

Rhodium-catalysed hydroamination–hydroarylation of norbornene with aniline, toluidines or diphenylamine

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(Received May 24, 1993)

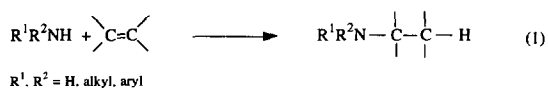
Abstract

The condensation of aniline, toluidines or diphenylamine with norbornene tetrahydrofuran is promoted by a system generated from Li^nBu , ArNH_2 and $[(\text{PEt}_3)_2\text{RhCl}]_2$. Aniline and *m*- and *p*-toluidines lead to a mixture of hydroamination and hydroarylation products whereas *o*-toluidine and diphenylamine lead to the hydroarylation product only. When conducted in the amine as solvent, the reaction is catalytic with respect to both lithium and rhodium.

Key words: Rhodium; Norbornene; Hydroarylation; Hydroamination; Catalysis

1. Introduction

The direct addition of a N–H bond of amines across the C=C bond of unactivated olefins (hydroamination) has attracted a great deal of interest [1,2]. Indeed, a catalytic version of this reaction could be a valuable alternative to the classical industrial synthesis of alkylamines by dehydration of alcohols in the presence of amines since alcohols are generally prepared from olefins:



However, efforts to effect this transformation in a general and efficient manner have met with only limited success [1]. Until recently, the basic approaches consisted in activating either the amine via alkali metal amido species [3] or the olefin by coordination to transition metals.

The first examples of transition-metal-catalysed homogeneous hydroamination reactions were reported by Coulson [4] in 1971. They concern the rhodium- or iridium-catalysed hydroamination of ethylene with sec-

ondary amines. This reaction, however, is limited to ethylene and is strongly dependent upon the $\text{p}K_a$ of the amine. An interesting approach to the catalytic hydroamination of activated olefins (acrylonitrile *etc.*) with cationic palladium amine complexes has been reported very recently [5]. These systems, however, failed to catalyse the hydroamination of simple unfunctionalized olefins.

Formation of a molecule containing the moiety H–C–C–NR₂ can occur by reductive elimination from either an amido(alkyl)metal complex $\text{L}_n\text{M}(\text{C}-\text{CH})(\text{NR}_2)$ or an aminoalkyl(hydrido)metal $\text{L}_n\text{M}(\text{H})(\text{C}-\text{C}-\text{NR}_2)$ species. In both cases, these intermediate alkylmetal complexes may be generated from $\text{L}_n\text{M}(\text{H})(\text{NR}_2)$ derivatives of transition metals able to coordinate olefins. The crucial step is thus the formation of the metal–nitrogen bond. Casalnuovo *et al.* [6] recently demonstrated the oxidative addition of aniline with some electron-rich Ir^I complexes and further developed a catalytic system for the hydroamination of norbornene with aniline [6].

Formation of an H–C–C–NR₂-containing molecule can also conceivably occur by *in-situ* aminolysis of an aminoalkyl derivative $\text{L}_n\text{M}(\text{C}-\text{C}-\text{NR}_2)$ [7]:

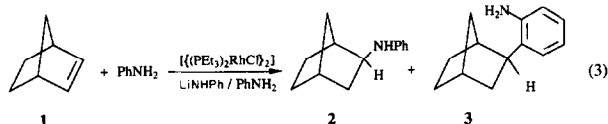


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A different catalytic process can thus be considered, which does not involve *per se* an N–H oxidative addition, provided that the transition metal amide L_nM-NR_2 can insert the olefin into the metal–nitrogen bond. Marks and coworkers [8] have recently developed an efficient organolanthanide-catalysed hydroamination–cyclization of α,ω -aminoalkenes based on the same principle.

Amides of the late transition metals are known. They are usually prepared by reaction of a lithium amide with a transition metal halide [7]. In the case of rhodium, however, the only isolated and well-characterized amido complex is the unstable $[(PPh_3)_2Rh\{N(SiMe_3)_2\}]$ [9]. We recently studied the reaction of $LiNPh$ with the Wilkinson and related $Rh(I)$ complexes. No stable anilidorhodium complex could be isolated, but solution-stable anionic anilidorhodium species were generated [10].

The study of the reactivity of these systems towards norbornene, chosen for the purpose of comparison with the results of Casalnuovo *et al.* [6], led us recently to briefly report an unexpected reaction which affords a mixture of hydroamination and hydroarylation products [11]:



We wish to report here full details of that reaction, together with further results obtained with toluidines and diphenylamine.

2. Results and discussion

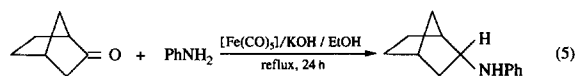
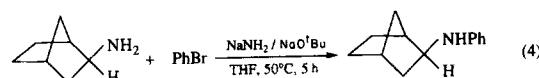
The first experiments were conducted in tetrahydrofuran (THF) which was the solvent used for the study of the reaction of $LiNPh$ with the Wilkinson complex [10]. The principle of the reactions reported below is the reaction of Li^tBu at $-10^\circ C$ with a mixture of aniline and a chloro(phosphine)rhodium(I) complex in THF to generate an anilidorhodium species. This procedure has been shown (nuclear magnetic resonance (NMR)) to generate the same species as when $LiNPh$ is added to a solution of aniline and the chloro(phosphine)rhodium(I) complex in THF [10]. Norbornene is then added at room temperature and the reaction mixture heated at reflux with stirring.

Exploratory experiments conducted with 1.3 equivalents of Li^tBu , ten equivalents of aniline and 55 equivalents of norbornene (per Rh) did not promote conversion of norbornene after 6 days in refluxing THF. This result showed that the anilidorhodium species, generated with this $LiNPh:Rh$ ratio and analysed (NMR)

as a $[(PPh_3)_2Rh(NHPh)]_2$ [10], is inactive for the condensation of aniline with norbornene. On the contrary, using a Li^tBu :aniline:Rh ratio of 5:10:1 allowed the slow formation of two products (gas chromatography (GC) analysis) **2** and **3** (about 30:70 ratio) which correspond to 1:1 adducts of aniline with norbornene (GC–mass spectroscopy (MS) analysis, $m/z = 187$).

As the conversion of norbornene appeared low, we were first led to perform control experiments. After 6 days in refluxing THF, a mixture of $LiNHPh$, $PhNH_2$ and norbornene (1:1:11 molar ratio) did not give condensation products. Similarly, the reaction of $PhNH_2$ with norbornene in the presence of $[(PPh_3)_3RhCl]$ (2:11:1 molar ratio) did not lead to condensation products after 6 days in refluxing THF. It thus appeared that the formation of **2** and **3** requires all the reagents. Study of the reaction medium prepared under these conditions indicated the formation of an unique solution-stable anionic anilidorhodium species for which the formula $Li[(PPh_3)_2Rh(NHPh)]_2$ has been proposed on the basis of ^{31}P and ^{103}Rh NMR analysis [10].

Although the molecular peaks were the same for **2** and **3**, the fragmentation patterns were clearly different (*vide infra*). In order to compare their GC retention times and mass spectra with those of authentic samples of the expected products, the isomeric *exo*- and *endo*-2-phenylaminonorbornanes were prepared according to the following equations [12,13] and characterized by IR, NMR (1H and ^{13}C) and mass spectroscopy (see Section 4):

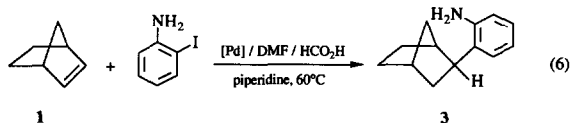


However, under the conditions used, the GC retention times of *exo*- and *endo*-2-phenylaminonorbornanes are the same. Their mass spectra are also quite similar and correspond to those obtained for **2**. It was thus obvious that **2** was one of the isomeric 2-phenylaminonorbornanes (or a mixture of both) whereas **3** corresponded to another structure.

The reaction products **2** and **3** were separated by liquid chromatography, and **2** was definitively identified as pure *exo*-2-phenylaminonorbornane.

The IR spectrum of **3** exhibited the characteristic $\nu(N-H)$ bands of a primary aromatic amine (3468 and 3379 cm^{-1}). Comparison of its 1H NMR spectrum (aromatic region) with those of *o*-, *m*-, and *p*-toluidines clearly indicated the structure of an *ortho*-sub-

stituted aniline. Two-dimensional (^1H and ^{13}C) NMR experiments in C_6D_6 at 250 MHz did not allow us to determine the stereochemistry at C(2). However, a ^1H NMR spectrum at 500 MHz indicated that benzylic hydrogen atom H(2) gives rise to an AB spectrum with coupling constants ($J = 5.3$ and 8.5 Hz) characteristic of an *exo* configuration [14]. The formula of **3** was definitively ascertained by comparison of its spectroscopic characteristics with those of an authentic sample of *exo*-2-(2'-aminophenyl) norbornane prepared by the palladium-catalysed condensation of 2-iodoaniline with norbornene [14] (see Section 4):



It must be noted that GC–MS is a very useful technique for differentiating between **2** and **3**. Indeed, the fragmentation pattern of **2** corresponds to that of an *N*-alkylaniline whereas the fragmentation pattern of **3** corresponds to that of alkylbenzenes.

Under the conditions used (*vide supra*), the overall yield was 10% *vs.* Rh after 6 days in refluxing THF. In order to improve the reactivity of the rhodium system, the influence of the natures of the (phosphine)_n-rhodium(I) precursor, of the phosphine and of the solvent were investigated.

It was first decided to examine the reactivity of the system generated from the dinuclear complex $[(\text{PPh}_3)_2\text{RhCl}]_2$ instead of $[(\text{PPh}_3)_3\text{RhCl}]$. Indeed, the system generated from the latter always contains one equivalent of dissociated triphenylphosphine [10] which

could interfere in the reaction, as shown by Casalnuovo *et al.* [6]. Indeed, these workers demonstrated that the intermediate azairidacyclobutane formed by reaction of norbornene with $[(\text{PEt}_3)_2\text{Ir}(\text{H})(\text{Cl})(\text{NHPh})]$ is decomposed on reaction with triethylphosphine and regenerates norbornene nearly quantitatively.

When norbornene (27.5 mmol) was allowed to react with the system generated from LiNHPh (2.5 mmol), PhNH₂ (2.5 mmol) and $[(\text{PPh}_3)_2\text{RhCl}]_2$ (0.25 mmol) for 6 days in refluxing THF, the overall yield of **2** + **3** reached 20% *vs.* Rh only (**2**:**3** $\approx$ 30:70).

The same trend was observed with complexes bearing triethylphosphine. Starting from $[(\text{PEt}_3)_3\text{RhCl}]$ gave a 20% overall yield *vs.* Rh while a 90% yield *vs.* Rh was obtained when using $[(\text{PEt}_3)_2\text{RhCl}]_2$. On the contrary, only traces of **2** and **3** were detected when $[(\text{PCy}_3)_2\text{RhCl}]_2$, $[(\text{dmpe})\text{RhCl}]_2$ or $[(\text{C}_8\text{H}_{14})_2\text{RhCl}]_2$ were used. Further experiments also indicated that changing the molar LiNHPh:PhNH₂: $[(\text{PEt}_3)_2\text{RhCl}]_2$:norbornene ratios from 5:5:0.5:55 to 10:5:0.5:55 or 5:5:0.5:110 gave similar results. In no case could a catalytic reaction be observed during 6 days in refluxing THF.

Nevertheless, the most active system detected so far (from $[(\text{PEt}_3)_2\text{RhCl}]_2$) was tested for the condensation of *o*-, *m*- and *p*-toluidines with norbornene in THF. In each case condensation products were formed but, depending on the toluidine used, the ratios of hydroamination to hydroarylation products were different (Table 1).

For *p*-toluidine, the reaction products were isolated and fully characterized by IR, NMR and mass spectroscopies. For the two other toluidines, the reaction

TABLE 1. Rhodium-promoted condensation of toluidines with norbornene ^{a,b}

ArNH ₂	Products (yield <i>vs.</i> Rh (selectivity))
	+ 95% (10:90)
	+ 50% (40:60)
	50% (0:100)

^a Reactions conducted for 7 days in refluxing THF with $[(\text{PEt}_3)_2\text{RhCl}]_2$ as rhodium precursor.

^b LiNHAr:ArNH₂: $[(\text{Et}_3\text{P})_2\text{RhCl}]_2$:norbornene = 2.5:2.5:0.25:27.5 mmol; THF, 20 ml.

TABLE 2. Influence of the nature of the solvent for the condensation of aniline with norbornene ^a

Solvent	(2+3) yield (% vs. Rh)
THF ^b	90
1,2-Dimethoxy ethane ^b	70
Toluene ^b	110
Aniline ^c	850 ^d

^a Reactions conducted for 7 days at 70°C with $[(\text{PEt}_3)_2\text{RhCl}]_2$ as rhodium precursor in 20 ml of solvent.

^b $\text{LiNHAr}:\text{ArNH}_2:[(\text{PEt}_3)_2\text{RhCl}]_2:\text{norbornene} = 2.5:2.5:0.25:27.5$ mmol.

^c $\text{LiNHAr}:[(\text{PEt}_3)_2\text{RhCl}]_2:\text{norbornene} = 2.5:0.25:27.5$ mmol.

^d That is a 16% yield *vs.* norbornene.

products were identified on the basis of their mass spectra obtained through GC-MS.

Further experiments on the influence of the solvent showed us that the amine itself is by far superior to other classical solvents, as exemplified by the condensation of aniline with norbornene in various solvents (Table 2). Under these conditions, the reaction is slow but truly catalytic with respect to both lithium and rhodium. The 2:3 ratio is unaffected by the change of solvent and always remains at approximately 30:70.

The influence of the reaction temperature was also briefly studied for the condensation of aniline with norbornene in aniline. Increasing the temperature to 110°C increased the yield (1250%). However, higher temperatures (130°C) resulted in a decreased yield (700%), probably because of some decomposition of the catalytic system.

Although the reaction proved to be slow at 70°C, the overall turn-over frequency is comparable with that reported for the hydroamination of norbornene with aniline in THF with the iridium catalyst cited above [6]. Moreover, no deactivation of the system was observed after 20 days, leading to more than 30 turn-overs, *i.e.* a 55% yield *vs.* norbornene (Fig. 1).

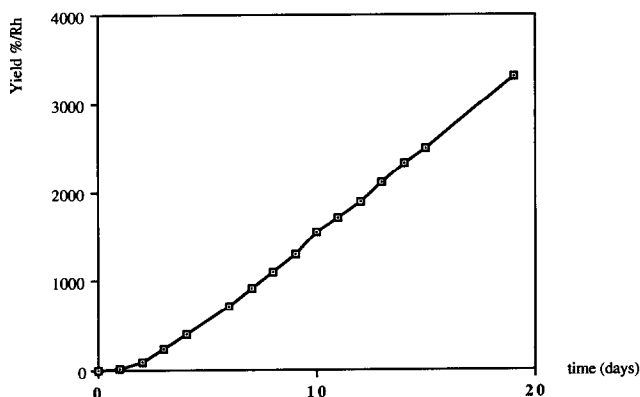
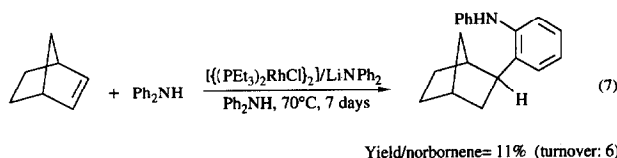


Fig. 1. Reaction yield for the condensation of aniline with norbornene in aniline as solvent.

The procedure used for aniline was also tested for a secondary aromatic amine, diphenylamine. In that case, the following reaction led only to the hydroarylation product:



Based on NMR data (see Section 4), this condensation product was shown to exhibit the *exo* configuration, as does the hydroarylation product of norbornene with aniline.

The amidorhodium systems tested in this study thus allow the condensation of aniline, toluidines and diphenylamine with norbornene. In most cases, the reaction leads to a mixture of hydroamination and hydroarylation products. The hydroarylation product is always the major product and, in two cases, it is the only product formed.

To the best of our knowledge, this unexpected hydroarylation reaction is only preceded by the *ortho* alkylation of aniline with ethylene in the presence of either granulated aluminium or aluminium anilide under forcing conditions (*e.g.* 170 bar and 300°C) [15,16].

3. Mechanistic considerations

The considerations below concern the condensation of aniline with norbornene to produce both an hydroamination product 2 and an hydroarylation product 3.

³¹P NMR monitoring of catalytic runs never allowed us to observe any (phosphine)rhodium complex other than the anilidorhodium species generated before adding norbornene and believed to be $\text{Li}[(\text{PEt}_3)_2\text{Rh}(\text{NHPH})_2]$ [10].

In fact, the only clear information is that no isomerization of 2 to 3 (and vice versa) occurs when each of them, taken separately, is treated with the system generated from $[(\text{PEt}_3)_2\text{RhCl}]_2$ and LiNHPH (five equivalents per Rh) under the usual reaction conditions.

The mechanistic proposal can thus only be related to that proposed by Casalnuovo *et al.* [6] for the iridium-catalysed condensation of aniline on norbornene, a reaction which has been demonstrated to occur via an azairidacyclobutane complex (Fig. 2).

This last $18e^-$ complex could be isolated because reductive elimination leading to 2-phenylaminonorbornene is difficult [6]. In fact, the catalytic reaction must be conducted in the presence of a Lewis acid (ZnCl_2) which is supposed to generate a coordinatively unsaturated $16e^-$ complex from which the reductive elimination can occur [6].

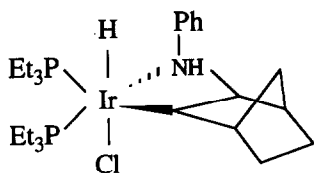


Fig. 2. Aziridacyclobutane complex occurring in iridium-catalysed condensation of aniline on norbornene.

In our case, the reductive elimination occurs spontaneously, an observation which can be accounted for by the hypothesis that the intermediate azarhodacyclobutane is an unsaturated $16e^-$ complex and, in turn, that the active species is a $14e^-$ complex (Scheme 1).

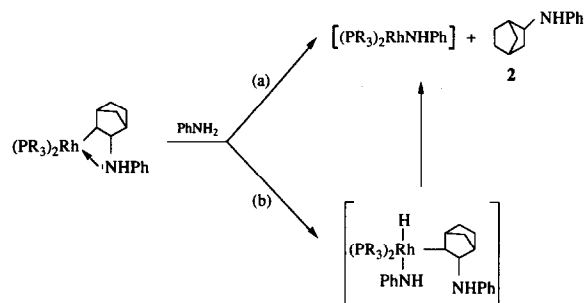
Formation of 2-phenylaminonorbornene (**2**) from the $16e^-$ -metallacyclic intermediate could then occur (Scheme 2) either by aminolysis of the rhodium–carbon bond (path (a)) or by reductive elimination after oxidative addition of aniline on the rhodium centre (path (b)).

It thus appears that there are some mechanistic differences between the iridium- and rhodium-based systems for the hydroamination of norbornene with aniline to give **2**.

However, the most striking difference between these two systems is that the rhodium-based one simultaneously and predominantly leads to an hydroarylation product, **3**, the formation of which involves an orthoalkylation.

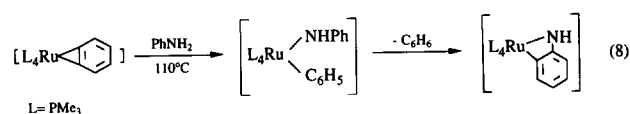
The first hypothesis would be to consider the direct formation of a (2-aminophenyl)rhodium species by reaction of an ortholithiated aniline with the rhodium(I) precursor. This is very unlikely. Indeed, whereas *N,N*-dialkylanilines are known to be *ortho* lithiated under the action of alkylolithiums, no example is known for aniline itself [17].

The more probable reaction pathway thus involves an orthometallation from an anilidorhodium species. The orthometallation process is well documented in the case of transition metal-coordination triarylphosphines (see for example ref. 18). In the case of anilido ligands, however, only two cases have been reported so far [19,20]. For example, the reaction of aniline with

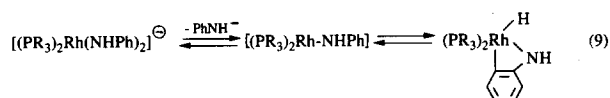


Scheme 2.

$[(PMe_3)_4Ru(\eta^2\text{-benzyne})]$ has been shown to produce an azaruthenabenzocyclobutane [20]:

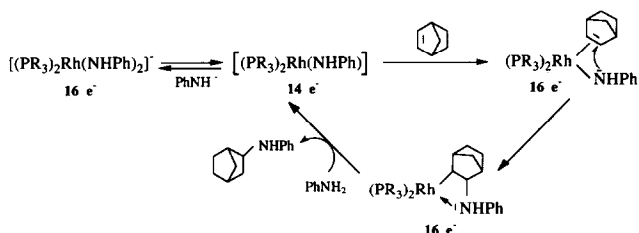


On the basis of the data in the literature, it can be postulated that the formation of **3** involves an orthometallation of the anilido ligand:

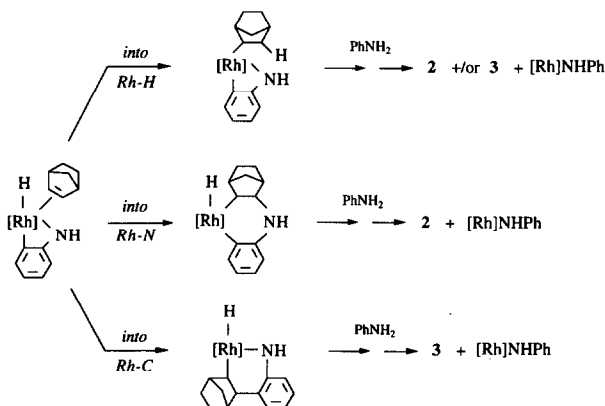


However, since no change was observed in the ^{31}P NMR spectra registered during the reaction, it must be concluded either that eqn. (9) is strongly shifted to the left and further reaction of the metallacycle with norbornene is very fast, or that the orthometallation occurs only after coordination of norbornene to the rhodium, this being the rate-determining step.

The postulated (norbornene)azarhodabenzocyclobutane could then evolve by insertion of the coordinated norbornene into the Rh–H, Rh–N or Rh–C bonds (Scheme 3).

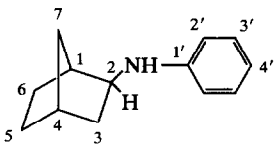


Scheme 1.



Scheme 3. The phosphine ligands have been omitted for clarity.

Data in the literature indicate that, for transition metals M, the relative bond strengths decrease in the order $M-Ph \approx M-H > M-N$ [21]. Insertion into the Rh–NPh bond is thus probably the easiest, consistent with the results of Cowan and Trogler [22] and Casanuovo *et al.* [6] who found that olefins insert into the Pt–NPh and Ir–NPh bonds of (hydrido)(anilido) complexes $[(PEt_3)_2Pt(H)(NPh)]$ and $[(PEt_3)_2Ir(H)(NPh)(Cl)]$ respectively.

TABLE 3. Data for *exo*-2-phenylaminonorbornane


	C (%)	H (%)	N (%)
Analysis, found	83.79	9.36	7.41
Analysis, C ₁₃ H ₁₇ N calculated	83.37	9.15	7.48

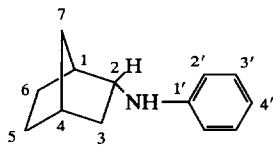
IR (neat); $\nu(N-H)$ (cm⁻¹)
3408

¹H NMR (250 MHz, CDCl₃)

δ (ppm)	Multiplicity	Integration	J (H–H) (Hz)	Assignment
7.14	ddm	2H	7.3; 8.5	H(3')
6.65	tm	1H	7.3	H(4')
6.58	dm	2H	8.5	H(2')
3.7	s (br)	1H	–	NH
3.22	ddd	1H	7.6; 2.5; 1	H(2)
2.27	s (br)	2H	–	H(1,4)
1.82	ddd	1H	12.7; 7.6; 2.4	H(3) <i>endo</i>
1.10–1.75	m	7H	–	H(5,6,7) H(3) <i>exo</i>

¹³C NMR (62.89 MHz, CDCl₃)

δ (ppm) ^a	Multiplicity ^b	J (C–H) (Hz) ^b	Assignment
147.6	m		C(1')
129.1	dd	157; 8	C(3')
116.9	dt	160; 7	C(4')
113.1	dt	155; 7	C(2')
56.6	d	140	C(2)
41.2	d	140	C(1)
41.1	t	125	C(3)
35.6	d	140	C(4)
35.3	t	130	C(7)
28.2	t (br)	135	C(5)
26.4	t	130	C(6)

MS (EI, 70 eV); m/z 187 (M⁺, 76%), 158 (23%), 132 (44%), 119 (77%), 106 (57%), 93 (100%), 77 (47%), 67 (29%)^a ¹³C{¹H} NMR.^b ¹³C NMR.TABLE 4. Data for *endo*-2-phenylaminonorbornane


	C (%)	H (%)	N (%)
Analysis, found	83.45	9.40	7.41
Analysis, C ₁₃ H ₁₇ N calculated	83.37	9.15	7.48

IR (neat); $\nu(N-H)$ (cm⁻¹)
3370

¹H NMR (250 MHz, CDCl₃)

δ (ppm)	Multiplicity	Integration	J (H–H) (Hz)	Assignment
7.26	ddm	2H	7.3; 8.6	H(3')
6.7	tm	1H	7.3	H(4')
6.70	dm	2H	8.6	H(2')
3.9	s (br)	1H	–	NH
3.77	dm	1H	10	H(2)
2.60	s (br)	1H	–	H(1)
2.35	s (br)	1H	–	H(4)
2.15–2.30	m	1H	–	H(3) <i>exo</i>
1.25–1.85	m	6H	–	H(5,6,7)
0.8	ddd	1H	12.5; 4.5; 2.9	H(3) <i>endo</i>

¹³C NMR (62.89 MHz, CDCl₃)

δ (ppm) ^a	Multiplicity ^b	J (C–H) (Hz) ^b	Assignment
148.2	t	8	C(1')
129.1	dd	157; 8	C(3')
116.8	dt	160; 7	C(4')
112.9	dt	155; 7	C(2')
54.6	dm	140	C(2)
39.7	dm	140	C(1)
38.8	tm	125	C(3)
38.1	tm	130	C(7)
36.7	dm	135	C(4)
29.9	tm	135	C(5)
21.1	tm	130	C(6)

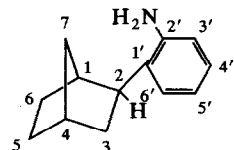
MS (EI, 70 eV); m/z 187 (M⁺, 55%), 158 (20%), 132 (38%), 119 (76%), 106 (64%), 93 (100%), 77 (48%), 67 (21%)^a ¹³C{¹H} NMR.^b ¹³C NMR.

However, insertion into the Rh–N bond (Scheme 3) cannot account for the formation of **3**. Insertion into the Rh–H or Rh–Ph bonds (or both) must be considered. Moreover, since **3** (and related hydroarylation products obtained from toluidines or diphenylamine) is always the major product, it appears that the orientation of the reaction is determined by factors other than the bond strengths.

4. Experimental details

4.1. General procedures

All reactions were conducted under argon (argon U, L'Air Liquide) using Schlenk tube and vacuum line techniques. Reactions conducted at temperatures

TABLE 5. Data for *exo*-2-(2'-aminophenyl)norbornane


	C (%)	H (%)	N (%)
Analysis, found	83.20	9.30	7.23
Analysis, C ₁₃ H ₁₇ N calculated	83.37	9.15	7.48

IR (neat): $\nu(\text{N-H})$ (cm⁻¹)
3468, 3379

¹H NMR (250 MHz, C₆D₆)

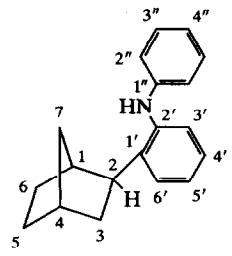
δ (ppm)	Multi-plicity	Integration	J (H-H) (Hz)	Assignment
7.21	d (br)	1H	7.6	H(6')
7.16	td	1H	7.6; 1.5	H(4')
6.92	td	1H	7.6; 1.3	H(5')
6.57	dd	1H	7.6; 1.3	H(3')
3.1	s (br)	2H	—	NH ₂
2.40–2.50	m	2H	—	H(1), H(2) <i>endo</i>
2.27	s (br)	1H	—	H(4)
1.40–1.70	m	5H	—	H(3) <i>exo</i> , H(3) <i>endo</i> H(5) <i>exo</i> , H(6) <i>exo</i> H(7) <i>syn</i>
1.20–1.30	m	2H	—	H(5) <i>endo</i> , H(6) <i>endo</i>
1.16	dm	1H	9.6	H(7) <i>anti</i>

¹³C NMR (62.89 MHz, C₆D₆)

δ (ppm) ^a	Multi-plicity ^b	J (C-H) (Hz) ^b	Assignment
145.1	pseudo-t	8	C(2')
131.6	m	—	C(1')
126.9	dd	157; 8	C(4')
125.9	dm	155	C(6')
118.7	dm	160	C(5')
116.0	dd	155; 8	C(3')
42.6	d (br)	125	C(2)
41.1	d (br)	140	C(1)
38.3	t (br)	130	C(3)
37.6	d (br)	140	C(4)
36.8	tm	125	C(7)
30.8 and 30.0	t (br)	130	C(5) and C(6)

MS (EI, 70 eV): *m/z*

187 (M⁺, 28%), 130 (17%), 119 (22%), 106 (100%), 93 (24%), 77 (18%), 39 (32%), 28 (21%).

^a ¹³C{¹H} NMR.^b ¹³C NMR.TABLE 6. Data for *exo*-2-[2'-N-(phenylamino)phenyl]norbornane


	C (%)	H (%)	N (%)
Analysis, found	86.50	8.10	5.25
Analysis, C ₁₉ H ₂₁ N calculated	86.65	8.04	5.32

IR (neat): $\nu(\text{N-H})$ (cm⁻¹)
3435

¹H NMR (250 MHz, CDCl₃)

δ (ppm)	Multi-plicity	Integration	J (H-H) (Hz)	Assignment
7.20–7.40	m	5H	—	H aromatic
7.15	td	1H	7.5; 1.6	H aromatic
6.95–7.05	m	2H	—	H aromatic
6.92	tm	1H	7.4	H aromatic
5.4	s (br)	1H	—	NH
2.80	dd	1H	8.8; 5.4	H(2)
2.53	s (br)	1H	—	H(1)
2.40	s (br)	1H	—	H(4)
1.86	ddd	1H	11.4; 8.8; 2.1	H(3) <i>endo</i>
1.50–1.80	m	4H	—	H(3) <i>exo</i> , H(5) <i>exo</i> H(6) <i>exo</i> , H(7) <i>syn</i>
1.30–1.45	m	3H	—	H(5) <i>endo</i> , H(6) <i>endo</i> H(7) <i>anti</i>

¹³C NMR (62.89 MHz, CDCl₃)

δ (ppm) ^a	Multi-plicity ^b	J (C-H) (Hz) ^b	Assignment
144.3	pseudo-t	8	C(1'')
140.7	pseudo-t	6	C(2')
137.4	s (br)	—	C(1')
129.3	dd	162; 7.5	C(3'')
126.0	dd	160; 7.5	C(4')
125.8	dm	157	C(6')
121.8	dd	160; 7.5	C(5')
120.3	dt	160; 5	C(4'')
119.5	dd	157; 7.5	C(3')
117.4	dt	157; 5	C(2'')
42.0	d (br)	135	C(2)
40.8	d (br)	140	C(1)
38.8	t (br)	132	C(3)
37.0	d (br)	140	C(4)
36.4	tm	132	C(7)
30.3	t (br)	130	C(5) or C(6)
29.1	t (br)	132	C(5) or C(6)

MS (EI, 70 eV): *m/z*

263 (M⁺, 100%), 234 (19%), 194 (19%), 182 (65%), 115 (10%), 91 (15%), 77 (16%), 55 (23%).

^a ¹³C{¹H} NMR.^b ¹³C NMR.

higher than 70°C were performed in a 100 ml 316 STI autoclave. All reagents and solvents were distilled (or recrystallized) according to classical procedures and thoroughly deaerated before use. *n*-Butyllithium (Janssen; about 1.6 M in hexane) was used after titration [23]. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was purchased from Johnson Matthey. The rhodium precursors were prepared according to, or by adaptation of, literature procedures: $[(\text{PPh}_3)_3\text{RhCl}]$ [24]; $[(\text{PEt}_3)_3\text{RhCl}]$ [25]; $[(\text{PPh}_3)_2\text{RhCl}]_2$ [25]; $[(\text{PEt}_3)_2\text{RhCl}]_2$ [25]; $[(\text{C}_8\text{H}_{14})_2\text{RhCl}]_2$ [26]. Column chromatography separations were performed on 40–60 μm silica gel (SDS).

IR spectra were recorded on a Perkin–Elmer IRFT 1725 instrument. ^{31}P , ^1H and ^{13}C NMR spectra were recorded on a Bruker WM 250 instrument. The ^1H NMR spectrum at 500 MHz was measured on a Varian Unity 500 apparatus. GC analyses were performed on a Hewlett–Packard 5890 gas chromatograph (flame ionization detector) equipped with a 50 m capillary column (OV1). Peaks areas were determined using a Spectra Physics computing integrator. GC–MS (electron impact (EI)) analyses were carried out on a Hewlett–Packard 5890 gas chromatograph coupled to a 5970 Hewlett–Packard mass-selective detector. CHN elemental analyses were performed on a Perkin–Elmer 2400 series II instrument.

The data obtained are given in Tables 3–6.

4.2. Condensation of aromatic amines with norbornene

The typical procedure is exemplified by the reaction of aniline, with norbornene in THF. Aniline (5 mmol) is added under argon to a solution of $[(\text{PEt}_3)_2\text{RhCl}]_2$ (0.25 mmol) in freshly distilled THF (15 ml). The solution is cooled to -10°C and Li^nBu (2.5 mmol) (1.6 M in hexane) is added dropwise with a syringe. After warming to room temperature, norbornene (27.5 mmol) in THF (5 ml) is added and the reaction mixture is then heated to reflux with stirring.

At the end of the reaction (see text), the reaction mixture is poured onto ice and acidified with hydrochloric acid to pH 1. The aqueous phase is washed several times with diethyl ether. Dilute sodium hydroxide is then added to the aqueous phase to pH 10, and the amines extracted with diethyl ether and dried over potassium carbonate overnight. After evaporation of the solvents, the amines are separated by column chromatography over silica with a hexane–diethyl ether (95 : 5) mixture as eluent. The amines elute in the order unreacted aniline, 3 and 2.

Acknowledgments

The authors wish to thank the Conseil Régional Midi-Pyrénées for financial support, and the Ministère de la Recherche et de la Technologie for a fellowship to K.P.

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