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Phosphine- and thiophosphorane-amine ligands: Lithiation and coordination to Rh(I)

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ABSTRACT

A series of phosphine-amine and thiophosphorane-amine ligands ($PR_2(X)CH_2NHR'$, X = lone pair, S, R = Ph, Cy, R′ = *t*Bu, Ph) differing by the nature of the phosphorus and nitrogen substituents were synthesized. Their lithiation, in order to generate the corresponding amido ligand mainly led to dissociation with formation of phosphide or thiophosphinite anion and imine. DFT calculations confirmed that this pathway is in most cases thermodynamically favoured. But for a phosphine-amido anion featuring alkyl substituents on the P atom and phenyl on the nitrogen, calculations showed that the dissociation is strongly disfavoured (ΔG = +24.3 kcal mol^{-1}). Actually, $\{PCy_2CH_2NPhLi\}$ was isolated in high yield and fully characterized. This phosphine-amido ligand and the corresponding amine derivative were then coordinated to Rh(I) metal centre.

1. Introduction

Mixed ligands combining soft and hard donor atoms have received much attention because of their ability to stabilize a wide range of metals. Moreover, the presence of electronically different coordination sites may promote unusual reactivity at the metal centre. In this context, a variety of mixed ligands associating phosphine donors with amido groups was synthesized (Scheme 1). In particular, Fryzuk and co-workers, developed $[PN^{Si}P]$ and $[N_2P_2]$ ligands based on the $-SiMe_2CH_2-$ backbone, which gave group 4 and 5 metal complexes able to activate N_2 [1]. Zirconium complexes featuring a more rigid [NPN] ligand were also reported [2]. The [PNP] ligand developed by Liang et al. [3] and Ozerov and co-workers [4] may appear similar since it also features aromatic rings linked by heteroatoms but the nitrogen atom is central and the phosphorus donors are located at the periphery [5]. This ligand proved to be very versatile since its coordination to electron deficient metal centres such as group 4, 5 [6–8] and actinides [9] or to electron rich metals such as group 9 and 10 [4,10] was described. When di(isopropyl) groups are present as substituents on phosphorus, insertions of rhodium(I) and iridium(I) in NC or NH bonds were observed [10a]. Such [PNP] rhodium(I), iridium(I), or platinium(II) complexes were also shown to achieve CH activation [10b,11]. Apart from these two families of phosphine/amido ligands, [PN] [12], [PNN] [13], [PNNP] [14] and $[N_3P]$ [15] structures (Scheme 1) were also described and their coordination chemistry studied. Having already developed mixed ligands combining soft phosphine and hard iminophosphorane donors ligands [16], we were interested in elaborating phosphine-amido and thiophosphorane-amido ligands featuring various substituents at the P and N atoms. We now wish to report on the synthesis of the phosphine- and thiophosphorane-amine adducts, a study of their lithiation, and the coordination of $\{PCy_2CH_2NLiPh\}$ (Cy = cyclohexyl, Ph = phenyl) and the corresponding amine towards the [Rh(COD)Cl] metal fragment.

2. Results and discussion

The synthesis of phosphine-amine PR_2CH_2NHR' ligands was achieved by adding the amine to the hydroxymethylphosphine (Scheme 2). Nevertheless the synthetic procedure was found to highly depend on the nature of the substituents at both the phosphorus and the nitrogen atoms. Indeed, because of the presence of a reactive NH function in the formed product, reaction conditions have to be carefully monitored in order to avoid the formation of the corresponding [PCNCP] ligands (product resulting of the double condensation $[PCNCP] = R_2PCH_2N(R')CH_2PR_2$). With volatile *tert*-butylamine, the reaction was performed at room temperature in dichloromethane with 1.5 equiv. of amine (Scheme 2a), so that [PCNCP] was not observed. The amino-phosphines **1a** and **1b** were then isolated in excellent yield as pale yellow oils. They were characterized by a singlet in $^{31}P\{H\}$ NMR at $\delta(CH_2Cl_2) = -16.7$ and −5.3 ppm for R = Ph and Cy, respectively. With aniline, this syn-

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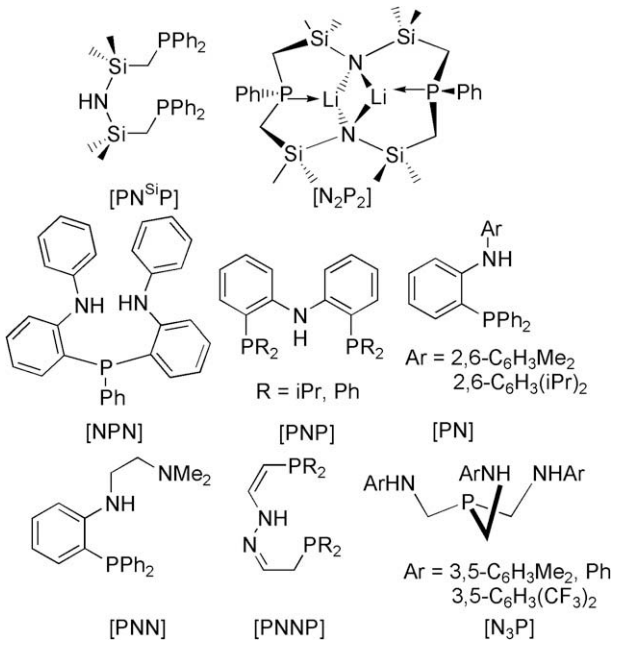
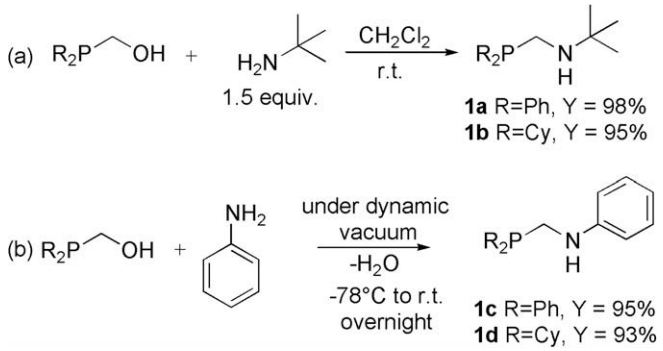


Scheme 1. The structural diversity of mixed phosphine-amine ligands.



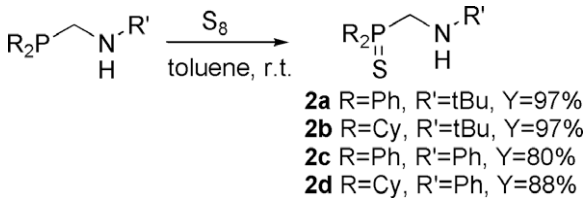
Scheme 2. Synthesis of phosphine-amine ligands **1**.

thetic procedure could not be employed since excess of aniline proved to be difficult to eliminate (either by washing or under vacuum). So, the reaction was achieved by adding a stoichiometric amount of aniline. When the addition was performed at room temperature, substantial amount of the [PCNCP] by-product was obtained which could be easily removed by precipitation in methanol/hexane, but the yields remained low. Consequently, another procedure was employed, aniline was added on a frozen solution of hydroxymethylphosphine (PCy_2CH_2OH was used neat and PPh_2CH_2OH was dissolved in dichloromethane). The reaction mixture was allowed to warm to room temperature overnight under dynamic vacuum to eliminate water (Scheme 2b). With these conditions, inspired by the work of Johnson and co-workers [15] compounds **1c** and **1d** could be isolated in high yields as pale yellow oils.

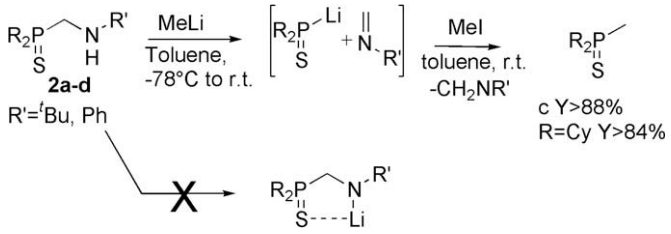
The completion of the reaction was checked by $^{31}P\{H\}$ NMR and shows the formation of a unique product exhibiting a singlet at $\delta(CH_2Cl_2) = -19.7$ and -3.2 ppm for R = Ph and Cy, respectively. As all the other compounds of this study, the phosphine-amine derivatives **1a**–**d** were characterized by multinuclear NMR ($^{31}P\{H\}$, ^{1}H, $^{13}C\{H\}$), mass spectroscopy and elemental analysis. The corresponding thiophosphorane-amine ligands **2a**–**d** were then easily obtained by reacting **1a**–**d** with sulfur in toluene at room temperature (Scheme 3). The reaction is accompanied by a strong deshielding of the phosphorus atom in **2a**–**d**, the resonance appearing in $^{31}P\{^{1}H\}$ NMR spectrum as a singlet at around 40 ppm and 60 ppm for PPh_2 and PCy_2 derivatives, respectively. Compounds **2a**–**d** were then isolated as white products in good yields (80–97%) after purification by silica gel chromatography.

Thiophosphorane-amido derivatives were expected to result from deprotonation of thiophosphorane-amines **2a**–**d** using methyllithium in toluene at −78 °C (Scheme 4). The reaction mixture became clear yellow upon lithiation, and showed in $^{31}P\{H\}$ NMR a unique product characterized by a singlet at δ(toluene) = 22.9 and 37.5 ppm starting from **2a**,**c** and **2b**,**d**, respectively. In order to identify these compounds methyliodide was added. It induced a rapid color fading of the solution and precipitation of lithium iodide salt. After filtration and removal of all volatiles under vacuum, a colorless oil was obtained in each case. Analysis of ^{1}H NMR spectrum showed the absence of the R′ substituent, thus **2a**, **2c** on one hand and **2b**, **2d** on the other hand gave the same product (Scheme 4). All NMR data were in good agreement with the formation of corresponding methylthiophosphoranes characterized by a singlet in $^{31}P\{H\}$ NMR spectrum at $\delta(C_6D_6) = 35.5$ and 54.7 ppm for the diphenyl and dicyclohexyl derivatives, respectively. In these derivatives, the methyl group is easily recognizable and appears as a doublet in ^{1}H NMR at $\delta(C_6D_6) = 2.27$ ($^{2}J_{P,H} = 13$ Hz) and 1.06 ppm ($^{2}J_{P,H} = 12$ Hz) for R = Ph and Cy, respectively. Therefore, the amido derivative was not stable and dissociated to give the thiophosphinite anion and the corresponding imine (Scheme 4), which evaporated under vacuum. Despite several attempts to modify the experimental conditions (base or solvent), no improvement was made and the issue of the reaction remained unchanged.

In parallel to the experimental lithiation study, we also computed the thermodynamics of the dissociation of the postulated thiophosphorane-amido anions $\{R_2P(X)CH_2NR'^-\}$. DFT calculations were conducted with the B3PW91 functional associated with the 6-31++G(d,p) basis set for all atoms. The real molecules were considered except for the cyclohexyl derivatives for which these substituents were replaced by methyl groups. These calculations evidenced the role of the substituent at the nitrogen atom (Table 1). Therefore, with *tert*-butyl group at this position, full optimization of the postulated anions derived from amines **2a**,**b** led to spontaneous dissociation into two compounds: the thiophosphinite anion and the imine. In the case of a phenyl substituent at the N atom,



Scheme 3. Synthesis of thiophosphorane-amine ligands **2**.



Scheme 4. Lithiation of thiophosphorane-amine **2a**–**d**.

Table 1
Thermodynamic data for the dissociation of thiophosphorane-amido and phosphine-amido anions ($R_2P(X)CH_2NR'$) (derived from **1a–d** and **2a–d,** respectively) into phosphide or thiophosphinite anion and imine.

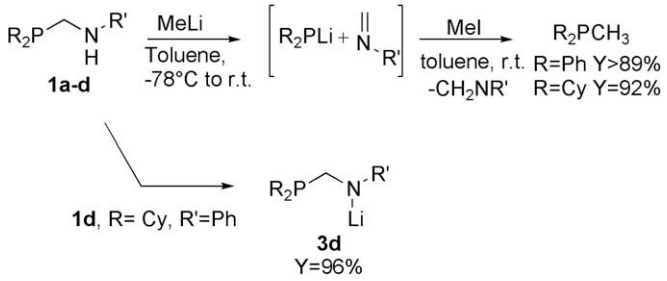
Corresponding amine derivatives	Calculated anions	ΔH[a]	ΔG[a]
2a	$Ph_2P(S)CH_2NtBu^-$	Dissociation[b]	
2b	$Me_2P(S)CH_2NtBu^-$	Dissociation[b]	
2c	$Ph_2P(S)CH_2NPh^-$	−0.8	−9.7
2d	$Me_2P(S)CH_2NPh^-$	9.8	2.4
1a	$Ph_2PCH_2NtBu^-$	Dissociation[b]	
1b	$Me_2PCH_2NtBu^-$	9.2	1.7
1c	$Ph_2PCH_2NPh^-$	8.7	0.9
1d	$Me_2PCH_2NPh^-$	31.6	24.3

[a] in kcal mol^{-1}.
[b] Full geometry optimization of the anion actually leads to its dissociation into phosphide or thiophosphinite anion and imine.

stable structures were found for the corresponding anions (see Table 1, **2c** and **2d**). However, the dissociation is thermodynamically favoured on ΔG grounds for the anion derived from **2c** (ΔG = −9.7 kcal mol^{-1}) and only slightly endergonic for that derived from **2d** (ΔG = 2.4 kcal mol^{-1}). On the whole, these conclusions are consistent with the experimental results since the amido derivatives generated from **2a–d** were found to dissociate and gave the thiophosphinite anion as the unique phosphorus derivative when the temperature reached 25 °C.

Similar calculations were then performed on the anions derived from the phosphine-amine compounds **1a–d** (Table 1). No stable minimum was found for the {$Ph_2PCH_2NtBu^-$} anion formed from **1a**, the optimization leading to dissociation into the phosphide anion and the imine. On the other hand, stable structures were found for the anions derived from **1b** and **1c** but the ΔG variation for the dissociation process is close to zero (+1.7 and +0.9 kcal mol^{-1}, respectively). Finally, in striking contrast with all the other results, the dissociation of the anion derived from **1d** was predicted to be strongly disfavoured (ΔG = +24.3 kcal mol^{-1}). According to the calculations, only the lithiation of **1d** should give a stable amido anion.

In order to check these theoretical predictions, the lithiation of the whole **1a–d** series was carried out (Scheme 5). Reactions were performed in the previously described conditions and followed by $^{31}P\{H\}$ NMR spectroscopy. Deprotonation of **1a** with methyllithium induced a small color change of the solution from colorless to pale yellow. $^{31}P\{H\}$ NMR spectrum of the crude mixture showed the formation of a single product exhibiting a singlet at δ(toluene) = −40 ppm, which corresponds to lithium diphenylphosphide. To ascertain the dissociation, methyl iodide was added: the formation of diphenylmethylphosphine was confirmed by mass and NMR spectroscopy. The lithiation of **1c** also led to dissociation, lithium diphenylphosphide being observed as the major product in the $^{31}P\{H\}$ NMR spectrum of the crude mixture after reaching room temperature. Nevertheless, in this case, another small singlet at δ(toluene) = −16 ppm, which may correspond to the desired phosphine-amido derivative, could be seen at the early stage of the reaction. However, a few minutes later, this product had disappeared leaving only lithium diphenylphosphide which was reacted with methyliodide. The lithiation of **1b** also conducted to a single product characterized by a singlet at δ(toluene) = −27 ppm, which upon addition of methyliodide gave dicyclohexylmethylphosphine characterized by a singlet at $\delta(C_6D_6)$ = −27.6 ppm in the $^{31}P\{^1H\}$ NMR spectrum and a doublet at $\delta(C_6D_6)$ = 0.9 ppm ($^2J_{P,H}$ = 16.5 Hz) in the ^1H NMR spectrum corresponding to the methyl protons. Thus, the lithiation of **1a–c** only led to dissociation as anticipated by calculations.



Scheme 5. Lithiation of phosphine-amine **1a–d**.

Finally, addition of one equivalent of methyllithium to a solution of **1d** in toluene at −78 °C, gave a pale yellow solution, which exhibited in the $^{31}P\{^1H\}$ NMR spectrum only one broad singlet at δ(toluene) = −6.9 ppm, a resonance which does not correspond to that of the lithium dicyclohexylphosphide. Thus, as predicted by calculations this phosphine-amido derivative proved to be stable. Compound **3d** was indeed isolated in 96% yield by evaporation of toluene and precipitation in hexanes. It was characterized by multinuclear NMR spectroscopy ($^{31}P\{^1H\}$, ^1H, $^{13}C\{^1H\}$ and ^7Li), showing in particular a broad singlet in ^7Li NMR spectrum at δ(toluene) = 1.74 ppm and a broad singlet for methylene hydrogen at $\delta(C_6D_6)$ = 3.53 ppm in ^1H NMR spectrum.

Definitive evidence concerning the structure of **3d** was given by a X-ray crystal structure analysis. As can be seen in Fig. 1 which presents an ORTEP plot of the molecule and the most relevant metric parameters, **3d** adopts in the solid state a dimeric structure organized around a square N_2Li_2 arrangement (deviation to planarity 0.74°). The unit cell is composed of four dimeric units which are very similar but differ by the orientation of the solvent molecules coordinated to the lithium atoms. Each lithium atom is coordinated by one diethyl ether molecule, and two nitrogen atoms from the phosphine-amido ligands. The N–Li, N–C, and P–C bond lengths

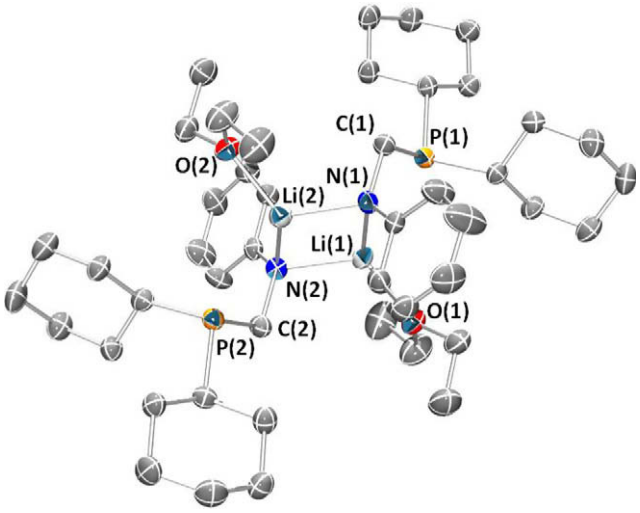


Fig. 1. Ortep plot of **3d**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (°): Li(1)–N(1) = 2.075(6); Li(1)–N(2) = 2.034(7); Li(2)–N(1) = 2.015(7); Li(2)–N(2) = 2.046(6); N(1)–C(1) = 1.459(4); P(1)–C(1) = 1.861(3); N(2)–C(2) = 1.468(4); P(2)–C(2) = 1.870(4); N(1)–Li(2)–N(2) = 103.6(3); N(2)–Li(1)–N(1) = 101.9(3); Li(2)–N(1)– Li(1) = 77.1(2); Li(1)–N(2)– Li(2) = 77.4(2); N(1)–C(1)– P(1) = 107.9(2); N(2)–C(2)– P(2) = 107.4(2).

are very similar to those observed by Johnson et al. for the tris(anion) $P(CH_2NPhLi)_3$ [17].

Interestingly, Poli and co-workers [18] have shown some years ago that α-aminodiphenylphosphine ligands or their anionic species set up a solution equilibrium with Ph_2PH or Ph_2PLi and the corresponding imine. They demonstrated that the reversible P–C bond break can be suppressed or at least reduced by decreasing the electron density at the nitrogen and central carbon atoms by introducing electron-withdrawing substituents at these positions or by coordination to Cu(I) through the P atom. Similarly to their results, removing electron density from the nitrogen atom was determinant also in our case. But in the **1a–d** series, electron donating substituents at the phosphorus atom are required as well, since with phenyl substituents only dissociation was observed. This may explain why lithiation in the thiophosphorane series **2a–d** failed, pentavalent phosphorus is, whatever its substitution scheme, too electron deficient to give a stable amido compound. Noteworthy, the tris(amido) derivative $P(CH_2NPhLi)_3$ prepared by Johnson and co-workers [17] features as **3d** the suitable combination of substituents; alkyl substituents on the phosphorus and an aryl ring at the nitrogen atom.

Having in hand a phosphine-amido ligand its coordination to Rh(I) was studied. Addition of half-equivalent of the $[Rh(COD)Cl]_2$ complex to a toluene solution of **3d** induced a rapid color change to deep red. ^{31}P NMR spectroscopy showed the clean formation of a new complex labelled **4**. This species was isolated as a red solid in 88% yield by evaporation of toluene followed by trituration in hexanes. Note that astonishingly no precipitation of any LiCl salt was observed in toluene. The chemical shift of the coordinated phosphorus atom is also rather unusual, since it gives a doublet at $\delta(C_6D_6) = -35.2$ ppm ($^1J_{P,Rh} = 127.5$ Hz). In the ^1H NMR spectrum the coordination is accompanied by a deshielding of the methylene protons ($\Delta\delta \sim 1$ ppm) compared to the free ligand. The vinylic protons of the cyclooctadienyl ligands appear as two multiplets at $\delta(C_6D_6) = 3.78$ and 5.58 ppm. The ^7Li NMR of complex **4** revealed a broad singlet at $\delta(d^8\text{-toluene}) = -0.66$ ppm. Unfortunately crystals suitable for X-ray analysis could not be grown. Indeed, crystallization attempts by slow diffusion of hexanes into THF solutions of complex **4** led before the formation of any crystal to a slow fading of the initial red solution, from which single crystals could be grown. X-ray analysis evidenced the formation of complex **5** featuring the phosphine-amine ligand **1d**.

To obtain better information on this transformation, **5** was independently synthesised by addition of one half-equivalent of $[Rh(COD)Cl]_2$ to a solution of **1d** in dichloromethane. After half an hour at room temperature, the $^{31}P\{H\}$ NMR spectrum of the crude mixture showed the disappearance of the starting material and the formation of a sole product characterized by a doublet at $\delta(CH_2Cl_2) = 24.0$ ppm ($^1J_{P,Rh} = 144.0$ Hz). Complex **5** was isolated as a yellow solid in 80% yield after evaporation of dichloromethane and washing with hexanes. The NMR data are very similar to those of **4**, except the presence of the amine proton at $\delta(CDCl_3) = 4.84$ ppm ($^3J_{H,H} = 5.0$ Hz), which is highly deshielded compared to the free ligand **1d** ($\delta(CDCl_3) = 3.68$ ppm). The coordination has on the other hand only little effect on the central methylene group of the phosphine-amine ligands; the protons appear as a doublet at 3.37 ppm ($^2J_{P,H} = 5.0$ Hz) and the carbon at 35.9 ppm ($^1J_{C,P} = 26.5$ Hz). Finally the structure of **5** was definitely established by X-ray crystallographic study. A view of **5** is given in Fig. 2 and the most significant parameters are listed in the legend below. As expected for d^8 metals, the geometry around the metal centre is square planar, the four coordination site being occupied by the phosphorus, the chlorine atoms and the two double bonds of the cyclooctadiene (COD). These bonds were measured at 1.396(4) and 1.357(4) Å, the longer (C20–C21) being located *trans* to the chloride. Accordingly, the Rh1–C20 and Rh1–C21 bonds

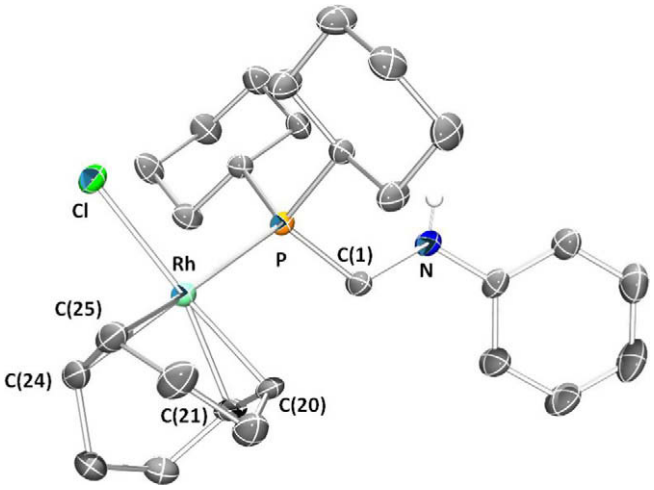
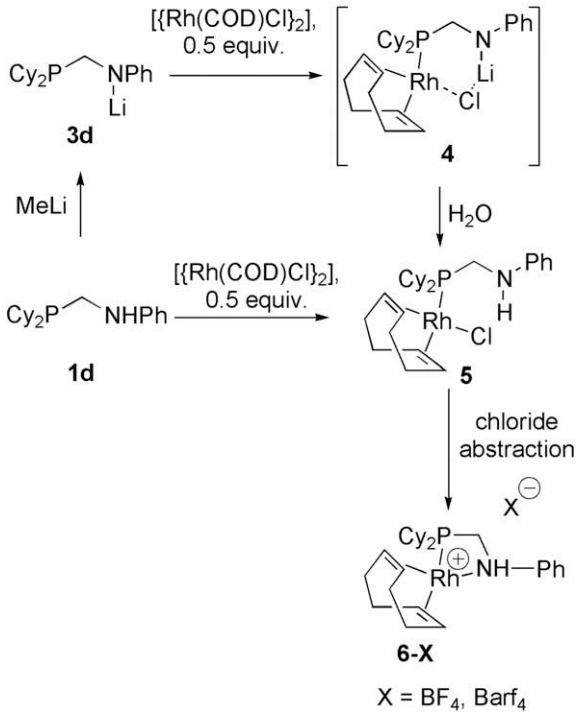


Fig. 2. Ortep plot of complex **5**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity (except the NH). Selected distances (Å) and angles (°): P(1)–Rh(1) = 2.3145(6); Rh(1)–Cl = 2.3878(6);Rh(1)–C(20) = 2.129(2); Rh(1)–C(21) = 2.113(2); Rh(1)–C(24) = 2.240(2); Rh(1)–C(25) = 2.207(3); P(1)–C(1) = 1.845(2); N(1)–C(1) = 1.444(3); N(1)–C(1)–P(1) = 116.6(2), P(1)–Rh–Cl = 89.88(2), C(1)–P(1)–Rh = 115.91(8).

are shorter (2.129(2) and 2.113(2) Å, respectively) than those *trans* to P, namely Rh1–C24 and Rh1–C25 were measured at 2.240(2) and 2.207(3) Å, respectively. The reflects the higher *trans* influence of the phosphine ligand compared to the chloride one.

Noteworthy, addition of water to pure complex **4** cleanly led to **5** as evidenced by multinuclear NMR spectroscopy, in particular this induced a huge deshielding of the phosphorus nucleus ($\Delta\delta = 79$ ppm). Interestingly X-ray analysis of complex **5** prepared from **4** evidenced the presence of the chloride ligand. All these data prompted us to propose for **4** a structure in which the LiCl salt remains in the coordination sphere of the rhodium, Scheme 6 shows a possible structure [19].



Scheme 6. Coordination to rhodium(I).

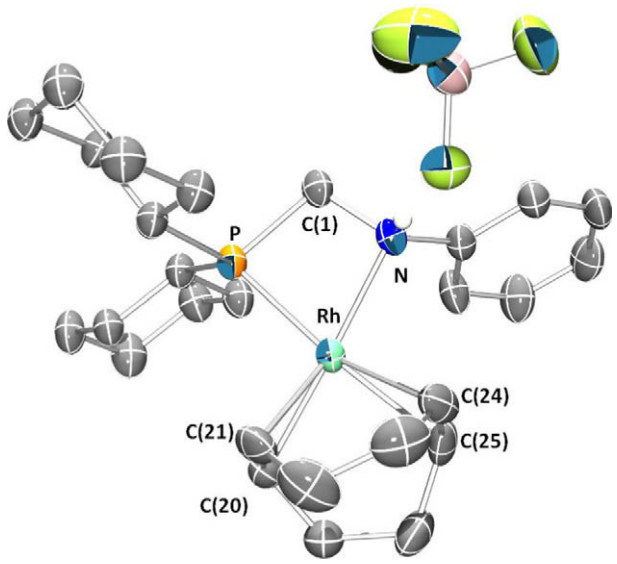


Fig. 3. Ortep plot of complex **6-BF$_4$**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity (except the NH). Selected distances (Å) and angles (°): P(1)–Rh = 2.290(1); N(1)–Rh = 2.161(3); Rh(1)–C(20) = 2.119(3); Rh(1)–C(21) = 2.126(3); Rh(1)–C(24) = 2.219(3); Rh(1)–C(25) = 2.230(4); P(1)–C(1) = 1.840(3); N(1)–C(1) = 1.516(4); N(1)–C(1)–P(1) = 101.1(2), P(1)–Rh(1)–N(1) = 71.41(8), C(1)–P(1)–Rh(1) = 86.9(1); C(1)–N(1)–Rh(1) = 100.6(2).

Then, chloride abstraction from **5** was attempted using first a silver salt. Nevertheless, the formation of the expected cationic complex labelled **6-BF$_4$** was accompanied by a silver by-product, which was impossible to eliminate. Therefore the chloride abstraction was finally cleanly achieved by reacting complex **5** with one equivalent of NaBarf$_4$ (Barf$_4$:Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) in dichloromethane. With this procedure only complex **6-Barf$_4$** formed, and was isolated in 84% yield as an orange solid after work-up. It was characterized by multinuclear NMR spectroscopy and elemental analysis. X-Ray quality crystals of **6-Barf$_4$** could not be grown whatever the technique used. But, fortunately, suitable crystals could form by slow diffusion of hexanes into a dichloromethane solution containing **6-BF$_4$**, the structure of this complex is depicted in Fig. 3. Complex **6-BF$_4$** adopts a square planar geometry, the four coordination sites being occupied by the phosphine, the amine of the PN ligand and the two olefins of the COD. Contrary to **5**, **6** is monocationic. Moreover, the coordination of the amine function induced an elongation of the C(1)–N(1) bonds from 1.444(3) Å in **5** to 1.516(4) Å in **6-BF$_4$**. The formation of the 4-membered metallacycle also significantly decreases the P(1)–C(1)–N(1) and C(1)–P(1)–Rh(1) angles: 101.2(2)° and 86.9(1)°, respectively in **6-BF$_4$** (*vs.* 116.6(2)° and 115.91(8)° in **5**). Concerning the coordination of the COD, the Rh–C$_{olefin}$ bonds located *trans* to P (2.225 Å) are on average longer than those *trans* to N (2.168 Å). The olefin bond lengths are only slightly different, the one located *trans* to P being a little shorter (1.359(6) Å) compared to the one *trans* to N (1.387(6) Å). This implies a stronger *trans* influence of the phosphorus compared to the nitrogen.

3. Conclusion

In conclusion we synthesized a series of phosphine-amine and thiophosphorane-amine ligand and studied their deprotonation. The formed amido derivatives appeared unstable and in most of the cases lithium phosphide or thiophosphinite and imine formed. This dissociation was evidenced by trapping experiments with methyliodide. But, as predicted by DFT calculations in the phosphine-amine series, we were able to isolate a stable amido derivative **3d** by tuning the substituent both at the P and N atoms. This lithium salt was fully characterized including by X-ray analysis evidencing a dimeric structure. Then, both the amido **3d** and amine **1d** ligands were successfully coordinated to Rh(I) centres. For complex **4** featuring phosphine-amido ligand, experimental observations and NMR data suggest the presence of the LiCl in the coordination sphere of the metal. Noteworthy, cationic [(P,NH)Rh(COD)]$^+$ complex could be obtained from **5** by chloride abstraction. Further studies will concern the use of lithium derivative **3d** as precursor for new classes of polydentate ligands.

4. Experimental

4.1. Synthesis

All reactions were routinely performed under argon or nitrogen by using standard Schlenck and glove-box techniques. Solvents were freshly distilled under dry nitrogen from Na/benzophenone (THF, hexanes), from Na (toluene), or from P_2O_5 (dichloromethane). Hydroxymethylphosphines were prepared according to literature procedures. [20] All other reagents and chemicals were obtained commercially and used without further purification. Nuclear magnetic resonance spectra were recorded on Bruker Avance 300 spectrometer operating at 300.0 MHz for ^{1}H, 75.5 MHz for ^{13}C and 121.5 MHz for ^{31}P. Solvent peaks were used as internal references for ^{1}H and ^{13}C chemical shifts (ppm). ^{31}P chemical shifts are relative to a 85% H_3PO_4 solution used as external standard. Coupling constants are given in Hz. The following abbreviations are used: bs = broad singlet, s = singlet, d = doublet, t = triplet, m = multiplet. Microanalyses were performed by the "Service d'analyse du CNRS", at Gif sur Yvette, France. Mass spectra were obtained on a HP 5989B spectrometer using ammonia as reagent gas.

4.2. R_2PCH_2NHtBu ***1a–d***

Tertbutylamine (1.5 equiv.) was added to a solution of. (hydroxymethyl)phosphine (1 equiv.) in dichloromethane (5 mL). The mixture was then stirred at room temperature for 1 h30. After completion of the reaction, the solution was dried on Na_2SO_4 and filtered under nitrogen. The solvent was removed in vacuo, yielding **1i** as colorless oil.

4.2.1. Ph_2PCH_2NHtBu (***1a***)

Tert-butylamine (0.365 mL, 3.47 mmol) and (hydroxymethyl)diphenylphosphine (500 mg, 2.31 mmol) gave **1a** (614 mg, 98%). Found: C, 75.39, H, 7.98, N, 5.41%. $C_{17}H_{22}NP$ requires C, 75.25; H, 8.17; N 5.161; δ_H (300 MHz, C_6D_6, 25 °C) 0.91 (9H, s, C(CH_3)$_3$), 3.22 (2H, d, $^2J_{P,H}$ 3.0 Hz, PCH_2), 7.08 (6H, m,m- and p-C*H*(PPh)), 7.58 (4H, td, $^3J_{H,H}$ 8.0 Hz, $^3J_{P,H}$ 1.5 Hz, o-C*H*(PPh)), NH signal could not be seen; δ_C (75.5 MHz, C_6D_6, 25 °C) 28.6 (s, C(CH_3)$_3$), 43.2 (d, $^1J_{C,P}$ 5 Hz, PCH_2), 51.0 (d, $^3J_{C,P}$ 10.5 Hz, *C*(CH_3)$_3$), 128.2 (s, p-C*H*(Ph)), 128.6 (s, m-C*H*(Ph)), 133.3 (d, $^2J_{C,P}$ 18.0 Hz, o-C*H*(Ph)), 138.8 (d, $^1J_{C,P}$ 14.5 Hz, C_{ipso}-(PPh)); δ_P (121.5 MHz, C_6D_6, 25 °C) −16.7; *m*/*z* (CI, NH_3) 272 $[MH]^+$, 186 $[(M-CH_2NHtBu)H]^+$.

4.2.2. Cy_2PCH_2NHtBu (***1b***)

Tert-butylamine (0.345 mL, 3.28 mmol) and (hydroxymethyl)dicyclohexylphosphine (500 mg, 2.19 mmol) gave **1b** (596 mg, 96%). Found: C, 71.77, H, 12.23, N, 5.12%. $C_{17}H_{34}NP$ requires C, 72.04; H, 12.09; N 4.94; δ_H (300 MHz, C_6D_6, 25 °C) 0.99 (9H, s, C(CH_3)$_3$), 1.17–1.36 (10H, m, CH_2(Cy)), 1.63 (2H, m, C*H*(Cy)), 1.70–1.91 (10H, m, CH_2(Cy)), 2.77 (2H, d, $^2J_{P,H}$ 2.0 Hz, PCH_2), NH signal could not be seen; δ_C (75.5 MHz, C_6D_6, 25 °C) 27.0 (s, *C*H$_2$(Cy)), 27.7 (t, $J_{P,C}$ 3.5 Hz, *C*H$_2$(Cy), 27.8 (s, *C*H$_2$(Cy)), 28.8 (s, C(CH_3)$_3$), 30.9

(d, $J_{P,C}$ 9.0 Hz, CH_2(Cy)), 33.2 (d, $^1J_{P,C}$ 14.5 Hz, CH(Cy)), 36.7 (d, $^1J_{P,C}$ 11.0 Hz, PCH_2), 51.0 (d, $^3J_{P,H}$ 10.5 Hz, $C(CH_3)_3$); δ_P (121.5 MHz, C_6D_6, 25 °C) −4.91; *m/z* (CI, NH_3) 284 $[MH]^+$, 198 $[(M–CH_2NHtBu)H]^+$.

4.2.3. Ph_2PCH_2NHPh (**1c**)

Aniline (0.210 mL, 2.31 mmol) was added on a frozen solution of (hydroxymethyl)diphenylphosphine (500 mg, 2.31 mmol) in dichloromethane (5 mL). The reaction mixture was then allowed to slowly warm and placed under dynamic vacuum overnight. After evaporation of dichloromethane, a colorless oil was obtained. Dichloromethane (5 mL) was then added; the solution was dried on Na_2SO_4, and filtered under nitrogen. Solvent evaporation gave **1c** (626 mg, 93%). Found: C, 78.56, H, 6.07, N, 4.68%. $C_{19}H_{18}NP$ requires C, 78.33; H, 6.23; N 4.81; δ_H (300 MHz, C_6D_6, 25 °C) 3.11 (1H, bs, N*H*), 3.36 (2H, d, $^2J_{P,H}$ 4.0 Hz, PCH_2), 6.16 (2H, d, $^2J_{P,H}$ 8.0 Hz, o-C*H*(NHPh)), 6.49 (1H, t, $^3J_{H,H}$ 8.0 Hz, p-C*H*(NHPh)), 6.84 (8H, m, m-C*H*(NHPh), p- and m-C*H*(PPh)), 7.14 (4H, m, o-C*H*(PPh)); δ_C (75.5 MHz, C_6D_6, 25 °C) 44.1 (d, $^1J_{P,C}$ 11.0 Hz, PCH_2), 113.5 (s, o-*C*H(NHPh)), 118.1 (s, p-*C*H(NHPh)), 128.8 (d, $^4J_{P,C}$ 6.5 Hz, p-*C*H(PPh)), 128.9 (d, $^3J_{P,C}$ 7.5 Hz, m-*C*H(PPh)), 129.5 (s, m-*C*H(NHPh)), 133.2 (d, $^2J_{P,C}$ 18.0 Hz, o-*C*H(PPh)), 137.4 (d, $^1J_{P,C}$ 14.0 Hz, C_{ipso}-(PPh)), 148.6 (d, $^3J_{P,C}$ 6.0 Hz, C_{ipso}-(NHPh) ppm. δ_P (121.5 MHz, C_6D_6, 25 °C) −19.4; *m/z* (CI, NH_3) 292 $[MH]^+$, 186 $[(M\text{-}CH_2NHPh)H]^+$.

4.2.4. Cy_2PCH_2NHPh (**1d**)

The same procedure as **1c** was followed except that aniline (0.210 mL, 2.19 mmol) was added to neat (hydroxymethyl)dicyclohexylphosphine (500 mg, 2.19 mmol) cooled at −78 °C. Compound **1d** (631 mg, 95%) was isolated as a colorless oil, yield. Found: C, 75.21, H, 9.97, N, 4.62%. $C_{19}H_{30}NP$ requires C, 75.33; H, 9.72; N, 4.81. δ_H (300 MHz, $CDCl_3$, 25 °C) 1.27 (10H, m, CH_2(Cy)), 1.68 (4H, m, CH_2, CH(Cy)), 1.77 (8H, m, CH_2(Cy)), 3.19 (2H, d, $^2J_{P,H}$ 5 Hz, PCH_2), 3.68 (1H, bs, N*H*), 6.63 (2H, d, $^3J_{H,H}$ 7.5 Hz, m-C*H*(NHPh)), 6.69 (1H, t, $^3J_{H,H}$ 7.5 Hz, p-C*H*(NHPh)), 7.18 (2H, t, $^3J_{H,H}$ = 7.5H z, o-C*H*(NHPh)). δ_C (75.5 MHz, $CDCl_3$, 25 °C) 26.4 (s, CH_2(Cy)), 27.0 (d, $J_{P,C}$ 2.5 Hz, CH_2(Cy)), 27.2 (d, $J_{P,C}$ 7.0 Hz, CH_2(Cy)), 29.0 (d, $J_{P,C}$ 7.0 Hz, CH_2(Cy)), 30.2 (d, $^1J_{P,C}$ 14.5 Hz, CH_2(Cy)), 32.6 (d, $^1J_{P,C}$ 11.0 Hz, CH(Cy)), 38.1 (d, $^1J_{P,C}$ 13.0 Hz, PCH_2), 112.6 (s, o-*C*H(NHPh)), 117.2 (s, p-*C*H(NHPh)), 129.1 (s, m-*C*H(NHPh)), 148.9 (d, $^3J_{P,C}$ 9.5 Hz, C_{ipso}-(NHPh)); δ_P (121.5 MHz, $CDCl_3$, 25 °C) −1.92; *m/z* (CI, NH_3) 304 $[MH]^+$.

4.3. $R_2P(S)CH_2NHR'$ **2a–d**

S_8 (1/8 equiv.) was added to a solution of amino-phosphine (1 equiv.) in toluene (5 mL). The mixture was stirred at room temperature for 30 minu. After completion of the reaction, solvent was removed. The obtained solid was purified by silica gel column chromatography (eluent: CH_2Cl_2) giving **2a–d** as white solids.

4.3.1. $Ph_2P(S)CH_2NHtBu$ (**2a**)

Sulfur (58.9 mg, 1.84 mmol) and amino-phosphine (**1a**) (500 mg, 1.84 mmol) gave **2a** (541.5 mg, 97%). Found: C, 67.61, H, 7.12, N, 4.90%. $C_{17}H_{22}NPS$ requires C, 67.30; H, 7.31; N 4.62; δ_H (300 MHz, $CDCl_3$, 25 °C) 1.09 (9H, s, $C(CH_3)_3$), 3.49 (2H, d, $^2J_{P,H}$ 8.5 Hz, PCH_2), 7.47 (6H, m, m- and p-C*H*(PPh)), 7.88 (4H, dd, $^3J_{H,H}$ 8.0 Hz, $^3J_{P,H}$ 6.5 Hz, o-C*H*(PPh)), NH signal could not be seen. δ_C (75.5 MHz, $CDCl_3$, 25 °C) 28.6 (s, $C(CH_3)_3$), 45.6 (d, $^1J_{P,C}$ 68.5 Hz, PCH_2), 51.2 (d, $^3J_{P,C}$ 14.5 Hz, $C(CH_3)_3$), 128.4 (d, $^3J_{P,C}$ 12.0 Hz, m-*C*H(PPh)), 131.5 (d, $^2J_{P,C}$ 10.0 Hz, o-*C*H(PPh)), 131.6 (s, p-*C*H(PPh)), 132.0 (d, $^1J_{P,C}$ 73.5 Hz, C_{ipso}-(PPh)); δ_P(121.5 MHz, $CDCl_3$, 25 °C) 41.2; IC/MS: *m/z* (CI, NH_3) 304 $[MH]^+$, 218 $[M\text{-}(CH_2NHtBu)H]^+$.

4.3.2. $Cy_2P(S)CH_2NHtBu$ (**2b**)

Sulfur (50.8 mg, 1.58 mmol) and amino-phosphine (**1b**) (500 mg, 1.58 mmol) yielded **2b** (481 mg; 97%). Found: C, 64.58, H, 11.04, N, 4.28%. $C_{17}H_{34}NPS$ requires C, 64.72; H, 10.86; N 4.44; δ_H (300 MHz, C_6D_6, 25 °C) 0.89 (1H, bs, N*H*), 0.94 (9H, s, $C(CH_3)_3$), 1.00 (6H, m, CH_2(Cy)), 1.46–1.62 (12H, m, CH_2(Cy)), 1.78 (4H, m, CH_2 CH(Cy)), 1.98 (2H, m, CH_2(Cy)), 2.77 (2H, d, $^2J_{P,H}$ 8.0 Hz, PCH_2); δ_C (75.5 MHz, C_6D_6, 25 °C) 26.0 (d, $J_{P,C}$ 1.5 Hz, CH_2(Cy)), 26.2 (d, $J_{P,C}$ 3.0 Hz, CH_2(Cy)), 26.6 (d, $J_{P,C}$ 3.0 Hz, CH_2(Cy)), 26.7 (s, CH_2(Cy)), 26.8 (s, CH_2(Cy)), 28.4 (s, $C(CH_3)_3$)), 36.8 (d, $^1J_{P,C}$ 48.0 Hz, CH(Cy)), 38.8 (d, $^1J_{P,C}$ 56.5 Hz, PCH_2), 50.7 (d, $^3J_{P,C}$ 12.5 Hz, $C(CH_3)_3$); δ_P (121.5 MHz, C_6D_6, 25 °C) 58; *m/z* (CI, NH_3) 316 $[MH]^+$, 230 $[(M\text{-}CH_2NHtBu)H]^+$.

4.3.3. $Ph_2P(S)CH_2NHPh$ (**2c**)

Sulfur 49.6 mg, 1.55 mmol) and amino-phosphine (**1c**) (500 mg, 1.55 mmol) gave **2c** (401 mg, 80%). Found: C, 70.79, H, 5.37, N, 4.52%. $C_{19}H_{18}NPS$ requires C, 70.57; H, 5.61; N, 4.33; δ_H (300 MHz, $CDCl_3$, 25 °C) 4.03 (2H, d, $^2J_{P,H}$ 7.5 Hz, PCH_2), 4.63 (1H, bs, N*H*), 6.72 (2H, d, $^3J_{H,H}$ 7.5 Hz, o-C*H*(NHPh)), 6.81 (1H, t, $^3J_{H,H}$ 7.5 Hz, p-C*H*(NHPh)), 7.21 (2H, t, $^3J_{H,H}$ 7.5 Hz, m-C*H*(NHPh)), 7.41–7.60 (6H, m, m- and p-C*H*(PPh)), 7.89 (4H, dd, $^3J_{P,H}$ 13.0 Hz, $^3J_{H,H}$ 7.5 Hz, o-CH(PPh)); δ_C (75.5 MHz, $CDCl_3$, 25 °C) 45.9 (d, $^1J_{C,P}$ 63.0 Hz, PCH_2), 113.8 (s, o-*C*H(NHPh)), 118.8 (s, p-*C*H(NHPh)), 128.8 (d, $^3J_{C,P}$ 12.0 Hz, m-*C*H(PPh)), 129.2 (s, m-*C*H(NHPh)), 131.1 (d, $^1J_{C,P}$ 81.0 Hz, C_{ipso}-(PPh)), 131.3 (d, $^2J_{C,P}$ 10.0 Hz, o-*C*H(PPh)), 132.0 (d, $^4J_{C,P}$ 3 Hz, p-*C*H(PPh)), 147.3 (d, $^3J_{C,P}$ 11.5 Hz, C_{ipso}-(NHPh)); δ_P (121.5 MHz, $CDCl_3$, 25 °C) +36.7; *m/z* (CI, NH_3) 324 $[MH]^+$, 218 $[(M–CH_2NHPh)H]^+$.

4.3.4. $Cy_2P(S)CH_2NHPh$ (**2d**)

Sulfur (47.8 mg, 1.49 mmol) and amino-phosphine **1d** (500 mg, 1.49 mmol) led to 2 d (440 mg, 88%). Found: C, 68.26, H, 8.75, N, 4.39%. $C_{19}H_{30}NPS$ requires C, 68.26; H, 9.01; N, 4.18; δ_H (300 MHz, $CDCl_3$, 25 °C) 1.25 (6H, m, CH_2(Cy)), 1.44 (4H, m, CH_2(Cy)), 1.73 (2H, m, CH_2(Cy)), 1.91 (6H, m, CH and CH_2(Cy)), 1.99 (4H, m, CH_2(Cy)), 3.31 (2H, d, $^2J_{P,H}$ 7.0 Hz, PCH_2), 6.68 (2H, d, $^3J_{H,H}$ 7.5 Hz, o-C*H*(NHPh)), 6.80 (1H, t, $^3J_{H,H}$ 7.5 Hz, p-C*H*(NHPh)), 7.22 (2H, t, $^3J_{H,H}$ 7.5 Hz, m-C*H*(NHPh)), NH signal could not be seen; δC (75.5 MHz, $CDCl_3$, 25 °C) 25.6 (s, CH_2(Cy)), 26.1 (d, $J_{P,C}$ 3.5 Hz, CH_2(Cy)), 26.3 (d, $J_{P,C}$ 4.5 Hz, CH_2(Cy)), 26.5 (d, $J_{P,C}$ 4.0 Hz, CH_2(Cy)), 36.9 (d, $^2J_{P,C}$ 48.0 Hz, CH(Cy)), 37.6 (d, $^1J_{P,C}$ 51.0 Hz, PCH_2), 113.5 (s, o-*C*H(NHPh)), 118.3 (s, p-*C*H(NHPh)), 129.2 (s, m-*C*H(NHPh)), 147.8 (d, $^3J_{P,C}$ 11.0 Hz, C_{ipso}-(NHPh)); δ_P (121.5 MHz, $CDCl_3$, 25 °C) +59.6 ; *m/z* (CI, NH_3) 336 $[MH]^+$, 230 $[(M–CH_2NHPh)H]^+$.

4.4. Lithiation-electrophilic quench procedure

MeLi (1.6 M in Et_2O, 1 mmol) was added to a solution of amino-phosphine **1a–c** (1 mmol) or amino-thiophosphorane **2a–c** in toluene (3 mL) cooled at –78 °C. The reaction mixture turned pale yellow when warming to room temperature. The composition of the reaction mixture was determined by ^{31}P NMR spectroscopy. Then, methyliodide (1 mmol) was added at low temperature (−78 °C) inducing a fading of the color solution. Precipitated lithium salts were removed by filtration, and toluene was evaporated yielding methylphosphine or methylthiophosphorane derivatives as colorless oil or white solid, respectively.

4.4.1. Ph_2PCH_3

MeLi (0.625 mL, 1 mmol), **1a** (271 mg, 1 mmol) or **1c** (291 mg, 1 mmol) gave with MeI (0.062 mL, 1 mmol) the diphenylmethyl phosphine in respectively, 89% (178 mg) and 95% (190 mg) yield. δ_H (300 MHz, C_6D_6, 25 °C) 1.39 (3H, d, $^2J_{P,H}$ 3.0 Hz, CH_3), 7.03 (6H, m, m- and p-C*H*(PPh)), 7.58 (4H, td, $^3J_{H,H}$ 7.5 Hz, $^3J_{P,H}$ 1.5 Hz, o-C*H*(PPh)); δ_C (75.5 MHz, C_6D_6, 25 °C) 20.7 (d, $^1J_{P,C}$ 20.0 Hz, CH_3),

127.8 (s, p-*C*H(PPh)), 128.1 (d, $^2J_{P,C}$ 8.0 Hz , m-*C*H(PPh)), 131.6 (d, $^2J_{P,C}$ 18.0 Hz, o-*C*H(PPh)), 138.9 (d, $^1J_{P,C}$ 15.0 Hz, C_{ipso}-(PPh)); δ_P (121.5 MHz, C_6D_6, 25 °C) –27.6; *m*/*z* (CI, NH_3) 201 $[MH]^+$.

4.4.2. Cy_2PCH_3

MeLi (0.625 mL, 1 mmol), **1b** (283 mg, 1 mmol) gave with MeI (0.062 mL, 1 mmol) the dicyclohexylmethyl phosphine in 92% (195 mg). δ_H (300 MHz, C_6D_6, 25 °C) 0.82 (3H, d, $^2J_{P,H}$ 16.5 Hz, C*H*$_3$), 0.93–1.99 (22H, m, C*H*$_2$, and C*H*(Cy)); δ_C (75.5 MHz, C_6D_6, 25 °C) 13.0 (d, $^1J_{P,C}$ 12.0 Hz, *C*H$_3$), 25.5–30.0 (*C*H$_2$(Cy)), 37.5 (d, $^1J_{P,C}$ 12.5 Hz, *C*H(Cy)); δ_P (121.5 MHz, C_6D_6, 25 °C) −19.8; *m*/*z* (CI, NH_3) 213 $[MH]^+$.

4.4.3. $Ph_2P(S)CH_3$

MeLi (0.625 mL, 1 mmol), **2a** (315 mg, 1 mmol) or **2c** (323 mg, 1 mmol) gave with MeI (0.062 mL, 1 mmol) the diphenylmethylthiophosphorane in respectively, 90% (209 mg) and 88% (204 mg) yield. δ_H (300 MHz, C_6D_6, 25 °C) 2.27 (3H, d, $^2J_{P,H}$ 13.0 Hz, C*H*$_3$), 7.47 (6H, m, m- and p-C*H*(PPh)), 7.81 (4H, dd, $^3J_{P,H}$ 13.5 Hz $^3J_{H,H}$ 7.5 Hz, o-CH(PPh)); δ_C (75.5 MHz, C_6D_6, 25 °C): 21.7 (d, $^1J_{P,C}$ 60.0 Hz, *C*H$_3$), 128.6 (d, $^2J_{P,C}$ 12.0 Hz, m-*C*H(PPh)), 130.7 (d, $^2J_{P,C}$ 10.5 Hz, o-*C*H(PPh)), 131.4 (d, $^4J_{P,C}$ 3.0 Hz, p-*C*H(PPh)), 133.9 (d, $^1J_{P,C}$ 82.5 Hz, C_{ipso}-(PPh)); δ_P (121.5 MHz, C_6D_6, 25 °C) +35.5; *m*/*z* (CI, NH_3) 233 $[MH]^+$.

4.4.4. $Cy_2P(S)CH_3$

MeLi (0.625 mL, 1 mmol), **2b** (316 mg, 1 mmol) or **2d** (336 mg, 1 mmol) gave with MeI (0.062 mL, 1 mmol) the dicyclohexylmethylthiophosphorane in respectively, 84% (205 mg) and 87% (213 mg) yield. δ_H (300 MHz, C_6D_6, 25 °C) 0.99 (2H, m, C*H*$_2$(Cy)), 1.06 (3H, d, $^2J_{P,H}$ 11.5 Hz, C*H*$_3$), 1.19–2.02 (20H, m, C*H* and C*H*$_2$(Cy)); δ_C (75.5 MHz, C_6D_6, 25 °C) 12.9 (d, $^1J_{P,C}$ 49.5 Hz, *C*H$_3$), 25.5–30.0 (*C*H$_2$(Cy)), 37.5 (d, $^1J_{P,C}$ 50.5 Hz, *C*H(Cy)); δ_P (121.5 MHz, C_6D_6, 25 °C) +54.7; *m*/*z* (CI, NH_3) 245 $[MH]^+$.

*4.4.5. Cy_2PCH_2NLiPh (**3d**)*

MeLi (625 μL, 1 mmol) was added to a solution of amino-phosphine **1d** (303 mg, 1 mmol) in toluene (3 mL) cooled at −78 °C. After evaporation under vacuum, the product was precipitated in 5 mL of hexane, filtered-off under nitrogen, and dried under vacuum. Amido anion **3d** was obtained as a white solid (323.3 mg, 96%). Crystals of this product were obtained by slow evaporation of diethyl ether in the glove box. NMR analyses were performed on in situ generated anion. δ_H (300 MHz, C_6D_6, 25 °C) 1.19–1.44 (10H, m, C*H*$_2$(Cy)), 1.64 (2H, m, C*H*(Cy)), 1.71 (6H, m, C*H*$_2$(Cy)), 1.95 (4H, m, CH$_2$(Cy)), 3.53 (2H, bs, PC*H*$_2$), 6.55 (1H, t, $^3J_{H,H}$ 7.5 Hz, p-C*H*(NHPh)), 6.81 (2H, d, $^3J_{H,H}$ 7.5 Hz, o-C*H*(NHPh)), 7.31 (2H, t, $^3J_{H,H}$ 7.5 Hz, m-C*H*(NHPh)); δ_C (75.5 MHz, C_6D_6, 25 °C) 26.9 (s, *C*H$_2$(Cy)), 27.8 (t, $J_{C,P}$ 6.5 Hz, *C*H$_2$(Cy)), 30.5 (d, $J_{C,P}$ 10.5 Hz, *C*H$_2$(Cy)), 33.6 (d, $^1J_{C,P}$ 11.5 Hz, *C*H(Cy)), 44.9 (d, $^2J_{C,P}$ 4.5 Hz, PCH$_2$), 111.9 (s, o-*C*H(NHPh)), 113.1 (s, p-*C*H(NHPh)), 130.0 (s, m-*C*H(NHPh)), 161.4 (d, $^3J_{C,P}$ 17.0 Hz, C_{ipso}-(NHPh)); δ_P (121.5 MHz, C_6D_6, 25 °C) −6.8; δ_{Li} (116.6 MHz, toluene d_8, 25 °C) +1.74 (bs).

4.5. Coordination experiments

*4.5.1. $(Cy_2PCH_2NLiPh)RhCODCl$ (**4**)*

$[RhCODCl]_2$ (49.3 mg, 0.1 mmol) was added to a solution **3d** (62.0 mg, 0.2 mmol) in toluene (3 mL). The reaction mixture was stirred at room temperature for 30 min, and then the solvent was evaporated under vacuum. The product was precipitated in hexanes (mixture of isomers), filtered-off, and washed with hexanes (5 mL). After drying, **4** was obtained as a red solid (98 mg, 88%). δ_H (300 MHz, C_6D_6, 25 °C) 1.01 (6H, m, C*H*$_2$(Cy)), 1.19 (2H, m, C*H*$_2$(Cy)), 1.65 (12H, m, C*H*$_2$(Cy)), 1.87 (2H, m, C*H*(Cy)), 1.95 (4H, m, C*H*$_2$(COD)), 2.26 (4H, m, C*H*$_2$(COD)), 3.78 (2H, m, C*H*(COD)), 4.54 (2H, d, $^2J_{C,P}$ 6.0 Hz, PCH$_2$), 5.58 (2H, m, C*H*(COD)), 6.52 (2H, d, $^3J_{H,H}$ 7.0 Hz, o-C*H*(NHPh)), 6.83 (1H, t, $^3J_{H,H}$ 7.0 Hz, p-C*H*(NHPh)), 7.17 (2H, t, $^3J_{H,H}$ 7.0 Hz, m-C*H*(NHPh)); δ_C (75.5 MHz, C_6D_6, 25 °C) 26.4 (s, *C*H$_2$(Cy)), 26.8 (d, $J_{C,P}$ 10.5 Hz, *C*H$_2$(Cy)), 27.1 (d, $J_{C,P}$ 12.5 Hz, *C*H$_2$(Cy)), 28.5 (s, CH$_2$(COD)), 28.9 (d, $J_{C,P}$ 3.0 Hz, *C*H$_2$(Cy)), 30.2 (s, *C*H$_2$(COD)), 31.3 (d, $^1J_{C,P}$ 16.5 Hz, *C*H(Cy)), 32.8 (d, $J_{C,P}$ 3.0 Hz, *C*H$_2$(Cy)), 60.1 (d, $^1J_{C,P}$ 40.0 Hz, PCH$_2$), 65.5 (d, $^1J_{C,Rh}$ 11.5 Hz, *C*H(COD)), 98.1 (dd, $^1J_{C,Rh}$ 10.5 Hz, $^2J_{C,P}$ 7.0 Hz, *C*H(COD)), 113.4 (s, o-*C*H(NHPh)), 114.2 (s, p-*C*H(NHPh)), 129.0 (s, m-*C*H(NHPh)), 147.0 (d, $^3J_{C,P}$ 8.0 Hz, , C_{ipso}-(NHPh)); δ_P (121.5 MHz, C_6D_6, 25 °C) −35.2 (d, $^1J_{Rh,P}$ 127.5 Hz); δ_{Li} (116.6 MHz, toluene d_8, 25 °C) −0.66 (bs).

*4.5.2. $(Cy_2PCH_2NHPh)Rh(COD)Cl$ (**5**)*

$[RhCODCl]_2$ (98.5 mg, 0.2 mmol) was added to a solution of **1d** (121 mg, 0.4 mmol) in dichloromethane (5 mL). The mixture was stirred at room temperature for 30 min. Then, the solvent was removed under vacuum. The product was precipitated in hexanes (mixture of isomers), filtered-off, and washed with hexanes (5 mL). After drying, **5** was obtained as a yellow solid (188.9 mg, 86%). Crystals were obtained by slow diffusion of hexanes in saturated dichloromethane solution of **5**. Found: C, 59.28, H, 7.56, N, 2.23%. $C_{27}H_{42}ClNPRh$ requires C, 58.97; H, 7.70; N 2.55%; δ_H (300 MHz, C_6D_6, 25 °C) 0.99–1.55 (10H, m, C*H*$_2$(Cy)), 1.64 (8H, m, C*H*$_2$(Cy)), 1.87 (4H, m, C*H* and C*H*$_2$(Cy)), 2.06 (4H, m, C*H*$_2$(COD)), 2.18 (4H, m, C*H*$_2$(COD)), 3.37 (t, $^2J_{P,H} = {}^3J_{H,H}$ 5.0 Hz, PC*H*$_2$), 3.63 (2H, m, C*H*(COD)), 4.84 (1H, t, $^3J_{H,H}$ 5.0 Hz, N*H*), 5.67 (2H, m, C*H*(COD)), 6.67 (2H, d, $^3J_{H,H}$ 7.5 Hz, o-C*H*(NHPh)), 6.75 (1H, t, $^3J_{H,H}$ 7.5 Hz, p-C*H*(NHPh)), 7.17 (2H, m, m-C*H*(NHPh)); δ_C (75.5 MHz, C_6D_6, 25 °C) 26.6 (s, *C*H$_2$(Cy)), 27.5 (d, $J_{C,P}$ 9.5 Hz, *C*H$_2$(Cy)), 27.7 (d, $J_{C,P}$ 11.5 Hz, *C*H$_2$(Cy)), 28.6 (s, *C*H$_2$(COD)), 29.7 (s, *C*H$_2$(Cy)), 30.0 (s, *C*H$_2$(Cy)), 30.5 (s, *C*H$_2$(Cy)), 30.4 (s, *C*H$_2$(Cy)), 30.9 (s, *C*H$_2$(Cy)), 33.6 (s, *C*H$_2$(COD)), 34.0 (d, $^1J_{C,P}$ 19.5 Hz, *C*H(Cy)), 35.9 (dd, $J_{C,P}$ 18.0 Hz, $^2J_{C,Rh}$ 46.5 Hz, PCH$_2$), 68.2 (d, $^1J_{C,Rh}$ 14.0 Hz, *C*H(COD)), 104.1 (dd, $^1J_{C,Rh}$ 12.0 Hz, $^2J_{C,P}$ 7.0 Hz, *C*H(COD)), 113.9 (s, o-*C*H(NHPh)), 118.5 (s, p-*C*H(NHPh)), 129.6 (s, m-*C*H(NHPh)), 149.0 (d, $^3J_{C,P}$ 8.5 Hz, C_{ipso}-(NHPh)); δ_P (121.5 MHz, C_6D_6, 25 °C) +24.0 (d, $^1J_{P,Rh}$ 145.5 Hz).

*4.5.3. $[(Cy_2PCH_2NHPh)RhCOD][Barf_4]$ (**6-Barf$_4$**)*

$NaBarf_4$ (88.6 mg, 0.1 mmol) was added to a dichloromethane solution (4 mL) of **5** (55 mg, 0.2 mmol). The mixture was stirred at room temperature for 30 min. Then, NaCl salt was eliminated by filtration under nitrogen and the filtrate was evaporated under vacuum. The result product was precipitated in hexanes (mixture of isomers), filtered-off, and washed with hexanes (5 mL). After drying **6-Barf$_4$** was obtained as an orange solid (116 mg, 84%). Found: C, 51.13, H, 4.18, N, 0.85%. $C_{59}H_{54}BF_{24}NPRh$ requires C, 51.44; H, 3.95; N, 1.02; δ_H (300 MHz, CD_2Cl_2, 25 °C) 1.17–1.93 (22H, m, C*H* and C*H*$_2$(Cy)), 2.12 (4H, m, C*H*$_2$(COD)), 2.33 (4H, m, C*H*$_2$(COD)), 3.70 (1H, t, $^3J_{H,H}$ 8.0 Hz, N*H*), 4.14 (2H, m, C*H*(COD)), 4.33 (2H, m, C*H*(COD)), 4.75 (2H, dd, $^2J_{P,H}$ 5.0 Hz, $^3J_{H,H}$ 8.0 Hz, PC*H*$_2$), 7.02 (2H, d, $^3J_{H,H}$ 7.5 Hz, o-C*H*(NHPh)), 7.10 (1H, t, $^3J_{H,H}$ 7.5 Hz, p-C*H*(NHPh)), 7.32 (2H, t, $^3J_{H,H}$ 7.5 Hz, m-C*H*(NHPh)), 7.47 (4H, bs, p-C*H*(Barf$_4$), 7.64 (8H, bs, o-C*H*(Barf$_4$)); δ_C (75.5 MHz, CD_2Cl_2, 25 °C) 24.9 (s, *C*H$_2$(Cy)), 25.5 (d, $J_{C,P}$ 10.5 Hz, *C*H$_2$(Cy)), 25.8 (d, $J_{C,P}$ 13.5 Hz, *C*H$_2$(Cy)), 27.0 (s, *C*H$_2$(COD)), 27.9 (s, *C*H$_2$(COD), 28.4 (d, $J_{C,P}$ 3.0 Hz, *C*H$_2$(Cy)), 30.9 (dd, $J_{C,Rh}$ 17.0 Hz , $J_{C,P}$ 39.0 Hz, *C*H(Cy)), 59.7 (dd, $^2J_{C,Rh}$ 4.5 Hz, $^1J_{C,P}$ 29.0 Hz, PCH$_2$), 75.3 (dd, $^2J_{C,P}$ 12.5 Hz, $^1J_{C,Rh}$ 70 Hz, *C*H(COD)), 104.9 (m, *C*H$_2$(COD)), 118.0 (quintuplet, $^3J_{C,F}$ 3.5 Hz, p-*C*H(Barf$_4$)), 119.0 (s, o-*C*H(NHPh)), 125.1 (q, $^1J_{C,F}$ 272 Hz, *C*F$_3$(Barf$_4$)), 126.9 (s, p-*C*H(NHPh)), 129.5 (qq, $^3J_{C,B}$ 31.5 Hz, $^2J_{C,F}$ 2.5 Hz, m-*C*H(Barf$_4$)), 131.4 (s, m-*C*H(NHPh)), 135.3 (s, o-CH(Barf$_4$)), 146.5 (d, $^3J_{C,P}$ 8.0 Hz, C_{ipso}-(NHPh)), 162.3 (d, $^1J_{C,B}$ 50.0 Hz, C_{ipso}-(Barf$_4$)); δ_P (121.5 MHz, C_6D_6, 25 °C) -20.1 (d, $^1J_{P,Rh}$ 126.5 Hz).

Table 2
Crystal data and refinement details for the X-ray structure determinations of **3d** and **5**.

	3d[a]	**5**[a]	**6-BF$_4$**[a]
Formula	$C_{46}H_{78}Li_2N_2O_2P_2$	$C_{27}H_{41}ClNPRh$	$C_{27}H_{42}NPRh,BF_4$
M_r	766.92	548.94	601.31
λ (Å)	0.71069	0.71069	0.71069
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	*P*1	$P2_12_12_1$	*C*2/*c*
a (Å)	10.870(1)	11.707(1)	21.934(1)
b (Å)	19.739(1)	13.391(1)	15.441(1)
c (Å)	21.521(1)	16.639(1)	16.168(1)
α (°)	92.377(1)	90.00	90.00
β (°)	90.276(1)	90.00	91.877(1)
γ (°)	91.423(1)	90.00	90.00
V (Å$^{3)}$	4612.1(5)	2608.5(3)	5472.9(5)
Z	4	4	8
ρ_{calcd} (g cm$^{-3)}$	1.104	1.398	1.460
μ (cm^{-1})	0.131	0.833	0.726
F (0 0 0)	1680	1148	2496
Crystal size (mm$^{3)}$	0.22 × 0.18 × 0.16	0.26 × 0.20 × 0.20	0.22 × 0.20 × 0.12
θ Max (°)	30.02	30.03	30.01
Index ranges	$-15 \le h \le 15$ $-27 \le k \le 22$ $-30 \le l \le 28$	$-15 \le h \le 16$ $-18 \le k \le 12$ $-23 \le l \le 22$	$-30 \le h \le 26$ $-21 \le k \le 17$ $-15 \le l \le 22$
Reflns. collected	58 635	17 020	19v252
Independent reflns.	41 539 [R_{int} = 0.0338]	7621 [R_{int} = 0.0470]	7953 [R_{int} = 0.0534]
Data/ restraints/ parameters	5025/15/319	30 054/15/1961	6951/24/284
Goodness-of-fit on F^2 [b]	1.028	1.026	1.090
Final *R* indices [$I > 2\sigma I$)][c]	*R*1 = 0.0598; *wR*2 = 0.1665	*R*1 = 0.0318; *wR*2 = 0.0810	*R*1 = 0.0513; *wR*2 = 0.1452
Largest diff. peak/hole [e Å^{-3}]	0.513(0.060)/ −0.302(0.060)	0.579(0.079)/ −0.769(0.079)	1.271(0.124)/ −0.665(0.124)
Flack's parameter	0.05(5)	−0.03(2)	
CCDC number	748466	748467	748468

[a] Measurement was performed at 150.0(1) K.
[b] GOF = $[\sum w(F_0^2 - F_c^2)]^2/(n-p)]^{1/2}$.
[c] $R^1 = \sum ||F_0| - |F_c||/\sum |F_0|$; $wR_2 = [\sum w(F_0^2 - F_c^2)]/[\sum w(F_0)^4]^{1/2}$.

4.6. Computational details

All calculations were carried out using the Gaussian 03W set of programs [21] with the hybrid B3PW91 functional (that includes 20% of Hartree-Fock exchange) [22], the 6-31++G(d,p) basis set was used H, C, N, Li and P atoms. For each computed structure the minimum energy was characterized by vibration frequencies calculations.

4.7. X-ray crystallography

Data were collected on a Nonius Kappa CCD diffractometer using a Mo Kα (λ = 0.71069 Å) X-ray source and a graphite monochromator. Experimental details are described in Table 2. The crystal structure was solved using SIR 97 [23] and Shelxl-97 [24]. ORTEP drawings were made using ORTEP III for Windows [25].

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Appendix A. Supplementary material

Supplementary data (Crystallographic data for **3d**, **5** and **6-BF$_4$** as cif file. Complete Gaussian reference, optimized geometry, energies, and three lower frequencies of DFT calculated model compounds) associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.03.006.

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