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Variable temperature multidimensional NMR study of anionic Rh(I) anilido $[(R_3P)_2Rh(NHPh)_2]^-$, M^+ complexes

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Abstract

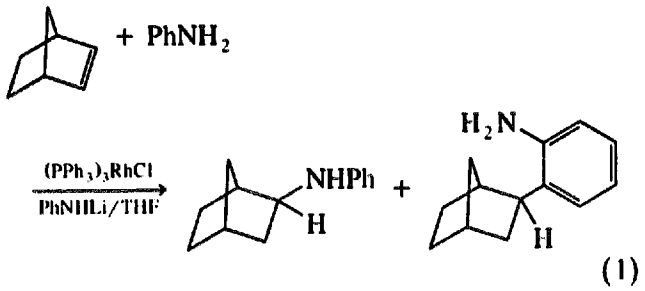
Variable temperature multidimensional NMR studies of $[(R_3P)_2Rh(NHPh)_2]^-$, Li^+ complexes enabled the detection of activation of one aromatic *ortho* proton of each anilido ligand. This activation is not attributable to a C–H_o–Rh agostic interaction, but rather to interaction with lithium, resulting from a short distance between the lithium atom and one of the aromatic *ortho* hydrogens of each anilido ligand.

Keywords: Amido rhodium(I) complexes; Phosphine complexes; Rhodates; Anilides; Hydroamination; Hydroarylation

1. Introduction

The hydroamination of alkenes is currently the focus of much interest, in particular because of its possible application in new industrial processes for the production of amines [1]. As part of our interest in this area, we recently reported the results of a study of the reactivity of in situ generated anilidorhodium species as possible catalysts for the condensation of aniline with alkenes [2,3].

In the presence of anilidorhodium species generated from $(Ph_3P)_3RhCl$ and excess PhNHLi in THF, the reaction of aniline with norbornene affords a mixture of the expected hydroamination product, and of another product which results from a hydroarylation reaction:



(1)

Similar results are obtained by generating the anilidorhodium species from $(Et_3P)_3RhCl$ and the best results in terms of turnover are obtained using aniline as solvent.

We recently investigated the nature of the complexes formed by reaction of PhNHLi with $(Ph_3P)_3RhCl$ and related rhodium(I) complexes. On the basis of extensive NMR studies, including ^1H, $^{31}P\{^1H\}$ and $^{103}Rh\{^1H\}$, we proposed that in the presence of excess PhNHLi (10 equiv.), a unique anionic rhodium complex $[(Ph_3P)_2Rh(NHPh)_2]^-$, Li^+ (1) is formed [4]. The latter complex was not isolated but is indefinitely stable (in the presence of excess PhNHLi) in refluxing THF or in a sealed tube at room temperature.

The formation of the hydroamination product (Eq. (1)) can be explained by a classical mechanism involving first coordination of the olefin to the coordinatively unsaturated rhodium center, followed by insertion into the Rh–N bond, leading to an alkylrhodium. Addition of aniline to this intermediate and subsequent elimination of the hydroamination product regenerates the anilidorhodium species as in a typical aminolysis of metal–alkyl bonds [5].

The formation of the hydroarylation product is less easy to rationalize. Since the *ortho* lithiation of aniline has never been observed [6], we tentatively proposed that a cyclometallation of the anilido ligand occurred during the reaction [3]:

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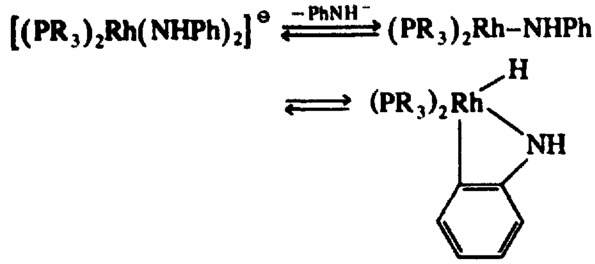

(2)

Although the cyclometallation of phenyl groups from triphenylphosphine coordinated to transition metals is well known [7], examples of cyclometallated anilido ligands are much more scarce. Nevertheless, Bergman and coworkers [8] have isolated such a complex, $(PMe_3)_4Ru(\eta^2\text{-}NHC_6H_4)$, and also report labelling experiments which strongly suggest a reversible cyclometallation of an anilide ligand on ruthenium [9]. In most cases of reversible cyclometallations, the expected agostic intermediates are not seen [10], though one variable temperature NMR study demonstrates the degenerate rearrangement between C–H ⋯ M–C and C–M ⋯ H–C in an iridium complex [11]. Since monitoring reaction (1) by ^{31}P NMR spectroscopy showed the

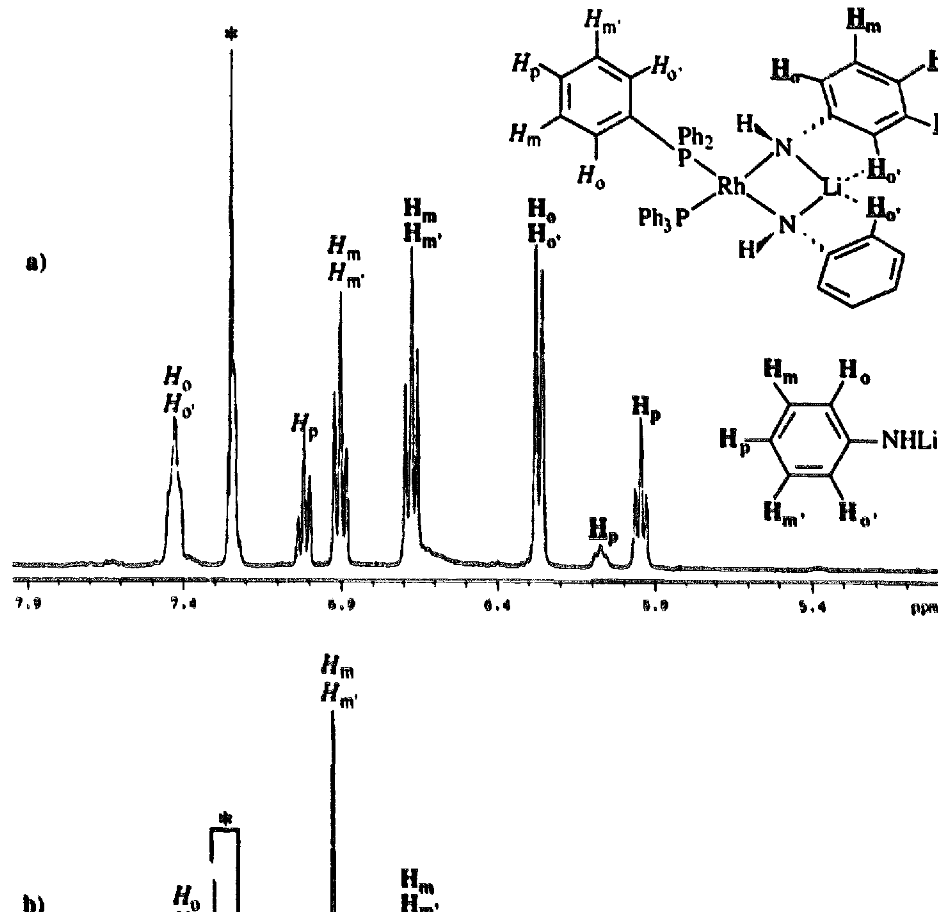

Fig. 1. 400 MHz ^{1}H NMR spectra (aromatic region) of a THF-d_8 solution of **1**: (a) at 298 K and (b) at 253 K. Assignments from 2-D (δ, δ) ^{1}H–^{1}H correlations (see text); * denotes non-coordinated PPh_3.

presence of only **1** and PPh_3, we undertook variable temperature NMR studies to probe for the possible activation of an *ortho* proton on the anilido ligands of $[(Ph_3P)_2Rh(NHPh)_2]^-$, Li^+.

2. Results and discussion

2.1. Variable temperature NMR spectroscopy of $[(Ph_3P)_2Rh(NHPh)_2]^-$, Li^+

As was previously reported, the $^{31}P\{^1H\}$ NMR spectra of a THF-d_8 solution of **1** (prepared from $(Ph_3P)_3RhCl$ with 10 equiv. PhNHLi in THF) in the presence of excess PhNHLi registered at different temperatures between 298 and 213 K showed no variation, except a very slight downfield shift ($\Delta\delta = 0.35$ ppm) of the doublet ($\delta = 55.1$ ppm at room temperature) due to **1** and a sharpening of the signal due to free PPh_3 [4].

The 400 MHz ^1H NMR spectrum of a crude solution of **1** in THF-d_8 at 298 K exhibits a complex set of signals in the aromatic proton region. Signals due to non-coordinated PPh_3 [δ (ppm) = 7.25 (m)] and to excess PhNHLi [δ (ppm) = 5.95 (t, 1H); 6.28 (d, 2H); 6.68 (t, 2H)] were identified by comparison with the spectra of authentic samples. In addition, some signals due to **1** are clearly observed [δ (ppm) = 6.08 (t); 6.90 (t); 7.02 (t); 7.42 (t)]. A 2-D (δ, δ) ^1H–^1H correlation at 298 K allowed the assignment of the three latter to the aromatic *ortho*, *meta* and *para* protons of coordinated triphenylphosphine respectively (Fig. 1(a)). The triplet at 6.08 ppm corresponds to the *para* proton on coordinated anilide while the signals of *ortho* and *meta* protons overlap with those due to excess PhNHLi.

As the temperature is lowered from 298 to 253 K, some signals (particularly those of excess lithium anilide, as verified independently) are severely broadened, while splitting of some other aromatic proton signals is observed (Fig. 1(b)) (no significant further split at lower temperatures). At 253 K, a 2-D (δ, δ) ^1H–^1H correlation (with integration) provided the following assignments for the aromatic protons of coordinated anilide, δ (ppm): H_o 5.28 (1H, d, $J = 8$ Hz); H_p 6.05 (1H, t, $J = 8$ Hz); $H_{o'}$ 7.65 (d, $J = 8$ Hz). Signals due to the *meta* protons H_m and $H_{m'}$ (δ (ppm) = 6.3 and 6.9 respectively) are partially buried beneath other signals. It is interesting to note that, at least at 253 K, the two anilido ligands are magnetically equivalent, suggesting a very symmetrical structure for **1** in solution at this temperature. It also appears that, on lowering the temperature, the two sides of the anilido ligands become inequivalent, indicating that the rotation around the Ph–NH[Rh] bonds is slow on the NMR time scale. Such a situation was previously observed for $(PMe_3)_4Ru(H)NHPh$ (at room temperature) and for the analogous aryloxy complex $(PMe_3)_4Ru(H)OC_6H_4Me$ (at low temperature) [9].

The very low chemical shift of the signal for one of the *ortho* protons (H_o δ (ppm) = 5.28) on coordinated anilide suggested the presence of an agostic H_o–Rh interaction. The other recognized criterion for agostic interactions being a significant decrease of the corresponding J_{C-H} coupling constant [12], a 2-D (δ, δ) ^{13}C–^1H correlation experiment was carried out at 193 K. Signals due to the *ortho* carbons of coordinated anilide (119.0 and 119.2 ppm) both have J_{C-H} coupling constant of 156 Hz, ruling out the possibility of an agostic interaction. The low chemical shift of the H_o anilido proton is thus suggested to be due to ring-anisotropy effects on experienced magnetic field from coordinated PPh_3. To confirm this hypothesis we carried out the same NMR study on an analogous complex containing a trialkylphosphine, $[(Et_3P)_2Rh(NHPh)_2]^-$, Li^+ (**2**), for which such magnetic field effects should not occur.

2.2. Variable temperature NMR spectroscopy of $[(Et_3P)_2Rh(NHPh)_2]^-$, Li^+

As previously reported [4], the reaction of 10 equiv. (/Rh) of PhNHLi with the dinuclear complex $[RhCl(PEt_3)_2]_2$ in THF affords **2**. This complex, however, is always contaminated by 15% of another (triethylphosphine)rhodium complex. At room temperature, the ^{31}P NMR spectrum of the THF-d_8 solution of **2** exhibits two doublets, the major one at $\delta = 38.8$ ppm ($J_{P-Rh} = 171$ Hz) corresponding to **2**, and the minor one at $\delta = 39.3$ ppm ($J_{P-Rh} = 169$ Hz). The ^{31}P NMR spectra of the above solution at different temperatures between 298 and 223 K showed no variation (approximately the same ratio of the two ^{31}P signals) but a sharpening of both doublets and a slight downfield shift ($\Delta\delta = 0.15$ ppm) of the signal of **2**.

The 400 MHz ^1H NMR spectrum of the above solution shows the coordinated anilido N–H signal at

Table 1
^1H NMR data of anilido ligands for $(R_3P)_2Rh(NHPh)_2Li$ (400 MHz, THF-d_8 at 223 K, δ (ppm))

Compound	R	H_o	H_m	H_p	$H_{m'}$	$H_{o'}$
1	Ph	5.28	6.3	6.05	6.9	7.65
2	Et	6.2	6.6	6.0	6.7	7.45

1.50 ppm and that due to excess PhNHLi at 3.15 ppm. The phosphine ethyl protons gave multiplets at 1.1 ppm (CH_3) and 1.4 ppm (CH_2), while the aromatic proton region exhibits the characteristic signals for free PhNHLi (triplet at 5.95 ppm (*para* proton), doublet at 6.28 ppm (*ortho* protons), triplet at 6.68 ppm (*meta* protons)) and some smaller signals among which is a well-defined triplet at 6.05 ppm ($J = 7.2$ Hz). At 223 K, the signals of free PhNHLi have broadened (as verified independently in a THF-d_8 solution of PhNHLi), and a doublet appeared at 7.45 ppm ($J = 7.3$ Hz) whereas the triplet at 6.05 ppm and all other small signals did not change significantly. Taking advantage of the strong broadening of the signals of excess PhNHLi, a 2-D (δ, δ) ^1H–^1H correlation at this temperature allowed unequivocal assignment of all the aromatic protons of the rhodium anilido ligands (Table 1). The triplet observed at 6.05 ppm at room temperature corresponds to the *para* proton H_p, whereas the other signals were buried beneath those of free PhNHLi. It is interesting to note that, as for **1**, the two anilido ligands appear to be equivalent, whatever the temperature, thus suggesting a very symmetrical conformation for **2**. As may be seen from Table 1, at 223 K the rotation around the RhN–Ph bond is slowed on the NMR time scale and the two sides of the anilido ligands are inequivalent. Even more interesting is that, contrary to what was observed for **1**, no aromatic signal of the rhodium anilido ligand experiences an upfield shift. This result confirms the hypothesis proposed for the upfield shift for the H_o of coordinated anilido ligands in **1** and firmly rules out the possibility of an observable agostic H_o–Rh interaction. The 2-D (δ, δ) ^1H–^1H correlation at 223 K also showed the presence of two impurities in the solution, one being free cyclo-octene (due to the preparation procedure of $[RhCl(PEt_3)_2]_2$ from $[RhCl(cyclooctene)_2]_2$) and another identified by aromatic signals at 5.6 and 6.8–7.0 ppm. These signals are present in the ^1H NMR spectra at room temperature and do not experience any shift when the temperature is lowered. Whether these signals are associated with the (triethylphosphine)rhodium side-product detected by ^{31}P NMR (vide supra) is not clear.

Examination of Table 1 also shows that for both **1** and **2** the $H_{o'}$ proton of coordinated anilido ligands is shifted downfield (at $\delta = 7.65$ ppm for **1** and $\delta = 7.45$ ppm for **2**). Such downfield shifts have many precedents in organolithium compounds and are explained by the electric field of the lithium cation which polarizes the aromatic C–H_o bonds, resulting in a reduced C–H_o bond order [13]. This has been particularly well studied for mixtures from addition of ^{t}BuLi to anisole, thioanisole or N,N-dimethylaniline at 209 K (conditions under which no lithiation occurs) [13]. The close proximity of the H_o hydrogen (and heteroatom-bonded methyl protons) to lithium has been clearly demonstrated by ^6Li–^1H two-dimensional heteroatom Overhauser effect spectroscopy (2-D HOESY). Although short ^6Li–^1H distances have been detected by 2-D HOESY with isotopes in their natural abundance (e.g. for 2-lithio-1-phenylpyrrole [14]), we did not succeed in using this method for **1** because of sensitivity and concentration problems. Unfortunately, attempts to get rid of the excess PhNHLi were unsuccessful, always leading to decomposition of **1**.

Therefore, although the above hypothesis appears the more likely, the possibility that the deshielding of the *ortho* protons of coordinated anilide in **1** is due to interaction with the excess PhNHLi was also considered.

2.3. NMR study of $[(Ph_3P)_2Rh(NHPh)_2]^-$, Na^+(TMEDA)

We studied the reaction of $(Ph_3P)_3RhCl$ with PhNHNa(TMEDA) with the hope of obtaining crystals of a sodium analogue of **1** which could be separated from the excess sodium anilide [15]. Although we did not succeed in obtaining crystals suitable for X-ray diffraction analysis, we could isolate the complex $[(Ph_3P)_2Rh(NHPh)_2]^-$, Na^+(TMEDA) (**3**) free from sodium anilide. The ^{31}P NMR spectrum (C_7D_8) exhibits the expected doublet at $\delta = 57.55$ ppm ($J = 171$ Hz). The ^1H NMR spectrum (C_7D_8) at room temperature exhibits a complex set of signals in the aromatic region, but clearly indicates the absence of excess sodium anilide. More interestingly, variable temperature ^1H NMR experiments show the same features for **3** as for **1**. At 235 K, the signal of one *ortho* anilido proton is shifted upfield ($\delta = 5.2$ ppm) whereas that of the other is shifted downfield ($\delta = 8.0$ ppm). Therefore, the deshielding experienced by one of the *ortho* protons of each anilido ligand in **1**, **2** and **3** is not due to interaction with excess lithium (or sodium) anilide, but rather to intramolecular C–H–M^+ interactions. Such interactions seem more likely than intermolecular C–H–M^+ interactions (aggregation) since the same features are observed in an electron-donor solvent, THF-d_8, for **1** and in toluene-d_8 for **3**. The above considerations suggest that the lithium (or sodium) atom is not merely a counterion, but is intrinsically involved in stabilizing these anionic complexes, a situation previously assumed for $(dtbpe)MPh_2Li(OEt)_2$ complexes (M = Rh, Ir, dtbpe = 1,2-bis(ditertiobutylphosphino)ethane) for which the aromatic *ortho* protons also exhibit high δ values (8 ppm for the Rh complex) as compared with those of the *meta* and *para* protons (6.4–6.6 ppm) [16].

The proposed solution structure of complexes **1**–**3** is shown in Fig. 2. Molecular model examination shows that the "*anti*" form can be proposed as well. This model also accounts for the shielding of the other anilido *ortho* protons in the case of **1** and **3** (R = Ph).

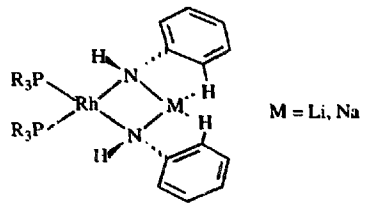

Fig. 2. Proposed solution structure for $[(R_3P)_2Rh(NHPh)_2]M$ complexes, "*syn*" form.

2.4. Conclusion

The NMR study of $[(R_3P)_2Rh(NHPh)_2]^-$, M^+ complexes has enabled the detection of activation of one aromatic *ortho* proton of each anilido ligand. This activation is not attributable to a C–H_o–Rh agostic interaction, but rather to interaction with lithium, resulting from a short distance between the lithium atom and one of the aromatic *ortho* hydrogens of each anilido ligand.

3. Experimental

3.1. General procedures and reagent syntheses

All manipulations were performed under argon using standard Schlenk and vacuum line techniques or in a Vacuum Atmospheres HE-493 workstation DRITRAIN. THF was dried and deoxygenated by distillation from sodium–benzophenone ketyl under argon. Pentane was dried and deoxygenated by distillation from P_2O_5 under nitrogen. Deuterated benzene (C_6D_6, 99.6 at.% D) and deuterated toluene (C_7D_8, 99.6 at.% D) were purchased from S. d. S and dried over 4 Å molecular sieves. The dried, deuterated solvents were then degassed using three "freeze–pump–thaw" cycles. Deuterated THF was purchased from S. d. S. and used without further purification.

$(Ph_3P)_3RhCl$ and $[(Et_3P)_2Rh](\mu\text{-}Cl)]_2$ were prepared by standard literature methods [17,18]. Aniline (Janssen Chimica) was dried by refluxing over calcium hydride overnight and distilled under partial vacuum. ^{n}Butyllithium (1.6 M in hexane) (Janssen Chimica) was used after titration [19]. NaH (60% dispersion in oil) was purchased from Aldrich. TMEDA (Aldrich) was predried over 4 Å sieves and distilled from sodium immediately prior to use.

^{1}H NMR spectra were recorded on Bruker AC-200, Bruker WM-250, or Bruker AMX-400 spectrometers. With benzene-d_6 as solvent the spectra were referenced to C_6D_5H at 7.15 ppm, with toluene-d_8 to the CD_2H residual proton at 2.09 ppm and with THF-d_8 to the OCH_2 signal at 3.6 ppm. $^{31}P\{^1H\}$ NMR spectra were recorded at 81.015 MHz on the Bruker AC-200, 101.25 MHz on the Bruker WM-250, and 151.8709 MHz on the Bruker AMX-400, and were referenced to external $P(OMe)_3$ at +141.0 ppm relative to 85% H_3PO_4 or to external H_3PO_4 in D_2O.

3.2. Generation of anilidorhodium complexes 1 and 2

Lithium anilide (10 equiv./Rh), prepared in situ from aniline in THF (5 ml) and ^{n}BuLi in hexane, was added by canula to a THF solution (10 ml) of the rhodium complex (0.5 mmol in Rh), and cooled to −10°C. The mixture was allowed to return to room temperature, by which time the original dark red colour had changed to a light orange. NMR samples were prepared by placing 1 ml portions of the mixture in a small Schlenk tube and removing the solvent under vacuum, followed by the addition of the appropriate deuterated solvent to the residues.

3.3. Preparation of $[(Ph_3P)_2Rh(NHPh)_2]^-$, Na^+-(TMEDA) (3)

NaNHPh was prepared from NaH and aniline in THF (10 ml). TMEDA (1 equiv.) was added to the anilide solution to complex the sodium ion before addition of this solution by canula to a cooled THF solution of $(Ph_3P)_3RhCl$, as described above. After the solution warmed to room temperature (light orange colour) the solution was stirred for a further 30 min before the solvent was removed under vacuum. The yellow–orange residues were extracted with 20 ml of pentane, the resulting yellow solution being filtered through Celite and concentrated slightly. Slightly waxy yellow crystals were obtained from cooling this solution. The product is extremely air-sensitive and labile towards loss of NaNHPh · TMEDA in solution, which prevented accurate yields being recorded.

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