

Reaction of Lithium Anilide with $(\text{PPh}_3)_3\text{RhCl}$ and Related Rhodium(I) Complexes

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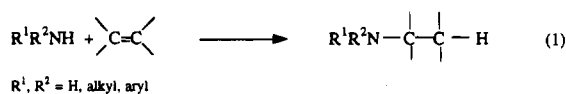
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The reaction of LiNHPH with four Rh(I) complexes, $(\text{PPh}_3)_3\text{RhCl}$, $[(\text{PPh}_3)_2\text{RhCl}]_2$, $(\text{PEt}_3)_3\text{RhCl}$, and $[(\text{PEt}_3)_2\text{RhCl}]_2$, in THF has been studied by NMR spectroscopy. The reaction of LiNHPH (1.3 equiv/Rh) with $(\text{PPh}_3)_3\text{RhCl}$ or $[(\text{PPh}_3)_2\text{RhCl}]_2$ leads to an equilibrium mixture of *syn*- and *anti*- $[(\text{PPh}_3)_2\text{Rh}(\text{NHPH})_2]$, which is slowly converted to $[(\text{PPh}_3)_2\text{Rh}]_2(\mu\text{-Cl})(\mu\text{-NHPH})$. When these reactions are conducted with a large excess (10 equiv/Rh) of LiNHPH , a single complex forms, for which the formula $[(\text{PPh}_3)_2\text{Rh}(\text{NHPH})_2]^- \text{Li}^+$ is proposed on the basis of ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{103}\text{Rh}\{^1\text{H}\}$ NMR data. This complex can also be generated by treatment of the mixture of *syn*- and *anti*- $[(\text{PPh}_3)_2\text{Rh}(\text{NHPH})_2]$ with an excess of LiNHPH . Reaction of LiNHPH (1.3 equiv/Rh) with $(\text{PEt}_3)_3\text{RhCl}$ leads to $(\text{PEt}_3)_3\text{RhNHPH}$, which is in equilibrium with the starting complex. In the presence of excess LiNHPH (10 equiv/Rh), $(\text{PEt}_3)_3\text{RhCl}$ reacts to give an equilibrium mixture of $(\text{PEt}_3)_3\text{RhNHPH}$ and $[(\text{PEt}_3)_2\text{Rh}(\text{NHPH})_2]^- \text{Li}^+$. Reaction of LiNHPH (1.3 equiv/Rh) with $[(\text{PEt}_3)_2\text{RhCl}]_2$ leads to a mixture of $[(\text{PEt}_3)_2\text{Rh}(\text{NHPH})_2]$ and $[(\text{PEt}_3)_2\text{Rh}]_2(\mu\text{-Cl})(\mu\text{-NHPH})$. When conducted with excess LiNHPH (10 equiv/Rh), this reaction gives $[(\text{PEt}_3)_2\text{Rh}(\text{NHPH})_2]^- \text{Li}^+$ as the major product. In the presence of excess LiNHPH , the two anionic complexes $[(\text{PR}_3)_2\text{Rh}(\text{NHPH})_2]^- \text{Li}^+$ ($\text{R} = \text{Ph}, \text{Et}$) are stable for days in refluxing THF.

Introduction

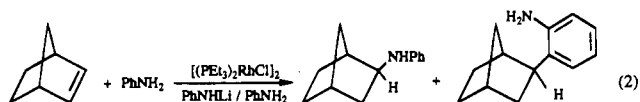
Since the synthesis of $\text{Ti}(\text{NPh}_2)_4$, the first reported transition-metal amide, in 1935,¹ a great deal of interest has been devoted to this class of compounds.² Amide $(\text{NRR}')^-$ donor ligands have found widespread use with early transition metals. In contrast, few amides of the late transition metals have been reported,³ and it has been proposed that the interaction of the hard amide ligand with the soft late transition metals leads to weak metal–nitrogen bonds.^{3,4} Furthermore, amido complexes of late transition metals have been shown to undergo facile β -elimination, leading to metal hydrides.⁵ Complexes such as these might gain some stability with electron-withdrawing groups on the nitrogen atom and/or substituents on nitrogen that do not allow β -elimination to occur, such as aryl groups.

Late transition-metal amides are of interest because of their possible connection with catalytic hydroamination processes (eq 1),^{6,7} as exemplified by the recent work of Casalnuovo *et al.* on iridium complexes.⁸



In fact, the first transition-metal-catalyzed homogeneous hydroamination of ethylene was achieved using a rhodium precursor.⁹ We recently reported that the reaction of aniline

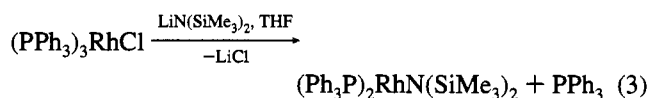
with norbornene in the presence of a catalytic system generated *in situ* by combining $[(\text{PEt}_3)_2\text{RhCl}]_2$ with LiNHPH (5 equiv/Rh) leads to a mixture of hydroamination and hydroarylation products (eq 2).¹⁰



The mechanism of these hydroamination/hydroarylation reactions is presently unknown. We decided to investigate the nature of the catalytic system(s) generated by reacting LiNHPH with the Rh(I) catalyst precursors used for reaction 2. Despite many attempts, we have not yet succeeded in isolating stable complexes from these reactions. We have thus been led to study the species in solution by NMR spectroscopy, and we report here the results of our $^{31}\text{P}\{^1\text{H}\}$ NMR investigations, together with some $^{103}\text{Rh}\{^1\text{H}\}$ NMR data.

Results and Discussion

The reaction of a lithium amide with a transition metal halide is the most widespread route to transition-metal amides.^{2,3} In the case of rhodium, the first well-characterized amide complex was prepared by such a metathesis (eq 3).¹¹



This $14 e^-$ complex, characterized by NMR and cryoscopy, is reported to be stable in the solid state but unstable in solution (*e.g.* $t_{1/2} \approx 12 \text{ h}$ at 25°C in benzene). NMR data indicates that the two phosphorus atoms are equivalent ($J(\text{P}-\text{Rh}) = 180.7$

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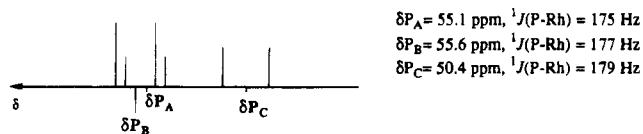


Figure 1. Schematic representation of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (at 308 K) of the THF solution obtained by reaction of 1.3 equiv of LiNHPH with $(\text{PPh}_3)_3\text{RhCl}$ (Bruker WM 250, 101.25 MHz).

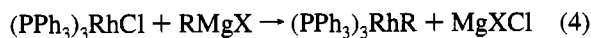
Hz), as are the protons of the methyl groups. By analogy with the isoelectronic complex $[(\text{PPh}_3)_2\text{CoN}(\text{SiMe}_3)_2]$, characterized by X-ray crystallography,¹² the authors suggest a trigonal planar geometry about the metal atom.¹¹ However, our studies of the reaction of lithium anilide with (monophosphine)_nRh(I) complexes in THF¹³ have shown this system to behave somewhat differently from the above system.

Reaction of Lithium Anilide with $(\text{PPh}_3)_3\text{RhCl}$. Initial experiments led us to try three different reactions of $(\text{PPh}_3)_3\text{RhCl}$ ¹⁴ with lithium anilide, varying the amount of anilide used.

With 1.3 Equiv of LiNHPH . The reaction of 1.3 equiv of LiNHPH with $(\text{PPh}_3)_3\text{RhCl}$ in THF at room temperature generates a clear, reddish-brown solution. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of that solution, recorded after 0.5 h, indicates the presence of three $(\text{PPh}_3)_n\text{Rh}$ species: a metastable one, A, and two more stable ones, B and C. In addition, a broad signal corresponding to dissociated triphenylphosphine ($\delta \approx -1.5$ ppm) is observed. For clarity, a schematic representation of the NMR spectrum has been drawn (Figure 1).

The solution was stirred at room temperature for 24 h, at which points its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (at 308 K) showed that A had disappeared. The spectrum exhibits only the doublets corresponding to species B and C, together with the signal due to dissociated triphenylphosphine. The relative intensities of the signals of B and C were unchanged (ca. 2/1). Variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR experiments showed that a decrease in the temperature of this mixture caused the signal due to dissociated triphenylphosphine to become sharper, while the signal due to B became broader and finally disappeared at 203 K, leaving only that corresponding to C. Allowing the NMR tube to return to room temperature restored the initial spectrum with the signals of B and C in approximately a 2/1 ratio.

These results clearly indicate that triphenylphosphine is liberated during the reaction of LiNHPH with $(\text{PPh}_3)_3\text{RhCl}$ to give two species B and C in equilibrium. Due to the lack of pertinent literature data, we could only speculate as to the nature of the detected species A. The reaction of LiNHPH with $(\text{PPh}_3)_3\text{RhCl}$ is similar to that of Grignard reagents with the same complex; these reactions are proposed to give tetrahedral or trigonal pyramidal complexes (eq 4).^{15,16}



Thus, one possible formula for A is $(\text{PPh}_3)_3\text{RhNHPH}$, in which the three phosphorus ligands are equivalent. Dissociation of a triphenylphosphine ligand from A would generate a $14 e^-$

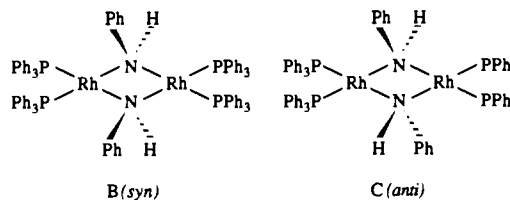
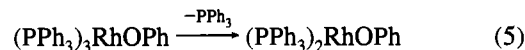
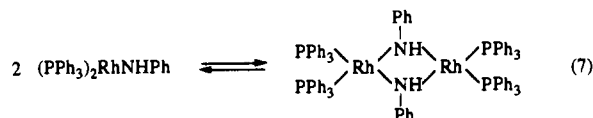


Figure 2. Proposed formula for the rhodium(I) species B and C.

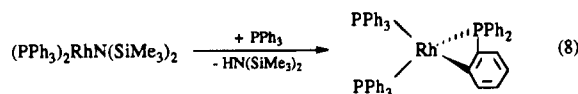
species that would be prone to dimerization, as in the case of tris(triphenylphosphine)phenoxorhodium (eqs 5, 6).¹⁶



On the basis of this literature data, two structural possibilities were considered for B and C. The first is that one species might be the monomer $(\text{PPh}_3)_2\text{RhNHPH}$, while the other is the dimer $[(\text{PPh}_3)_2\text{RhNHPH}]_2$.



This hypothesis (eq 7) is unlikely because of the expected instability of the $14 e^-$ mononuclear complex, similar to (but less crowded than) $(\text{PPh}_3)_2\text{RhN}(\text{SiMe}_3)_2$, which has been reported to be unstable and to undergo an orthometalation reaction (eq 8).²



In the reaction of $(\text{PPh}_3)_3\text{RhCl}$ with LiNHPH , we never observed $^{31}\text{P}\{^1\text{H}\}$ NMR signals corresponding to orthometalated complexes;¹⁷ apparently that process is not occurring in this system.

A second, and more probable, hypothesis for the structures of B and C is that they are two isomeric dimers, a situation previously reported for anilidopalladium and anilidogallium complexes.^{18,19} In the latter case, an equilibrium between the two isomers is observed, the *anti* form being the more stable. By analogy, complexes B and C are proposed to be the two geometric isomers of a dinuclear, bis(amido)-bridged complex (Figure 2).

After this reaction mixture was stirred at room temperature for several days, the $^{31}\text{P}\{^1\text{H}\}$ NMR signals due to B and C disappeared, leaving signals due to a new species, D. This spectrum (Figure 3) is somewhat complex, apparently due to an AA'BB'XX' spin system arising from a dinuclear structure.

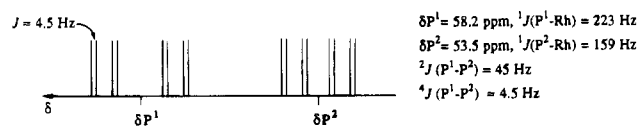


Figure 3. Schematic representation of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of D (THF) (Bruker WM 250, 101.25 MHz).

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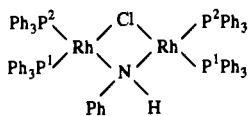


Figure 4. Proposed formula for D.

Studies using 2D (δ, δ) $^{31}\text{P}\{^1\text{H}\}$, $^{103}\text{Rh}\{^1\text{H}\}$ NMR spectroscopy indicate in this complex the presence of a unique type of rhodium center, associated with two inequivalent phosphorus ligands.

The variation in $^1\text{J}(\text{P}-\text{Rh})$ coupling constants (159 and 223 Hz) suggests quite different *trans* influences experienced by the two types of phosphorus ligand. On the basis of this data, the structure shown in Figure 4 is proposed for D. The assignments P¹ and P² arise from the smaller *trans* influence of Cl⁻ relative to HPhN⁻ (*vide infra*). The above 2D (δ, δ) $^{31}\text{P}\{^1\text{H}\}$, $^{103}\text{Rh}\{^1\text{H}\}$ NMR studies indicate that the observed fine coupling (approximately 4.5 Hz) is due to long-range P-P interactions, $^4\text{J}(\text{P}^1-\text{P}^2)$.

With 10 Equiv of LiNHPH. The reaction of LiNHPH (10 equiv/Rh) with $(\text{PPh}_3)_3\text{RhCl}$ in THF at room temperature generates a dark red solution. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this solution exhibits only one doublet, corresponding to the species A, and a broad signal attributed to dissociated triphenylphosphine. Under these conditions, A is stable and does not decompose, even after 6 days in refluxing THF.

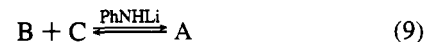
We initially proposed that A was a tris(triphenylphosphine)-anilidorhodium complex. However, in the presence of 10 equiv of LiNHPH, A is the only rhodium complex generated, and its formation apparently involves dissociation of triphenylphosphine. Thus A clearly bears less than three phosphorus ligands per rhodium atom and cannot have the above formula.

Variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR experiments show a sharpening of the free triphenylphosphine signal as the temperature of this reaction mixture is lowered; the signal due to A does not change in shape, though the doublet shifts downfield slightly ($\Delta\delta = 0.35$ ppm at 213 K). In the spectrum obtained at 203 K, integration of the signals indicates an approximately 2/1 ratio between coordinated and dissociated triphenylphosphine. This supports the idea that species A thus bears two phosphorus ligands per rhodium atom, a hypothesis which was later confirmed using 2D (δ, δ) $^{31}\text{P}\{^1\text{H}\}$, $^{103}\text{Rh}\{^1\text{H}\}$ NMR (*vide infra*).

The ^1H NMR spectrum of A was also obtained. As butane impurities, hexanes, and THF in the reaction mixture might obscure NH signals due to A in this spectrum, the solvents were removed under vacuum and replaced with THF-*d*₈. The $^{31}\text{P}\{^1\text{H}\}$ spectrum of the resulting sample corresponds to that of A. The 200 MHz ^1H NMR spectrum recorded at room temperature exhibits a complex set of signals in the aromatic proton region. Signals in this region due to noncoordinated PPh_3 and to excess LiNHPH (see the Experimental Section) were identified by comparison with the spectra of authentic samples. In addition, some signals due to complex A are observed; others (due to ortho and meta protons on the coordinated anilide) are probably buried beneath those due to excess LiNHPH. Two signals due to NH are clearly observed at 4.17 and 1.50 ppm. The approximately 4:1 ratio of the intensities of these peaks is as expected for the mixture of a complex (A) containing two anilido ligands and eight equivalents of excess LiNHPH. The chemical shift of 1.50 ppm for the signal due to NH of coordinated anilide falls in the range observed for similar complexes of late transition metals.²⁰ In addition, signals due to THF are observed in this ^1H NMR spectrum; it is not clear whether this is residual or Li-coordinated solvent. A $^2\text{H}\{^1\text{H}\}$ NMR spectrum of A (in THF), from the reaction of $(\text{PPh}_3)_3\text{RhCl}$

with 10 equiv of LiNHPH, shows two broad singlets in a approximately 4:1 ratio, attributable to ND signals due to excess and complexed anilide, respectively.

The most striking observation, however, is the stability of A in the presence of excess anilide, since, in the presence of 1.3 equiv of LiNHPH, A can only be transiently observed and rapidly decomposes to a mixture of the dimers B and C. We thus were led to examine the possible reversible transformation of B and C into A. A THF solution of B and C was prepared and treated with excess LiNHPH (5 equiv). The solution was stirred for 2 h at room temperature, at which point the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the solution did exhibit the signals of A, B, and C. These observations strongly suggest that an equilibrium exists between the three species (eq 9). Furthermore, this reaction (eq



9) appears to be slow, which suggests that the initial formation of A does not occur through (B + C) when a large excess of LiNHPH is added.

Also relevant to the possible structure of A is the following: addition, at room temperature, of a large excess of triphenylphosphine (12 equiv/Rh) to a THF solution containing only A, and stirring for 2 h does not promote any change in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum.

All the above observations can be accounted for by the following hypotheses: Because of steric hindrance, the mononuclear $[(\text{PPh}_3)_3\text{Rh}(\text{NHPH})]$ is not stable, and rapidly loses a triphenylphosphine ligand to generate a bis(triphenylphosphine)-anilidorhodium(I) species. (Another explanation could be that the chloride substitution occurs only after dissociation of a triphenylphosphine ligand.) The unsaturated complex $[(\text{PPh}_3)_2\text{Rh}(\text{NHPH})]$ thus generated is not stable and rapidly dimerizes to give the two geometric isomers B and C. However, in the presence of excess LiNHPH, $[(\text{PPh}_3)_2\text{Rh}(\text{NHPH})]$ can be stabilized by coordination of a second anilido ligand (less crowded than PPh_3) to give the anionic complex A, $[(\text{PPh}_3)_2\text{Rh}(\text{NHPH})_2]^- \text{Li}^+$. Complex A can also be generated by addition of excess LiNHPH to a mixture of (B + C).

Since A was also observed to form transiently during the reaction of $(\text{PPh}_3)_3\text{RhCl}$ with 1.3 equiv of LiNHPH, we were interested to discover if A could be observed in the reaction of $(\text{PPh}_3)_3\text{RhCl}$ with only 0.9 equiv of lithium anilide.

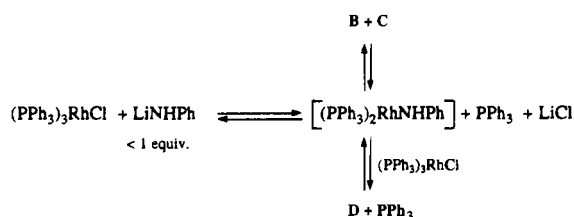
With 0.9 Equiv of LiNHPH. Reaction of $(\text{PPh}_3)_3\text{RhCl}$ with 0.9 equiv of LiNHPH leads to a red solution. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of that solution indicates the presence of several species but the absence of complex A. In addition to signals corresponding to small amounts of unreacted $(\text{PPh}_3)_3\text{RhCl}$, of dissociated triphenylphosphine, and of B and C are signals which correspond to species D, the major product.

Variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR experiments conducted on this reaction mixture showed a variation in the relative intensities of the different signals. In particular, as the temperature was lowered, signals due to species B disappeared and the signal due to free triphenylphosphine sharpened, as expected (*vide supra*). Moreover, the signals corresponding to $(\text{PPh}_3)_3\text{RhCl}$ increased in intensity. This last phenomenon has been reproducibly observed and suggests that the reactions are reversible. A similar observation has recently been reported for the reaction of $(\text{PPh}_3)_3\text{RhCl}$ with catecholborane.²¹

(20) See, for example: (a) Glueck, D. S.; Bergman, R. G. *Organometallics* **1991**, *10*, 1479. (b) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *Organometallics* **1991**, *10*, 1875. (c) Boncella, J. M.; Villanueva, L. A. *J. Organomet. Chem.* **1994**, *465*, 297.

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Scheme 1



It thus appears that complex equilibria exist between the different species in this solution and that A cannot be observed when less than 1 equiv of LiNHPH is added to $(\text{PPh}_3)_3\text{RhCl}$. (However, addition of 5 equiv of LiNHPH to this solution at room temperature causes the formation of A. After 24 h of stirring, only species A, B, and C are observed by $^{31}\text{P}\{^1\text{H}\}$ NMR, A being by far the major species, thus confirming eq 9.) A possible series of equilibria for the reaction mixture obtained from adding less than 1 equiv of LiNHPH to $(\text{PPh}_3)_3\text{RhCl}$ is outlined in Scheme 1. This proposal takes into account that we have observed (*vide supra*) a slow reaction of mixtures of (B + C) to give D. Addition of a small excess of LiCl to this reaction mixture does cause the equilibria to shift, $(\text{PPh}_3)_3\text{RhCl}$ being formed.

Since, in THF or benzene solutions, $(\text{PPh}_3)_3\text{RhCl}$ easily dissociates triphenylphosphine to yield the dimer $[(\text{PPh}_3)_2\text{RhCl}]_2$, which precipitates,²² we also studied the reaction of lithium anilide with that dinuclear complex. As described below, it turns out that this reaction (with 1.3 or 10 equiv of LiNHPH/Rh) gives the same overall results as the reactions conducted with $(\text{PPh}_3)_3\text{RhCl}$.

Reaction of Lithium Anilide with $[(\text{PPh}_3)_2\text{RhCl}]_2$. The reaction of $[(\text{PPh}_3)_2\text{RhCl}]_2$ with 1.3 equiv (/Rh) of LiNHPH generates a mixture of complexes B and C, which slowly reacts to give complex D. No dissociated triphenylphosphine is detected, in agreement with the hypothesis that species (B + C) are bis(triphenylphosphine)rhodium derivatives.

Reaction of $[(\text{PPh}_3)_2\text{RhCl}]_2$ with 10 equiv (/Rh) of LiNHPH leads to the formation of a single product, complex A. However, in this case, dissociated triphenylphosphine is observed. Integration of coordinated and dissociated triphenylphosphine signals in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum recorded at 203 K indicated a ca 4/1 ratio. This observation was confirmed by showing that addition of excess LiNHPH to a mixture of (B + C), generated from $[(\text{PPh}_3)_2\text{RhCl}]_2$ (and therefore free of noncoordinated triphenylphosphine), also produces dissociated triphenylphosphine.

The above observation was rather unexpected and obviously led us to question again the number of triphenylphosphine ligands present in complex A. To answer this question, a solution of A, generated by reaction of 10 equiv (/Rh) of LiNHPH with $[(\text{PPh}_3)_2\text{RhCl}]_2$, was analyzed by ^{31}P -detected, indirect, two-dimensional (δ, δ) $^{31}\text{P}\{^1\text{H}\}$, $^{103}\text{Rh}\{^1\text{H}\}$ NMR spectroscopy. The 2D spectrum obtained by an HMQC sequence (Figure 5a) indicates, in *F1*, a single $^{103}\text{Rh}\{^1\text{H}\}$ signal ($\delta = 225$ ppm) and a doublet in *F2* for the $^{31}\text{P}\{^1\text{H}\}$ signal ($\delta = 50.5$ ppm, $J(\text{P}-\text{Rh}) = 175$ Hz).

The chemical shift of the $^{103}\text{Rh}\{^1\text{H}\}$ signal lies in the expected range for Rh(I) complexes, but no further information can be deduced from this signal.²³ The 2D spectrum obtained by an HSQC sequence (Figure 5b) exhibits a doublet in *F1* with an apparent coupling constant of 350 Hz, which is twice the value

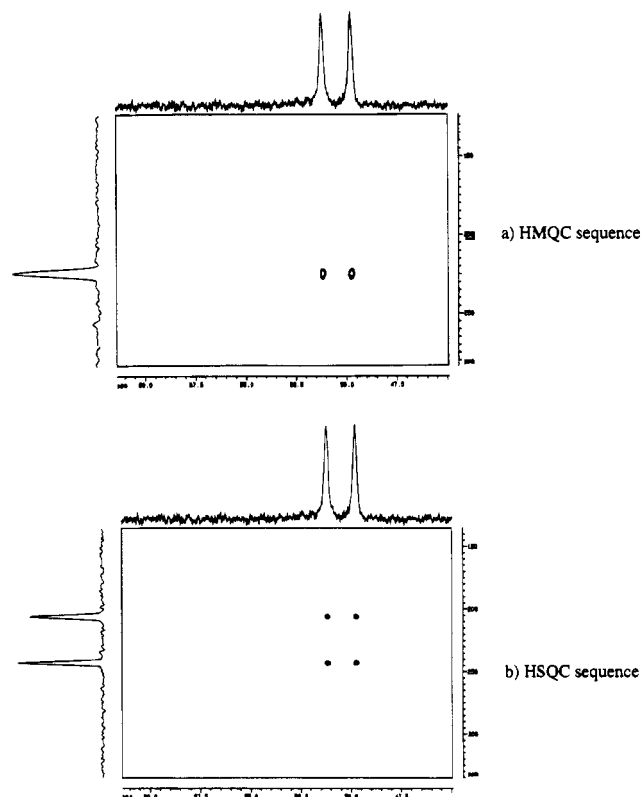


Figure 5. 2D (δ, δ) ^{31}P , $^{103}\text{Rh}\{^1\text{H}\}$ NMR spectra of A (Bruker AMX 300, 121.4967 MHz).

observed for the phosphorus signal, a doublet, in *F2*. For a retro-INEPT sequence, this situation is characteristic of a $1/0/-1$ triplet which appears as a doublet without inversion.²⁴ These results indicate an A_2X system and thus confirm the presence of two equivalent triphenylphosphine ligands bound to the rhodium atom in A.

Since noncoordinated triphenylphosphine is observed in the reaction of 10 equiv (/Rh) of LiNHPH with $[(\text{PPh}_3)_2\text{RhCl}]_2$, it must be concluded that the resulting, homogeneous solution contains both a bis(triphenylphosphine)rhodium species, A, and another rhodium species without phosphorus ligands. There is precedence for this hypothesis: amidocobalt complexes without phosphine ligands have been prepared, *e.g.*, the dinuclear $[\text{Co}(\text{NR}_2)_2]_2$ ($\text{R} = \text{Ph}, \text{SiMe}_3$).²⁵

The main results of the reaction of lithium anilide with either $(\text{PPh}_3)_3\text{RhCl}$ or $[(\text{PPh}_3)_2\text{RhCl}]_2$ are summarized in Scheme 2. What is interesting is that no bis(triphenylphosphine)anilidorhodium species analogous to $(\text{PPh}_3)_2\text{RhN}(\text{SiMe}_3)_2$ is detected, although it is probably a reaction intermediate. When generated, this species must rapidly dimerize to $[(\text{PPh}_3)_2\text{RhNHPH}]_2$, (B + C), which is stable in solution for at least 24 h but which slowly reacts with available Cl^- to give a chloride-containing, dinuclear species $[(\text{PPh}_3)_2\text{Rh}]_2(\mu\text{-Cl})(\mu\text{-NHPH})$, D. However, the most important observation is that, in the presence of excess LiNHPH, a solution-stable, anionic anilidorhodium species A is formed for which the formula $[(\text{PPh}_3)_2\text{Rh}(\text{NHPH})_2]^- \text{Li}^+$ is proposed. Some other anionic complexes of Rh(I) have previously been synthesized,^{26,27} *e.g.*, by reaction of organolithium reagents with dinuclear rhodium complexes bearing bulky chelating phosphines (eq 10).²⁷

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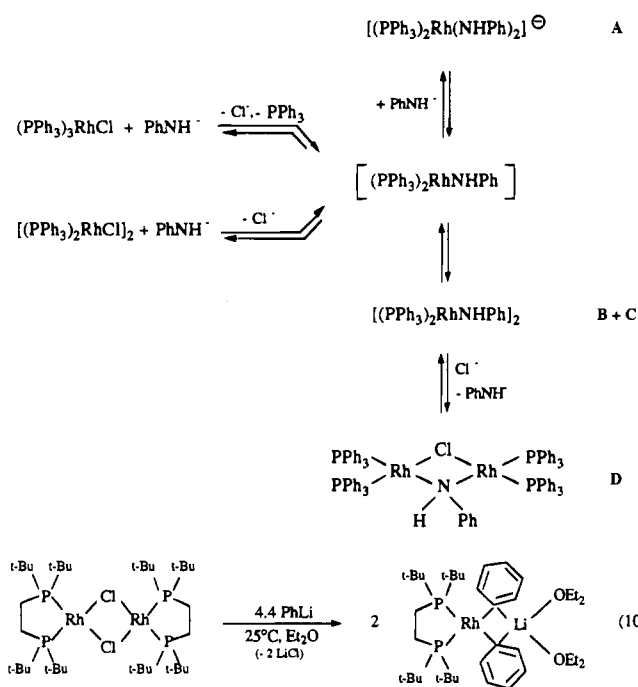
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Scheme 2



Another intriguing feature of the reactions of $(PPh_3)_3RhCl$ with lithium anilide is that no species corresponding to a simple substitution of the chloride atom of $(PPh_3)_3RhCl$ by the anilide anion is detected. This may be due in part to steric limitations, so this study was extended to the reaction of lithium anilide with similar Rh(I) complexes in which the triphenylphosphine ligands (cone angle = 145°) were replaced by triethylphosphines (cone angle = 132°).²⁸

Reaction of Lithium Anilide with $(PEt_3)_3RhCl$. As above, these experiments were conducted either with 1.3 or with 10 equiv ($/Rh$) of LiNHPPh.

With 1.3 Equiv of LiNHPPh. The reaction of 1.3 equiv of LiNHPPh with $(PEt_3)_3RhCl$ in THF at room temperature generates a clear, reddish-brown solution. The $^{31}P\{^1H\}$ NMR spectrum of this mixture exhibits two sets of signals, each corresponding to an AB_2X system (Figure 6). The first set corresponds to $(PEt_3)_3RhCl$, while the second set can be attributed to the substitution product, E' , $(PEt_3)_3RhNHPPh$. As expected from literature data,²⁹ the $^1J(P^1-Rh)$ coupling constant for E' is lower than $^1J(P^1-Rh)$ for $(PEt_3)_3RhCl$ (152 vs 188 Hz). No signal due to dissociated triethylphosphine is observed. It should be noted that, like $(PPh_3)_3RhCl$ and $(PEt_3)_3RhCl$, E' apparently exhibits a square planar geometry, as opposed to the tetrahedral or trigonal pyramidal structure proposed for $(PPh_3)_3RhPh$.^{15,16}

The composition of this solution remains unchanged (as monitored by $^{31}P\{^1H\}$ NMR) over several hours at room temperature, suggesting that an equilibrium exists between the two species (eq 11). At the concentrations used, the generated lithium chloride is soluble in THF. Addition of excess lithium chloride to this equilibrium mixture causes an immediate color

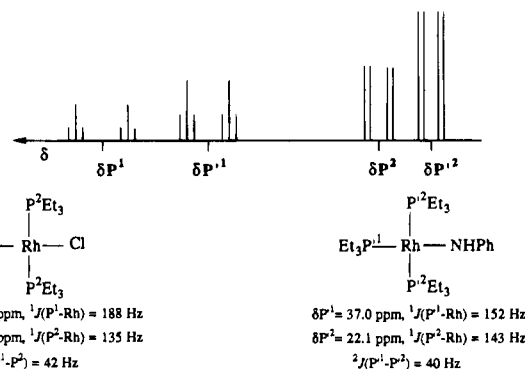
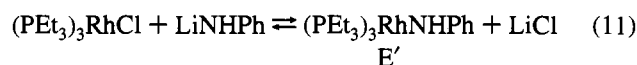


Figure 6. Schematic representation of the $^{31}P\{^1H\}$ NMR spectrum (at 298 K) of the THF solution obtained by reaction of 1.3 equiv of LiNHPPh with $(PEt_3)_3RhCl$ (Bruker WM 250, 101.25 MHz).

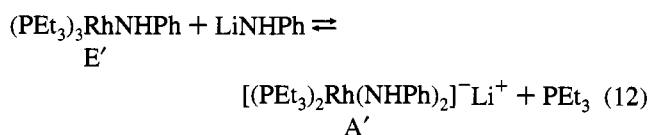
change from reddish brown to a light yellow-orange (the colour of $(PEt_3)_3RhCl$ in THF), and the $^{31}P\{^1H\}$ NMR spectrum of the resulting solution shows the chloride complex to be the principal species in solution. The tris(triethylphosphine)anilido



rhodium complex E' has not yet been isolated. Nevertheless, its observation in solution perhaps illustrates the first step of the reaction of LiNHPPh with tris(phosphine)RhCl complexes, showing that such reactions do not require *a priori* dissociation of a phosphine ligand (or conversion to a dinuclear complex).

With 10 Equiv of LiNHPPh. The reaction of 10 equiv of LiNHPPh with $(PEt_3)_3RhCl$ in THF at room temperature leads to a clear, reddish-brown solution. The $^{31}P\{^1H\}$ NMR spectrum of this solution exhibits signals due to three species. In addition to signals corresponding to E' (*vide supra*), a doublet is observed at 38 ppm ($J(P-Rh) = 171$ Hz), attributable to a new species A' , together with a broad signal due to dissociated triethylphosphine. This liberation of triethylphosphine indicates that A' bears fewer than three phosphorus ligands. By analogy with the previously observed chemistry of $(PPh_3)_3RhCl$, the species A' is proposed to be the anionic bis(triethylphosphine)bis-(anilido)rhodium complex, $[(PEt_3)_2Rh(NHPH)_2]^- Li^+$.

At room temperature, the relative intensities of the $^{31}P\{^1H\}$ NMR signals of A' and E' in this reaction mixture are nearly 1:2. At lower temperatures, this ratio increases and A' becomes by far the major species, while the signal of dissociated triethylphosphine sharpens. These observations are interesting, as they suggest the presence of an equilibrium that was not observed for the analogous (triphenylphosphine)anilidorhodium species (eq 12).



Reaction of Lithium Anilide with $[(PEt_3)_2RhCl)_2]$. **With 1.3 Equiv of LiNHPPh.** The $^{31}P\{^1H\}$ NMR spectrum of the solution obtained from the addition of 1.3 equiv ($/Rh$) of lithium anilide to $[(PEt_3)_2RhCl)_2]$ indicates the presence of four phosphine-containing species. Two minor products are A' (*vide supra*) and, unexpectedly, $(PEt_3)_3RhCl$. Variable-temperature $^{31}P\{^1H\}$ NMR experiments show that the two major products in the reaction mixture are in equilibrium. One of these products, referred to as D' , gives rise to two slightly split (small $J \approx 3$ Hz) doublets of doublets in the $^{31}P\{^1H\}$ NMR spectrum (Figure 7), a pattern similar to that observed for D (*vide supra*).

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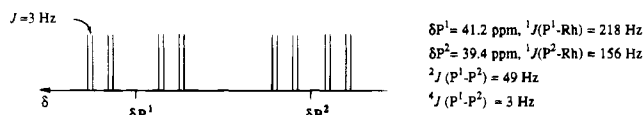


Figure 7. Schematic representation of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (298 K) of D' (Bruker WM 250, 101.25 MHz).

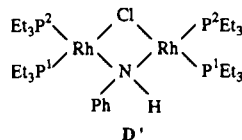


Figure 8. Proposed formula for D' .

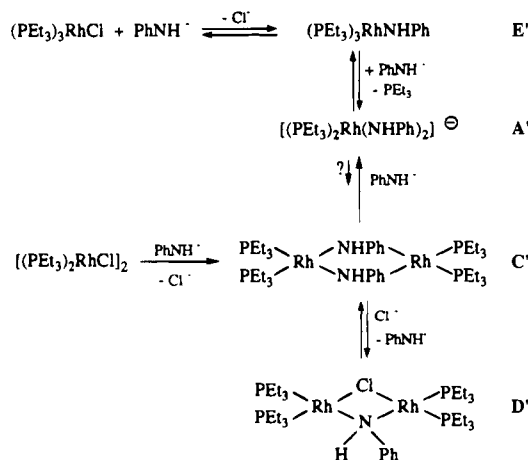
On the basis of these data, D' is believed to be the analogous dinuclear complex $[(\text{PEt}_3)_2\text{Rh}]_2(\mu\text{-Cl})(\mu\text{-NHPH})$ (Figure 8).

The $^{31}\text{P}\{^1\text{H}\}$ NMR signal of the second major species in this reaction mixture is a doublet ($\delta = 36$ ppm, $^1J(\text{P-Ph}) = 176$ Hz). Comparison with the spectroscopic features of the triphenylphosphine anilidorhodium complexes A–D suggests that this species is a dimer, C' , $[(\text{PEt}_3)_2\text{RhNHPH}]_2$. In the reaction of 1.3 equiv ($/\text{Rh}$) of LiNHPH with $[(\text{PPh}_3)_2\text{RhCl}]_2$, the isomeric dimers B and C form, which, after several days, react to give the chloride-containing, dinuclear complex, D (*vide supra*). In the present case, the two major products are C' and D' . The observation of only one signal for $[(\text{PEt}_3)_2\text{RhNHPH}]_2$ may be accounted for by a fast interconversion between the *syn* and *anti* isomers. This phenomenon may be due to a more labile coordination bond between the nitrogen ligand and the rhodium center, which is more electron-rich when coordinated by triethylphosphine ligands than by triphenylphosphine ligands.

With 10 Equiv of LiNHPH . The reaction of $[(\text{PEt}_3)_2\text{RhCl}]_2$ with LiNHPH (10 equiv/ Rh) in THF at room temperature leads to a clear, reddish-brown solution. $^{31}\text{P}\{^1\text{H}\}$ NMR analysis showed this solution to contain A' as the major species, contaminated by traces of other, unidentified species. As expected, no dissociated triethylphosphine was detected.

The reactivity of lithium anilide with $(\text{PEt}_3)_3\text{RhCl}$ and $[(\text{PEt}_3)_2\text{RhCl}]_2$ is summarized by the following reaction scheme (Scheme 3).

Scheme 3



Bis(triethylphosphine)anilidorhodium(I) complexes analogous to $(\text{PEt}_3)_2\text{RhN}(\text{SiMe}_3)_2$ were not observed in this system of reactions, irrespective of the $\text{Rh}(\text{I})$ precursor used and the amount of LiNHPH added. The results obtained from reacting 1.3 equiv of LiNHPH with $(\text{PEt}_3)_3\text{RhCl}$ indicate that the tris(triethylphosphine)anilidorhodium complex is not prone to dissociation of a phosphine ligand, as it was observed without

any trace of the dinuclear species C' or D' . In contrast, adding 1.3 equiv of LiNHPH to the dinuclear $[(\text{PEt}_3)_2\text{RhCl}]_2$ leads to those dinuclear species. These results suggest that the expected bis(triethylphosphine)anilidorhodium(I) intermediate is not stable and tends to dimerize, unless an excess of LiNHPH is present and stabilizes the monomer by formation of the anionic $[(\text{PEt}_3)_2\text{Rh}(\text{NHPH})_2]^- \text{Li}^+$, A' .

Conclusion

The results described here illustrate the complexity of the reaction of lithium anilide with mononuclear $(\text{PR}_3)_3\text{RhCl}$ and dinuclear $[(\text{PR}_3)_2\text{RhCl}]_2$ complexes. When conducted with a slight excess of LiNHPH (1.3 equiv), the reaction leads, depending on the nature of R and on reaction time, to equilibrated mixtures of anilidorhodium species, among which a mononuclear complex, $[(\text{PEt}_3)_3\text{RhNHPH}]$, E' , and dinuclear complexes bridged either by two anilido ligands or by one anilido and one chloro ligand (B' , C' , and D') were identified spectroscopically. In the presence of a large excess of LiNHPH (10 equiv), the above equilibria are shifted and the reaction leads a single, anionic, bis(phosphine)bis(anilido)rhodium(I) complex, $[(\text{PR}_3)_2\text{Rh}(\text{NHPH})_2]^- \text{Li}^+$ (A or A'). Complexes A and A' , though not isolable in the solid state, are stable for days in refluxing THF, provided that the appropriate excess of LiNHPH is present. Though these complexes were not isolated, solution $^{31}\text{P}\{^1\text{H}\}$ and $^{103}\text{Rh}\{^1\text{H}\}$ NMR spectroscopic investigations have allowed convincing structural assignments to be made.

Experimental Section

General Procedures. All reactions were conducted under argon (Argon U, L'Air Liquide) using Schlenk tube and vacuum line techniques. All reagents were distilled (or recrystallized) according to classical procedures and thoroughly degassed before use. THF was freshly distilled from sodium–benzophenone under argon. THF- d_6 (Euriso-Top) was used without further purification. *n*-Butyllithium (Janssen, ≈ 1.6 M in hexane) was used after titration.³⁰ Aniline (Janssen) was dried over CaH_2 and distilled under partial vacuum. Aniline- d_2 (Euriso-Top) was used without further purification. The rhodium precursors were prepared according to, or by adaptation of, literature procedures: $(\text{PPh}_3)_3\text{RhCl}$,³¹ $(\text{PEt}_3)_3\text{RhCl}$,³² $[(\text{PPh}_3)_2\text{RhCl}]_2$,³² $[(\text{PEt}_3)_2\text{RhCl}]_2$,³² $[(\text{C}_8\text{H}_{14})_2\text{RhCl}]_2$, the starting complex for the synthesis of the three latter complexes, was prepared from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ according to ref 33. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on Bruker AC 80 (^{31}P at 32.438 MHz) or WM 250 (^{31}P at 101.25 MHz) instruments, using 85% phosphoric acid in D_2O as an external reference. $^{103}\text{Rh}\{^1\text{H}\}$ NMR spectra were recorded on Bruker AMX 300 (^{31}P at 121.4967 MHz and ^{103}Rh at 9.4842 MHz) or Bruker AMX 400 (^{31}P at 151.8709 MHz and ^{103}Rh at 11.8553 MHz) instruments. The ^1H spectrum was recorded on a Bruker AC 200 (^1H at 200.133 MHz and referenced to the downfield peak of residual, nondeuterated THF at 3.75 ppm) and $^2\text{H}\{^1\text{H}\}$ NMR spectra were recorded on the Bruker AMX 400 instrument (^2H at 61.423 MHz and referenced to added C_6D_6 at 7.15 ppm).

Typical Reaction of LiNHPH with Rhodium(I) Complexes. Two procedures were used for the reaction of LiNHPH with the rhodium(I) precursors. Both gave identical results.

(a) Lithium anilide was prepared by addition of *n*-BuLi to an equimolar amount of aniline which had been cooled to -10 °C. The solution was stirred for 1 h at room temperature, and then the solvent (hexane) was removed under vacuum and the resulting powder was dissolved in THF (8 mL). This solution was then added to the rhodium complex (0.5 mmol in Rh) in THF (8 mL) at -10 °C, and the mixture was allowed to return to room temperature.

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Table 1. ^{31}P NMR Data of Rhodium(I) Precursors^a

Rh(I) precursors	δ , ppm (multiplicity), J , Hz
$(\text{PPh}_3)_3\text{RhCl}$	$\delta = 50$ (dt), $^1J(\text{P-Rh}) = 192$, $^2J(\text{P-P}) = 38$
$[(\text{PPh}_3)_2\text{RhCl}]_2$	$\delta = 33.4$ (dd), $^1J(\text{P-Rh}) = 143$, $^2J(\text{P-P}) = 38$
$(\text{PEt}_3)_3\text{RhCl}$	$\delta = 53.2$ (d), $^1J(\text{P-Rh}) = 196$
$[(\text{PEt}_3)_2\text{RhCl}]_2$	$\delta = 42.7$ (dt), $^1J(\text{P-Rh}) = 188$, $^2J(\text{P-P}) = 42$
	$\delta = 25.3$ (dd), $^1J(\text{P-Rh}) = 135$, $^2J(\text{P-P}) = 42$
	$\delta = 44.3$ (d), $^1J(\text{P-Rh}) = 194$

^a Bruker WM 250, 101.25 MHz, THF solutions at 298 K (reference: 85% H_3PO_4 in D_2O).

(b) Aniline (0.9–10 equiv/Rh) was added under argon to a solution of the rhodium complex (0.5 mmol in Rh) in freshly distilled THF (15 mL). The solution was cooled to -10 °C, and an equimolar (to the amount of aniline) amount of *n*-BuLi in hexane was added dropwise from a syringe. The reddish-brown solution was allowed to return to room temperature, stirred for 0.5–1 h, and then analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

To prepare a sample for ^1H NMR spectroscopy, a 1 mL portion of the reaction mixture was placed in a separate Schlenk flask. The THF was removed under vacuum and replaced with THF- d_8 . ^1H NMR ($\text{C}_4\text{D}_8\text{O}$, ppm): 7.67–7.59 (mult, H_{ortho} (coordinated PPh_3)), 7.49–7.41 (mult, H (free PPh_3)), 7.23 (t, $^3J_{\text{Hm-Hp}} = 7.2$ Hz, H_{para} (coordinated PPh_3)), 7.11 (t, H_{meta} (coordinated PPh_3)), 6.83 (t, H_{meta} (free LiNHPPh)), 6.43 (d, $^3J_{\text{Hm-Ho}} = 7.9$ Hz, H_{ortho} (free LiNHPPh)), 6.26 (t, $^3J_{\text{Hm-Hp}} = 6.7$ Hz, H_{para} (coordinated NHPPh)), 6.06 (t, $^3J_{\text{Hm-Hp}} = 7.0$ Hz, H_{para} (free LiNHPPh)), 3.79 (mult, THF), 3.00 (br s, $w_{1/2} = 11.5$ Hz, NH (free LiNHPPh)), 1.94 (mult, THF), 1.50 (s, $w_{1/2} = 6.9$ Hz, NH (coordinated NHPPh)).

Preparation of A- d_2 . Complex A containing deuterium-substituted amide ligands was prepared as above, using PhND_2 (d_2 -aniline). $^2\text{H}\{^1\text{H}\}$ NMR ($\text{C}_4\text{H}_8\text{O}$, ppm): 2.33 (br s, $w_{1/2} = 13$ Hz, ND free anilide), 1.16 (br s, $w_{1/2} = 16$ Hz, ND complexed anilide). The two signals are in an approximately 4:1 ratio.

Table 2. ^{31}P NMR Data of Anilidorhodium(I) Complexes^a

Rh(I) anilido species	δ , ppm (multiplicity), J , Hz
$[(\text{PPh}_3)_2\text{Rh}(\text{NHPH})_2]^- \text{Li}^+$	A $\delta = 55.1$ (d), $^1J(\text{P-Rh}) = 175$
$[(\text{PPh}_3)_2\text{Rh}(\text{NHPH})_2]$ (<i>syn</i>)	B $\delta = 55.6$ (d), $^1J(\text{P-Rh}) = 177$
$[(\text{PPh}_3)_2\text{Rh}(\text{NHPH})_2]$ (<i>anti</i>)	C $\delta = 50.4$ (d) $^1J(\text{P-Rh}) = 179$
$[(\text{PPh}_3)_2\text{Rh}]_2(\mu\text{-Cl})(\mu\text{-NHPH})$	D $\delta = 58.2$ (ddd), $^1J(\text{P-Rh}) = 223$, $^2J(\text{P-P}) = 45$, $^4J(\text{P-P}) = 4.5$
	$\delta = 53.5$ (ddd), $^1J(\text{P-Rh}) = 159$, $^2J(\text{P-P}) = 45$, $^4J(\text{P-P}) = 4.5$
$[(\text{PEt}_3)_2\text{Rh}(\text{NHPH})_2]^- \text{Li}^+$	A' $\delta = 38$ (d), $^1J(\text{P-Rh}) = 171$
$[(\text{PEt}_3)_2\text{Rh}(\text{NHPH})_2]$	C' $\delta = 36$ (d), $^1J(\text{P-Rh}) = 176$
$[(\text{PEt}_3)_2\text{Rh}]_2(\mu\text{-Cl})(\mu\text{-NHPH})$	D' $\delta = 41.2$ (ddd), $^1J(\text{P-Rh}) = 218$, $^2J(\text{P-P}) = 49$, $^1J(\text{P-P}) = 3$
	$\delta = 39.4$ (ddd), $^1J(\text{P-Rh}) = 156$, $^2J(\text{P-P}) = 49$, $^4J(\text{P-P}) = 3$
$(\text{PEt}_3)_3\text{RhNHPH}$	E' $\delta = 37$ (dt), $^1J(\text{P-Rh}) = 152$, $^2J(\text{P-P}) = 40$
	$\delta = 22.1$ (dd), $^1J(\text{P-Rh}) = 143$, $^2J(\text{P-P}) = 40$

^a Bruker WM 250, 101.25 MHz, THF solutions at 298 K (reference: 85% H_3PO_4 in D_2O).

The relevant $^{31}\text{P}\{^1\text{H}\}$ NMR data for the starting rhodium complexes and the detected anilidorhodium species are presented in Tables 1 and 2, respectively.

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