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Formation of Stable Rhodium η⁶-Arene Complexes with Aniline Derivatives

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Abstract. Three new, hitherto unknown, rhodium complexes with aniline and two of its derivatives (2,6-dimethylaniline and *N*-methylaniline) are presented. All complexes have been characterized by X-ray analysis.

Introduction

The use of Lewis bases like triethylamine as additives in combination with rhodium diphosphine complexes in asymmetric catalysis leads to inactive rhodium trinuclear species. These complexes are well known: they are highly stable and their formation probably takes place in a reversible consecutive reaction from the solvate complex [Rh(PP*)(solvent)$_2$]Anion (PP* = chelating diphosphine) and a Lewis base to give a μ_2-bridged dimer intermediate such as [Rh$_2$(PP*)$_2$(μ_2-Base)$_2$] which then evolves into a μ_3-bridged trimer [Rh$_3$(PP*)$_3$(μ_3-Base)$_2$]BF$_4$.[1,2] In a preceding equilibrium, the weaker Lewis base, e.g. MeO$^-$, is formed from the Lewis base triethylamine and the solvent MeOH which then acts as the bridging ligand.

Aniline and its derivatives are Lewis bases and therefore suitable candidates to promote the formation of such multinuclear rhodium complexes. However the interaction with solvate complexes could also lead to different species in which aniline coordinates to rhodium via the free electron pair on nitrogen or the π-electrons of the phenyl ring.

The aim of this work was to investigate the reaction of aniline, *N*-methylaniline and 2,6-dimethylaniline with solvate complexes of the type [Rh(PP*)(solvent)$_2$]BF$_4$ exemplified by the ligand DPPF (1,1′-Bis(diphenylphosphino)ferrocene) and their coordination mode to rhodium.

Results and Discussion

When a tenfold excess of 2,6-dimethylaniline is added to a solution of [Rh(DPPF)(MeOH)$_2$]BF$_4$ (0.01 mmol) in methanol (10 mL), a color change from yellow to light red takes place. ^{31}P NMR spectroscopy shows that only one species is present in solution (supp. info). By layering the solution with diethyl ether red crystals suitable for X-ray analysis are grown. The solid-state structure (Figure 1) surprisingly shows that neither the formation of a multinuclear complex takes place nor does the 2,6-dimethylaniline coordinate to rhodium via the nitrogen. Instead 2,6-dimethylaniline exclusively binds to rhodium through its phenyl ring. Similar rhodium-arene complexes with, among others, benzene and toluene, have been long known and, in some cases, characterized by X-ray analysis.[1a,3]

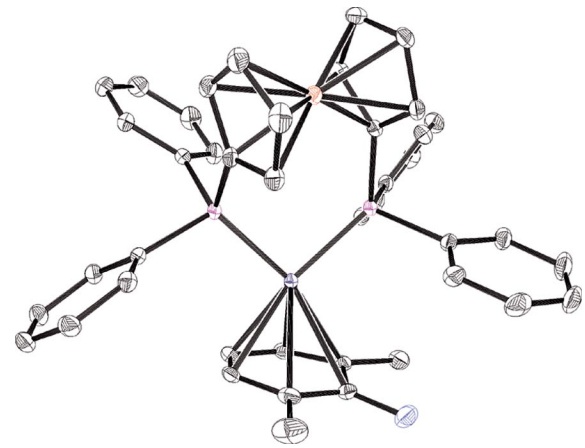

Figure 1. Molecular structure of the cation [Rh(DPPF)(2,6-dimethyl-η⁶-aniline)]BF$_4$; ORTEP, 30 % probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected distances and bond angles are summarized in Table 1. CCDC-861119.

The enantioselective hydrogenation of prochiral dehydroamino acid derivatives has been investigated for a long time both in academia and in industry. The amino group of this kind of substrates needs to be protected to prevent nitrogen coordination to rhodium and catalyst deactivation.[4] To rule out the possibility that in the case of 2,6-dimethylaniline coordination through the nitrogen was hampered by the steric hindrance of the two methyl groups thus favoring binding of the arene moiety, other substrates with a less hindered nitrogen, namely *N*-methylaniline and aniline, were tested. Indeed, even with these substrates the corresponding η⁶-arene complexes were isolated (Figure 2 and Figure 3).

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Data in Table 1 show that significant distances and angles in the three complexes are very similar.

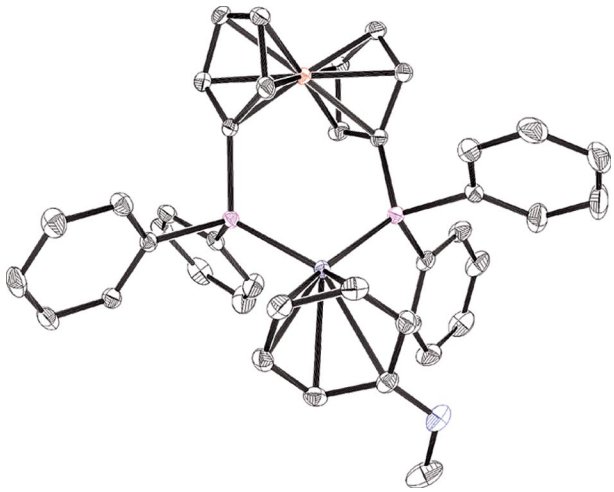

Figure 2. Molecular structure of the cation [Rh(DPPF)(*N*-methyl-η^6-aniline)]BF_4; ORTEP, 30 % probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected distances and bond angles are summarized in Table 1. CCDC-861121.

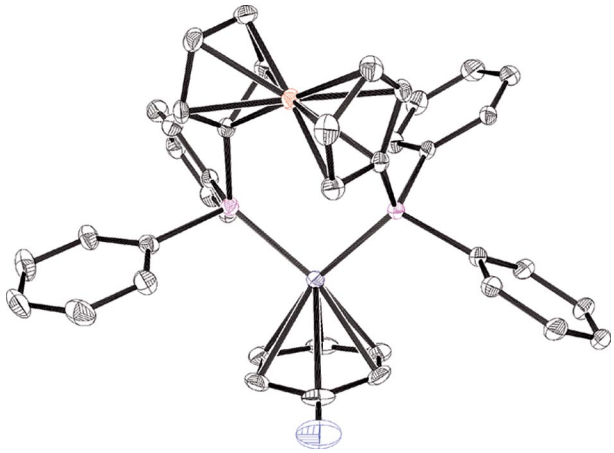

Figure 3. Molecular structure of the cation [Rh(DPPF)(aniline)]BF_4; ORTEP, 30 % probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected distances and bond angles are summarized in Table 1. CCDC-861120.

The apparent high stability of such rhodium-arene complexes and their iridium analogues might lead to deactivation phenomena in catalysis.[3,5] An example is provided by the industrial synthesis of Metolachlor. In the key step the so-called "MEA imine" ((*E*)-2-ethyl-*N*-(1-methoxypropan-2-ylidene)-6-methylaniline) is hydrogenated stereoselectively with a chiral iridium complex. The substrate is prepared by condensation of 2-ethyl-6-methylaniline (MEA) with methoxyacetone. During process optimization it has been shown that traces of MEA in the prochiral substrate load lead to a drop in the catalyst activity,[6,7] probably because of the formation of inactive (hydride ?) arene complexes.

Table 1. Selected distances /Å and bond angles /° of the isolated complexes with aniline and its derivatives.

Arene	Distance /Å Rh–P	Distance /Å Rh–η^6C	Angle /° P–Rh–P
aniline	2,230–2,254(2)	2,280–2,485(6)	95,48(5)
N-methylaniline	2,238–2,254(2)	2,260–2,522(4)	95,69; 97,22(4)
2,6-dimethylaniline	2,227–2,242(1)	2,263–2,552(3)	95,34(3)

Conclusions

In summary it has been shown that cationic rhodium diphosphine solvate complexes react with aniline and its derivatives to give stable arene complexes. X-ray structures of three such complexes containing the ligand DPPF and respectively aniline, *N*-methylaniline and 2,6-dimethylaniline are provided.

Supporting Information (see footnote on the first page of this article): ^{31}P NMR spectra of the rhodium diphosphine solvate complexes, crystallographic data, specification of data collection and structural refinement of the prepared X-Ray structures.

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