–7.51 (m, 6H), 7.55–7.61 (m, 6H), 7.80 (d, 2H, J_H-H = 8.8 Hz), 8.78 (br, 1H, NH). 13C NMR (100.4 MHz, CDCl3, ppm) δ 121.2, 126.3 (q, J = 3.8 Hz), 129.6 (d, J_C-P = 6.7 Hz), 130.7, 134.3, 134.5, 141.6, 208.5 (d, J_C-P = 40.3 Hz, C=S). The CF3 peak overlapped with another peak. 31P[1H] NMR (376.95 MHz, CDCl3, ppm) δ 9.20 (s). 31P[15N] NMR (161.70 MHz, CDCl3, ppm) δ 20.5 (s). Elemental analysis (%) calcd for C20H15F3NSP: C, 61.69; H, 3.88; N, 3.60. Found: C, 61.74; H, 4.00; N, 3.57%.

\( m\text{-ClC}_2\text{H}_4\text{NHC(S)PPh}_2 \) (2i): The mixture of diphenylphosphine Ph2PH (0.7 mmol, 122 µL) and 2-chlorophenylisothiocyanate (0.7 mmol, 92 µL) was stirred at room temperature in a Schlenk tube. After 24 h, all volatile materials were removed under reduced pressure. The residue was washed with n-hexane (1 mL × 3) at −70 °C and dried in vacuo to give 2i (226 mg, 91%) as a yellow powder. 1H NMR (400 MHz, CDCl3, ppm) δ 7.16–7.30 (m, 1H), 7.45–7.50 (m, 7H), 7.75–7.78 (m, 4H), 8.66 (br, 1H, NH). 13C NMR (100.4 MHz, CDCl3, ppm) δ 120.6, 122.4, 127.2, 129.5 (d, J_C-P = 7.67 Hz), 130.1, 130.6, 134.3, 134.5, 141.6, 207.9 (d, J_C-P = 40.3 Hz, C=S) ppm. 31P[1H] NMR (161.70 MHz, CDCl3, ppm) δ 19.4 (s). Elemental analysis (%) calcd for C20H15F3N: C, 64.14; H, 4.25; N, 3.53 found: C, 63.92; H, 4.33; N, 3.86%.

\( o\text{-ClC}_2\text{H}_4\text{NHC(S)PPh}_2 \) (2j): The mixture of diphenylphosphine Ph2PH (0.7 mmol, 122 µL) and 2-chloroethylenisothiocyanate (0.7 mmol, 92 µL) was stirred at room temperature in a Schlenk tube. After 2 h, all volatile materials were removed under reduced pressure. The residual yellow powder was washed with n-hexane (1 mL × 3) at −70 °C and dried in vacuo to give 2j (185 mg, 86%). 1H NMR (400 MHz, CDCl3, ppm) δ 3.53 (t, 2H, J = 9.2 Hz, CH2), 4.58–4.63 (m, 2H, CH2), 7.46–7.55 (m, 6H), 7.58–7.62 (m, 4H). The peak of NH overlapped with another peak. 13C NMR (100.4 MHz, CDCl3, ppm) δ 32.2, 58.0, 129.6 (d, J_C-P = 8.3 Hz,
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3.2.3. Synthesis of Pd(II) Complexes

[Pd(Ph₂PC(O)NHPPh-κP)]Cl₂ (3): A dichloromethane solution (2.5 mL) in a flask containing PdCl₂(COD) (57.2 mg, 0.20 mmol) and Ph₂PC(O)NHPPh 1a (123.2 mg, 0.40 mmol) was stirred at room temperature. After 5 min, all volatile materials were removed under reduced pressure. The residual yellow powder was washed with n-hexane and dried in vacuo to give 3 (153.7 mg, 0.195 mmol, 97%) as a yellow powder. 1H NMR (400 MHz, CDCl₃, ppm) δ 7.11−7.16 (m, 2H), 7.28−7.30 (m, 4H), 7.46−7.50 (m, 8H), 7.54−7.59 (m, 8H), 7.81−7.86 (m, 8H), 10.56 (br, 2H, NH). 31P[1H] NMR (100.4 MHz, CDCl₃, ppm) δ 120.3 (s), 125.6 (s), 126.3 (vt, J_C-P = 24.9 Hz), 128.7 (vt, J = 5.3 Hz), 129.2 (s), 131.8 (s), 135.0 (vt, J = 6.2 Hz), 137.6 (vt, J = 4.8 Hz), 164.9 (vt, J = 26.4 Hz, C=O). 31P[1H] NMR (162 MHz, CDCl₃, ppm) δ 25.5 (s). Elemental analysis (%) calcld for C₃₈H₃₂Cl₂N₂O₂P₂Pd: C, 57.92; H, 4.09; N, 3.56. Found: C, 57.66; H, 4.22; N, 3.50%.

[PdCl₂(Ph₂PC(S)NHPPh-κP)]Cl₂ (4): A dichloromethane solution (1.0 mL) in a test tube containing PdCl₂(COD) (14.3 mg, 0.050 mmol) and Ph₂PC(S)NHPPh 2a (32.2 mg, 0.100 mmol) was stirred at room temperature for 5 min. Yellow crystal 4 (14.3 mg, 0.029 mmol, 57%) was obtained by solvent diffusion over a few days from a CH₂Cl₂ layer and an overlayer of hexane. 1H NMR (400 MHz, −50 °C, CDCl₃, ppm) δ 7.36−7.53 (m, 10H), 7.88−7.90 (m, 2H), 7.99−8.04 (m, 3H), 13.13 (brs, NH, 1H). 31P[1H] NMR (100.4 MHz, 20 °C, CDCl₃, ppm) δ 119.8 (s), 120.3 (s), 123.7 (s), 129.6 (s), 129.6 (d, J_C-P = 12.5 Hz), 134.0 (s), 135.0 (d, J_C-P = 13.4 Hz), 135.5 (d, J_C-P = 4.8 Hz). The C=S peak was not observed. 31P[1H] NMR (162 MHz, 20 °C, CDCl₃, ppm) δ −41.3 (s). Elemental analysis (%) calcld for C₁₉H₁₆Cl₂NPPdS: C, 45.76; H, 3.23; N, 2.81. Found: C, 45.97; H, 3.57; N, 2.76%.

3.2.4. NMR Tube Experiments for Pd(II) Complexes

A CDCl₃ solution (0.5 mL) of Pd(COD)Cl₂ (7.1 mg, 0.025 mmol) and Ph₂PC(S)NHPPh 2a (8.1 mg, 0.025 mmol) was mixed with Ph₃P (internal standard, 8.1 mg, 0.029 mmol) in a vial at room temperature. After 5 min, 31P NMR was measured, which revealed that [Pd{Ph₂PC(S)NHPPh-κP}]Cl₂ (3) was formed in 48% NMR yield based on Pd.

A CDCl₃ solution (0.5 mL) of Pd(COD)Cl₂ (7.1 mg, 0.025 mmol) and Ph₂PC(S)NHPPh 2a (16.1 mg, 0.050 mmol) and P(=O)Ph₃ (internal standard, 8.1 mg, 0.029 mmol) was mixed in an NMR tube at room temperature. After 5 min, 31P NMR was measured, which revealed that [PdCl₂(Ph₂PC(S)NHPPh-κP)]Cl₂ (4) was formed in 94% NMR yield. A CDCl₃ solution (0.5 mL) of Pd(COD)Cl₂ (7.1 mg, 0.025 mmol) and Ph₂PC(S)NHPPh 2a (32.2 mg, 0.100 mmol) and P(=O)Ph₃ (internal standard, 8.1 mg, 0.029 mmol) was mixed in an NMR tube at room temperature. After 5 min, 31P NMR was measured, which revealed that [PdCl₂(Ph₂PC(S)NHPPh-κP)]Cl₂ (4) was formed in 94% NMR yield.

3.2.3. Synthesis of Pd(II) Complexes

[Pd(Ph₂PC(O)NHPPh-κP)]Cl₂ (3): A dichloromethane solution (2.5 mL) in a flask containing PdCl₂(COD) (57.2 mg, 0.20 mmol) and Ph₂PC(O)NHPPh 1a (123.2 mg, 0.40 mmol) was stirred at room temperature. After 5 min, all volatile materials were removed under reduced pressure. The residual yellow powder was washed with n-hexane and dried in vacuo to give 3 (153.7 mg, 0.195 mmol, 97%) as a yellow powder. 1H NMR (400 MHz, CDCl₃, ppm) δ 7.11−7.16 (m, 2H), 7.28−7.30 (m, 4H), 7.46−7.50 (m, 8H), 7.54−7.59 (m, 8H), 7.81−7.86 (m, 8H), 10.56 (br, 2H, NH). 31P[1H] NMR (100.4 MHz, CDCl₃, ppm) δ 120.3 (s), 125.6 (s), 126.3 (vt, J_C-P = 24.9 Hz), 128.7 (vt, J = 5.3 Hz), 129.2 (s), 131.8 (s), 135.0 (vt, J = 6.2 Hz), 137.6 (vt, J = 4.8 Hz), 164.9 (vt, J = 26.4 Hz, C=O). 31P[1H] NMR (162 MHz, CDCl₃, ppm) δ 25.5 (s). Elemental analysis (%) calcld for C₃₈H₃₂Cl₂N₂O₂P₂Pd: C, 57.92; H, 4.09; N, 3.56. Found: C, 57.66; H, 4.22; N, 3.50%.
3.3. Crystallography

Crystallographic data are summarized in Table 1. The single crystals of 1i, 2c, and 3–5 were obtained using the slow diffusion method (CH₂Cl₂/hexane for 3 and 5; acetone/ether for 4). Diffraction-intensity data were collected with Rigaku AFC11 with a Saturn 724 + CCD diffractometer (200(2) K for 1i, 2c; 110(2) K for 3–5), and semiempirical multi-scan absorption correction [36] was performed. The structures were solved using SIR97 [37] via subsequent difference Fourier synthesis, and refined with full matrix least-squares procedures on F². All non-hydrogen atoms were refined with anisotropic displacement coefficients. NH protons were determined via difference Fourier synthesis and refined isotropically. Hydrogen atoms (except for NH protons) were treated as idealized contributions and refined in a rigid group model. All software and sources of scattering factors were contained in the SHELXL-2018/3 [38] program package. The Cambridge Crystallographic Data Centre (CCDC) deposition numbers of 1i, 2c, and 3–5 are included in Table 1.

Table 1. Crystallographic data and details of structure refinement parameters of 1i, 2c, and 3–5

|             | 1i       | 2c       | 3         | 4-0.5(CH₂)CO | 5-CH₂Cl₂ |
|-------------|----------|----------|-----------|--------------|----------|
| empirical formula | C₃₂H₃₂ClNOP | C₁₉H₂₂ClNIPS | C₃₈H₃₅Cl₂N₂O₂P₂Pd | C₃₉H₃₅Cl₂N₂O₂P₂Pd | C₃₉H₃₅Cl₂N₂P₂S₂Pd |
| formula weight | 291.70 | 355.80 | 787.89 | 527.70 | 904.94 |
| T (K)        | 200(2)  | 200(2)  | 110(2)  | 110(2)  | 110(2)  |
| crystal system | triclinic | monoclinic | orthorhombic | triclinic | monoclinic |
| space group | P2₁/n | Pca₂ | P2₁/n | P2₁/n | P2₁/n |
| a (Å)        | 9.29470(10) | 9.2578(5) | 12.9390(2) | 15.6624(2) | 16.8190(2) |
| b (Å)        | 11.6190(2) | 21.2798(9) | 21.0466(4) | 21.0466(4) | 21.0466(4) |
| c (Å)        | 21.0466(4) | 21.0466(4) | 14.927(4) | 18.189(5) | 18.189(5) |
| α (°)        | 85.569(6) | 106.543(4) | 82.125(7) | 116.3332(15) | 92.7607(1) |
| β (°)        | 82.125(7) | 103.748(3) | 85.569(6) | 85.569(6) | 85.569(6) |
| γ (°)        | 67.021(6) | 103.748(3) | 67.021(6) | 67.021(6) | 67.021(6) |
| volume (Å³)  | 1448.16(9) | 1755.00(15) | 3390.98(12) | 2130.6(10) | 3924.0(17) |
| Z            | 4 | 4 | 4 | 4 | 4 |
| ρcalcd (mg m⁻³) | 1.338 | 1.347 | 1.543 | 1.645 | 1.352 |
| μ (mm⁻¹)     | 0.365 | 0.426 | 0.837 | 1.303 | 0.965 |
| F(000)       | 608 | 736 | 1600 | 1056 | 1832 |
| crystal size (mm³) | 0.37 × 0.27 × 0.12 | 0.27 × 0.18 × 0.17 | 0.12 × 0.07 × 0.02 | 0.13 × 0.07 × 0.03 | 0.21 × 0.16 × 0.06 |
| reflections collected | 17,154 | 13,335 | 27,555 | 22,263 | 39,512 |
| R(int)       | 0.0478 | 0.0503 | 0.0204 | 0.0278 | 0.0346 |
| wR2 (all data) | 0.1187 | 0.1062 | 0.0502 | 0.0600 | 0.0704 |
| goodness of fit | 1.106 | 1.094 | 1.042 | 1.046 | 1.094 |
| CCDC deposition number | 1959302 | 2193371 | 2168755 | 2168782 | 2168783 |

4. Conclusions

We achieved the catalyst-free synthesis of phosphinecarboxamide and phosphinecarbothioamide through the hydrophosphination of isocyanates and isothiocyanates. The important point in our system was to carry out the reaction without using a solvent (neat). This system showed the characteristics of easy handling, high yield, short reaction time, and good functional-group tolerance for the functionalized isocyanates and isothiocyanates. For the requirement of no catalyst nor solvent, the gram-scale synthesis of these compounds was also achieved. In addition, we synthesized and characterized palladium complexes with phosphinecarboxamide and phosphinecarbothioamide as ligands. In the reaction of Pd(COD)Cl₂ with 1a, [Pd₂(PC(S)NHPh-kP)₂Cl₂] (3) was obtained regardless of whether 1a was used in 1 or 2 equivalents. In contrast, in the reaction of Pd(COD)Cl₂ with 2a, [PdCl₂(PC(S)NHPh-kP,5)] (4) and [PdCl₂(PC(S)NHPh-kP,5)[PC(S)NHPh-kP]]Cl (5) were selectively obtained when 1 eq. and 2 eq. of 2a were used, respectively. It was revealed that 3 and 5 having intra- and/or inter-molecular hydrogen bonds showed thermal cis/trans isomerization.
Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/xxx/s1, Figure S1: 31P NMR spectra (CDCl3, 161.70 MHz) of 3 at 50 °C, 20 °C, and −50 °C, Figure S2: van’t Hoff plots for 3, Figure S3: van’t Hoff plots for 5, Figures S4–S27: NMR spectra of all new compounds.

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Sample Availability: Samples of the compounds are not available from the authors.

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