Formation of ArPdXL(amine) Complexes by Substitution of One Phosphane Ligand by an Amine in *trans*-ArPdX(PPh_3)$_2$ Complexes

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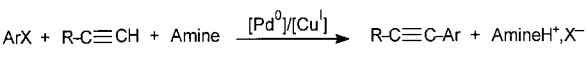
Keywords: Amines / Phosphanes / Palladium / Ligand substitution

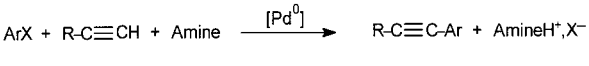
Amines (piperidine, morpholine, diisopropylamine, terbutylamine), which may be used as bases in copper-free palladium-catalyzed Sonogashira reactions, substitute one phosphane PPh_3 in *trans*-ArPdX(PPh_3)$_2$ complexes (Ar = Ph, 4-NC–C_6H_4, 4-MeOC–C_6H_4, 2-thienyl; X = I, Br, Cl) to generate ArPdX(PPh_3)(amine) complexes in a reversible reaction whose equilibrium constant is determined in chloroform, THF, and DMF. The equilibrium constant depends on Ar, X, the basicity, and the steric hindrance of the amine.

Palladium-catalyzed Sonogashira reactions (Scheme 1) require the presence of a base, which is very often an amine.[1,2]



Scheme 1.

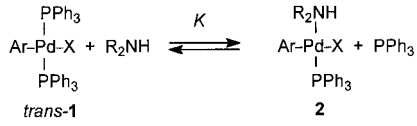
In copper-free Sonogashira reactions (Scheme 2), the role of the base is crucial, and specific amines are required.[3–10] Among them, secondary amines such as piperidine,[3,6,8–10] morpholine,[10] and diisopropylamine[8,10] proved to be very efficient. The amines are usually used in excess,[5,6,8,9] even as the solvent.[3,6,7] PPh_3 is often a ligand of the palladium catalyst when aryl iodides, bromides or triflates are used.[3,4,7–9]



Scheme 2.

The mechanism of the copper-free reaction is not well known. The first step of the reaction is an oxidative addition of ArX to a Pd^0 complex, which generates $ArPdXL_2$ complexes (e.g. L = PPh_3). However, the second step of the reaction is under debate. The amines employed in such reactions (e.g. piperidine, morpholine, etc.) are usually not able to deprotonate the alkyne to generate the anionic nucleophile RC≡C$^-$ that is able to react with $ArPdXL_2$ in a transmetallation step. It is for this reason that complexation of the alkyne to the *trans*-$ArPdXL_2$ complexes is supposed to proceed first with displacement of one ligand to give intermediate complexes: ArPdXL(η^2-HC≡CR).[10] The ligated alkyne would then be more easily deprotonated by the amine, and a new complex would be formed ArPd(–C≡CR)L_n (n = 1 or 2), which gives the coupling product ArC≡CR by reductive elimination. In the absence of any amine, a carbopalladation step[11,12] takes place, which leads to R–C($PdXL_2$)=CH–Ar complexes,[12] presumably by formation of ArPdXL(η^2-HC≡CR) complexes.[11]

Herein we report that amines react with *trans*-ArPdX(PPh_3)$_2$ (**1**) complexes by substitution of one PPh_3 to generate ArPdX(PPh_3)(amine) (**2**) complexes (Scheme 3). In other words, competition between the amine and the alkyne for the substitution of one phosphane group in ArPdX(PPh_3)$_2$ complexes may occur in palladium-catalyzed copper-free Sonogashira reactions.



Scheme 3.

The reactions of the secondary (piperidine, morpholine, and diisopropylamine) and primary amines (terbutylamine) with **1** were monitored by ^1H and ^{31}P NMR spectroscopy in DMF, THF, acetone, and chloroform, after successive additions of known amounts of amine. Besides the set of the ^1H NMR signals for the protons of the Ar group in **1**, a new set of signals appears at lower field, suggesting that a new complex **2** is formed. The magnitude of the ^1H NMR signals of **2** increases at the expense of those of complexes **1** as the amine concentration is increased. Concomitant ^{31}P NMR spectroscopy performed on the same solutions shows that signals for free PPh_3[13] are detected in the ^{31}P NMR spectra, together with a new singlet (δ_2 in Table 1) located

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Table 1. Equilibrium constants K and ^{31}P NMR shifts (101 MHz, H_3PO_4) of *trans*-ArPdX(PPh_3)$_2$ (δ_1)and ArPdX(PPh_3)(amine) (δ_2) generated by the reversible substitution of one PPh_3 group by the amine group (Scheme 3)

Entry	*trans*-ArPdX(PPh_3)$_2$	δ_1 [ppm]	ArPdX(PPh_3)(amine)	δ_2 [ppm][a]	K
Solvent		[D_7]DMF		[D_7]DMF	[D_7]DMF
1	PhPdI(PPh_3)$_2$	23.14	PhPdI(PPh_3)(piperidine)	32.56[b]	0.095
Solvent		[D_8]THF		[D_8]THF	[D_8]THF
2	PhPdI(PPh_3)$_2$	23.22	PhPdI(PPh_3)(piperidine)	33.18 [c]	0.14
Solvent		[D_6]acetone		[D_6]acetone	[D_6]acetone
3	PhPdI(PPh_3)$_2$	23.04	PhPdI(PPh_3)(piperidine)	32.83	n.d.[j]
Solvent		$CDCl_3$		$CDCl_3$	$CDCl_3$
4	PhPdI(PPh_3)$_2$	23.03	PhPdI(PPh_3)(piperidine)	32.45	0.11
5			PhPdI(PPh_3)(morpholine)	32.73	0.026
6			PhPdI(PPh_3)(tBuNH$_2$)	32.09[d]	0.002
7			PhPdI(PPh_3)(iPr$_2$NH)	31.72[e]	7×10^{-5}
8	PhPdBr(PPh_3)$_2$	23.72	PhPdBr(PPh_3)(piperidine)	32.08	0.28
9			PhPdBr(PPh_3)(morpholine)	32.37	0.014
10	PhPdCl(PPh_3)$_2$	23.73	PhPdCl(PPh_3)(piperidine)	31.76[f]	0.21
11			PhPdCl(PPh_3)(morpholine)	31.98	0.013
12	(4-NC–C_6H_4)PdI(PPh_3)$_2$	22.97	(4-NC–C_6H_4)PdI(PPh_3)(piperidine)	31.83[g]	0.023
13			(4-NC–C_6H_4)PdI(PPh_3)(morpholine)	32.25[h]	0.0038
14	(4-NC–C_6H_4)PdBr(PPh_3)$_2$	23.75	(4-NC–C_6H_4)PdBr(PPh_3)(piperidine)	31.48	0.038
15			(4-NC–C_6H_4)PdBr(PPh_3)(morpholine)	31.97	0.0033
16	(4-MeOC–C_6H_4) PdBr(PPh_3)$_2$	23.69	(4-MeOC–C_6H_4)PdBr(PPh_3)-(piperidine)	31.71[i]	n.d.[k]
17	(2-Th)PdI(PPh_3)$_2$[l]	21.97	(2-Th)PdI(PPh_3)(piperidine)	30.72	0.1

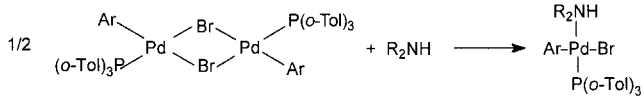
[a] δ_2 is the shift of the major isomer. [b] A minor isomer (16%) was observed at δ = 30.52 ppm. [c] A minor isomer (6%) was observed at δ = 32.22 ppm. [d] A minor isomer (11%) was observed at δ = 27.62 ppm. [e] Two other isomers (11%) were observed at δ = 28.20 and 30.10 ppm. [f] A minor isomer (13%) was observed at δ = 33.82 ppm.[g] A minor isomer (27%) was observed at δ = 31.31 ppm. [h] A minor isomer (40%) was observed at δ = 31.62 ppm. [i] A minor isomer (39%) was observed at δ = 31.42 ppm. [j] None determined because of the very low solubility of *trans*-PhPdI(PPh_3)$_2$ in acetone. [k] None determined because of the presence of some triphenylphosphane oxide. [l] Th means thienyl.

at lower field than those of the initial complexes **1** (δ_1 in Table 1). The magnitude of the singlet for free PPh_3 is similar to those of the new complexes **2** and both increase concomitantly at the expense of those of **1** as the amine concentration is increased. These experiments establish that one PPh_3 group is substituted by one amine group (Scheme 3).[14–18] The coordinated amine was characterized by its ^1H and ^{13}C NMR signals in isolated complexes **2**.

The reversibility of the substitution is proved by the fact that the amount of **2** increases at the expense of **1** when the amine concentration is increased, and addition of PPh_3 to solutions containing both complexes **1** and **2** results in an increase in the amount of **1** to the detriment of **2**. Addition of PPh_3 to the isolated complex 2-ThPdI(PPh_3)(piperidine) (Th = thienyl) results in the formation of *trans*-2-ThPdI(PPh_3)$_2$, and the release of the free piperidine is clearly detected by the ^1H NMR spectroscopy – further evidence of the equilibrium in Scheme 3. Complexes **1** and **2** are involved in equilibria that are slow relative to the time scale of NMR spectroscopy.

The substitution of the two PPh_3 was never observed,[19] even in the presence of a large amount of amine. Indeed, the integration of the ^{31}P NMR signal for the free phosphane never exceeded that of the monosubstituted complex ArPdX(PPh_3)(amine).

The substitution of PPh_3 in *trans*-ArPdX(PPh_3)$_2$ (**1**) by the amine occurs irrespective of the identity of X (= I, Br, Cl) and the aryl groups (Ar = Ph, 2-thienyl, 4-NC–C_6H_4, 4-MeOC–C_6H_4) investigated here (Table 1). One major complex of type **2** is generally generated (Table 1). Its structure, given in Scheme 3, was deduced from its ^{13}C NMR spectrum, in agreement with the value of the J_{CP} coupling, characteristic of a phosphane *cis* to the aryl group. In some cases, a second minor singlet near that observed at δ_2 is detected (Table 1), which suggests isomerisation of the ligands of **2** around the Pd^{II} centre, as observed for the P(*o*-Tol)$_3$ (*o*-Tol: *ortho*-tolyl) ligand.[20] Indeed, related complexes ArPdBr(amine)(P[*o*-Tol]$_3$) have been synthesized by a quite different reaction, not by ligand substitution but by cleavage of the bromide bridges by the amine in dimeric [ArPdBr(P[*o*-Tol]$_3$)]$_2$ complexes (Scheme 4).[20,21] The major isomer ArPd(amine)(P[*o*-Tol]$_3$) has the same structure as complexes **2** with the phosphane *trans* to the amine group.[20] Two other minor isomers only characterized by ^{31}P NMR singlets are also observed.[20]



Scheme 4.

The complexes ArPdX(PPh_3)(amine) **2** generated in situ were rather stable with time in chloroform. After some days, phosphane oxide was detected as a by-product, with the effect that the amount of complexes **2** had increased relative to that of complexes **1**, by the shift of the equilibrium in Scheme 3 to the right as a result of the oxidation of PPh_3. As an isolated complex, PhPdI(PPh_3)(piperidine) was stable for at least four days in chloroform.

The value of the equilibrium constant in Scheme 3, K = [**2**][PPh_3]/[**1**][amine] was determined by ^{31}P NMR spectroscopy by using the respective integration of the singlets of complexes **1** and **2**;[22] $K = x^2/(1-x)(n-x)$, where x is the molar fraction of **2** in the equilibrium: $x = 2S_2/(S_1 + 2S_2)$ [S_1 and S_2: magnitude of the singlet of **1** and **2**, respectively], n is the equiv. of amine added to **1**. The plot of x^2 versus $(1-x)(n-x)$ is linear, and K is determined from the slope of the straight line (Figure 1,Table 1).

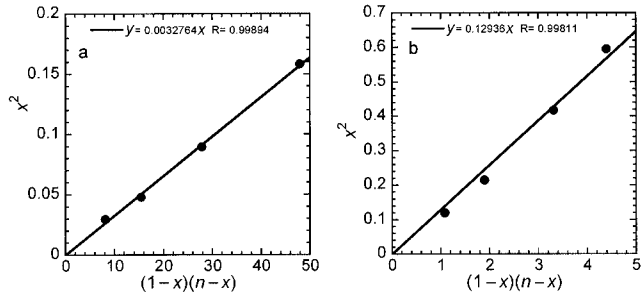


Figure 1.Determination of the equilibrium constant K between *trans*-ArPdX(PPh_3)$_2$**1** and ArPdX(PPh_3)(amine) **2** (Scheme 3) as monitored by ^{31}P NMR spectroscopy; plot of x^2 versus $(1-x)(n-x)$ [x is the molar fraction of **2** in the equilibrium; n is the equiv. of amine added to **1**]; K is determined from the slope; a) equilibrium between *trans*-(4-NC–C_6H_4)PdBr(PPh_3)$_2$ (initially 30 mM) and (4-NC–C_6H_4)PdBr(PPh_3)(morpholine) in $CDCl_3$ (n = 10, 20, 40, 80); b) equilibrium between *trans*-PhPdI(PPh_3)$_2$ (initially 20 mM) and PhPdI(PPh_3)(piperidine) in [D_8]THF (n = 2, 4, 10, 20)

The value of K is less than 1 (Table 1), which means that, under identical concentrations of ArPdX(PPh_3)$_2$ and amine, the equilibrium lies in favor of ArPdX(PPh_3)$_2$. However, in catalytic reactions where the concentration of the amine is always considerably higher than that of the catalytic palladium species, the equilibrium will be shifted toward the formation of ArPdX(PPh_3)(amine). As an example, if the concentration of the piperidine is 50 times higher than that of *trans*-PhPdI(PPh_3)$_2$ in DMF (corresponding to a catalytic reaction run with 2% of catalyst), then, with K = 0.095 (Table 1), one calculates that the concentration of PhPdI(PPh_3)(piperidine) will be 5.5 times higher than that of *trans*-PhPdI(PPh_3)$_2$.

The ligand substitution was studied under reversible conditions. We only have the thermodynamic data for the formation of complexes **2**. From the values of the equilibrium constant K collected in Table 1, it can be seen that for a given Ar group and X, K increases, and consequently the substitution is favored as the amine basicity[23] increases within the cyclic series (piperidine and morpholine: compare entries 4 and 5, 8 and 9, 10 and 11, 12 and 13, and 14 and 15). However, the magnitude of K follows the order (compare entries 4–7): piperidine > morpholine > $tBuNH_2$ >> iPr_2NH.

This does not reflect the amine basicity order since on one hand morpholine is less basic than tBuNH$_2$ and iPr$_2$NH, and on the other hand iPr$_2$NH is slightly more basic than tBuNH$_2$.[23] The steric hindrance of the amine may also affect the substitution. Indeed, *N*-methylmorpholine, even when used at high concentrations, could not displace the phosphane. The equilibrium constant is not significantly affected by the solvent (entries 1,2,4).

For a given X, amine and solvent, K decreases when the *para* substituent on the aryl group is an electron acceptor (entries 4 and 12, 5 and 13, 8 and 14, and 9 and 15).[24,25] The reaction was not tested with an electron-donor substituent because of the instability of the related *trans*-ArPdX(PPh_3)$_2$ due to scrambling between the Ph group of the ligand and the Ar group.[26,27]

The influence of X (X = I, Br, Cl) on the substitution was tested for a given Ar group, amine and solvent. Whereas for the substitution of PPh_3 by the piperidine K follows the order: Br > Cl > I (entries 4, 8,10; entries 12, 14), a reverse order: I > Br ≈ Cl (entries 5, 9, 11; entries 13,15) is found for the substitution by morpholine. The effect of the halides is hard to rationalize, since they cannot have a *trans* influence on the substitution of the phosphane due to the structure of the initial complexes **1**.[24,25]

In conclusion, ArPdX(PPh_3)(amine) complexes were generated by the reaction of amines with *trans*-ArPdX(PPh_3)$_2$ complexes. The reversible substitution of one PPh_3 group by one amine was characterized by the determination of the equilibrium constant between the two complexes. These results establish that in copper-free Sonogashira reactions, the formation of ArPdX(PPh_3)(amine) complexes has to be taken into account. There will be an evident competition between the alkyne and the amine for the substitution of one PPh_3 group in ArPdX(PPh_3)$_2$ complexes. The fact that the amine is often used in large excess[5,6,8,9] or as the solvent[3,6,7] encourages the substitution of the phosphane by the amine group. Work is in progress to better define the contribution of such new amine complexes in the mechanism of palladium-catalyzed reactions involving amines in copper-free Sonogashira reactions.

Experimental Section

General: All experiments were conducted under argon. The deuterated solvents DMF, THF, acetone and chloroform were obtained commercially and degassed just before use. The amines (piperidine; morpholine, diisopropylamine, terbutylamine), phenyl halides (X = I, Br, Cl), 4-NC–C_6H_4–X (X = Br, Cl), 4-MeOC–C_6H_4–Br, 2-iodothiophene were obtained commercially. The complexes *trans*-ArPdX(PPh_3)$_2$ were synthesized by reacting aryl halides with $Pd^0(PPh_3)_4$.[28–30]

General Procedure for the Ligand Exchange as Monitored by ^1H and ^{31}P NMR Spectroscopy: *trans*-PhPdI(PPh_3)$_2$ (8.3 mg, 0.01 mmol) was introduced in $CDCl_3$ (0.5 mL). The ^1H and ^{31}P NMR spectra were recorded at room temperature. Piperidine (2 μL, 0.02 mmol) was first added, followed by further additions of piperidine (0.02, 0.06 and 0.10 mmol, respectively). ^1H and ^{31}P NMR spectra were recorded after each addition of piperidine.

General Procedure for the Synthesis of ArPdX(PPh_3)(amine): Piperidine (500 μL, 5 mmol) was added to *trans*-PhPdI(PPh_3)$_2$ (83 mg, 0.1 mmol) in chloroform (5 mL). After 30 min, the solution was concentrated under vacuum. Precipitation in pentane gave 48 mg of PhPdI(PPh_3)(piperidine), as a gray-white solid (72 % yield). The isolated complex exhibits the same ^1H and ^{31}P NMR spectra as those recorded during ligand exchange in the NMR tube, but the

protons of the ligated piperidine are more clearly detected because of the absence of excess piperidine. A ^{13}C NMR spectrum was also recorded on the isolated complex to elucidate its structure.

The complexes with morpholine, $ArPdX(PPh_3)$(morpholine), could not be isolated as pure compounds because the equilibrium lies less in favor of their formation than for the formation of $ArPdX(PPh_3)$(piperidine). The reversibility explains the difficulty in their isolation. Consequently, most of them were characterized in situ in solution.

***trans*-PhPdI(PPh$_3$)$_2$:**[28] ^1H NMR (250 MHz, $CDCl_3$, TMS): δ = 6.21 (t, J = 7 Hz, 2 H, *m*-H of Ph), 6.33 (t, J = 7 Hz, 1 H, *p*-H of Ph), 6.60 (d, J = 7 Hz, 2 H, *o*-H of Ph), 7.23 (t, J = 7 Hz, 12 H, *m*-H in PPh_3), 7.32 (t, J = 7 Hz, 6 H, *p*-H in PPh_3), 7.50 (dd, J = 7, J = 6 Hz, 12 H, *o*-H in PPh_3) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, TMS): δ = 127.76 (t, J_{C3P} = 5 Hz, C_3 of Ph in PPh_3), 127.90 (t, J_{C3P} = 4 Hz, C_3 of Ph–Pd), 129.69 (s, C_4 of Ph in PPh_3), 131.31 (s, C_4 of Ph–Pd), 132.21 (t, J_{C1P} = 23 Hz, C_1 of Ph in PPh_3), 134.65 (t, J_{C2P} = 6 Hz, C_2 of Ph–Pd), 134.89 (t, J_{C2P} = 6 Hz, C_2 of Ph in PPh_3), 136.03 (t, J_{C1P} = 5 Hz, C_1 of Ph–Pd) ppm. ^{31}P NMR (101 MHz, $CDCl_3$, H_3PO_4): δ = 23.03 (s) ppm.

***trans*-(4-NC–C$_6$H$_4$)PdBr(PPh$_3$)$_2$:**[30] ^1H NMR ($CDCl_3$, TMS): δ = 6.41 (d, J = 8 Hz, 2 H, *m*-H), 6.80 (d, J = 8 Hz, 2 H, *o*-H), 7.30 (m, 18 H, *m*-H and *p*-H in PPh_3), 7.52 (dd, J = 7, J = 6 Hz, 12 H, *o*-H in PPh_3) ppm. ^{31}P NMR ($CDCl_3$, H_3PO_4): δ = 23.75 (s) ppm.

***trans*-(2-Th)PdI(PPh$_3$)$_2$:** ^1H NMR ($CDCl_3$, TMS): δ = 5.89 (d, J = 3.3 Hz, 1 H, 5-H in Th), 6.34 (dd, J = 5, J = 3.3 Hz, 1 H, 4-H in Th), 6.82 (d, J = 5 Hz, 1 H, 3-H in Th), 7.29 (m, 18 H, *m*-H and *p*-H in PPh_3), 7.53 (dd, J = 6, J = 5.5 Hz, 12 H, *o*-H in PPh_3) ppm. ^{31}P NMR ($CDCl_3$, H_3PO_4): δ = 30.72 (s) ppm.

PhPdI(PPh$_3$)(piperidine): Isolated complex, yield 72%. ^1H NMR (250 MHz, $CDCl_3$, TMS): δ = 1.25 (m, 2 H, γCH_2), 1.38 (m, 2 H, βCH_2), 1.55 (m, 2 H, βCH_2), 2.39 (ddd, J = 13 Hz, 2 H, HC–N–CH), 3.29 (d, J = 13 Hz, 2 H, HC–N–CH), 3.43 (br. s, 1H, NH), 6.67 (m, 3 H, *m*-H and *p*-H of Ph), 6.95 (br. d, J = 4.5 Hz, 2 H, *o*-H of Ph), 7.22 (t, J = 6 Hz, 6 H, *m*-H in PPh_3), 7.25 (m, 3 H, *p*-H in PPh_3), 7.46 (t, 6 H, *o*-H in PPh_3) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$, TMS): δ = 23.83 (CH_2–*C*H_2–CH_2 of piperidine), 24.75 (N–CH_2–*C*H_2 of piperidine), 49.34 (N*C*H_2 of piperidine), 127.53 (d, J_{C3P} = 1.5 Hz, C_3 of Ph–Pd), 127.76 (d, J_{C3P} = 10.5 Hz, C_3 of Ph in PPh_3), 127.99 (s, C_4 of Ph–Pd), 129.99 (s, C_4 of Ph in PPh_3), 132.1 (d, J_{C1P} = 50 Hz, C_1 of Ph in PPh_3), 134.28 (d, J_{C2P} = 4.6 Hz, C_2 of Ph–Pd), 134.78 (d, J_{C2P} = 11 Hz, C_2 of Ph in PPh_3), 160.58 (d, J_{C1P} = 2.3 Hz, C_1 of Ph–Pd) ppm. ^{31}P NMR (101 MHz, $CDCl_3$, H_3PO_4): δ = 32.45 (s) ppm. $C_{29}H_{31}INPPd$ (657.8): calcd. C 52.9, H 4.7, N 2.1; found C 51.9, H 4.2, N 1.8.

(4-NC–C$_6$H$_4$)PdBr(PPh$_3$)(morpholine): Isolated complex. ^1H NMR (250 MHz, $CDCl_3$, TMS): δ = 2.57 (ddd, J = 12 Hz, 2 H, HCNCH), 3.10 (d, J = 12 Hz, 2 H, HCNCH), 3.49 (dd, J = 12 Hz, 2 H, HCOCH), 3.73 (m, 2 H, HCOCH), 6.92 (d, J = 8 Hz, 2 H, *m*-H), 7.17 (d, J = 8 Hz, 2 H, *o*-H), 7.30 (m, 9 H, *m*-H and *p*-H in PPh_3), 7.52 (m, 6 H, *o*-H in PPh_3) ppm. ^{31}P NMR (101 MHz, $CDCl_3$, H_3PO_4): δ = 32.38 (s) ppm.

(2-Th)PdI(PPh$_3$)(piperidine): Isolated complex. ^1H NMR (250 MHz, $CDCl_3$, TMS): δ = 1.32 (m, 2 H, γCH_2), 1.65 (br. t, 4 H, βCH_2), 2.70 (ddd, J = 12 Hz, 2 H, HCNCH), 3.09 (s, 1 H, NH), 3.25 (d, J = 13.5 Hz, 2 H, HCNCH), 6.35 (d, J = 3.3 Hz, 1 H, 5-H in Th), 6.72 (dd, J = 5, J = 3.3 Hz, 1 H, 4-H in Th), 7.10 (d, J = 5 Hz, 1 H, 3-H in Th), 7.32 (m, 9 H, *m*-H and *p*-H in PPh_3), 7.52 (m, 6 H, *o*-H in PPh_3) ppm. ^{31}P NMR (101 MHz, $CDCl_3$, H_3PO_4): δ = 30.72 (s) ppm.

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[13] The ^{31}P NMR singlet of the free PPh_3 was located at –5.24 in [D$_8$]THF, –5.62 in [D$_9$]DMF, –5.46 in [D$_6$]acetone and –5.18 ppm in $CDCl_3$.
[14] The substitution of one phosphane group by one amine group in square-planar d^8 complexes *trans*-$RMXL_2$ (M = Pt, Pd; R = organic group; X = halide andL = PR'_3) is quite unusual.[15,16] What is often observed is the substitution of one halide ligand in *trans*-$RMXL_2$ (M = Pt, Pd; X = Br, Cl) complexes by an amine to generate cationic complexes [RM(amine)L_2]$^+X^-$, as in the reaction of pyridine (py) with *trans*-$ArPtCl(PEt_3)_2$ complexes that forms *trans*-[$ArPt(PEt_3)_2$(py)]$^+Cl^-$.[17,18]
[15] For substitutions reactions in square-planar d^8 complexes *trans*-$RMXL_2$ see: M. L. Tobe, "Reactions Mechanisms", in *Comprehensive Coordination Chemistry* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon Press, **1987**, vol. 1., pp. 281–329.
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[24] It has been established that the ligand in a *trans* position to the leaving group has a significant effect on the rate of the substitution reactions (*trans* effect). Here we are discussing thermodynamic factors (*trans* influence),[25] i.e. how the ligand *trans* to the leaving group can weaken the bond of the leaving group in the ground state of the reactant. In complexes **1**, the aryl group and the halide are in a *cis* position to the leaving group and would have a *cis* influence on the substitution. In general, the *cis* influence is less effective than the *trans* influence.[25]
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