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# P-N bridged dinuclear Rh-METAMORPhos complexes: NMR and computational studies

Frederic W. Patureau,<sup>[a,b,c]</sup> Jessica Groß,<sup>[b]</sup> Jan Meine Ernsting,<sup>[a]</sup> Christoph van Wüllen,\*<sup>[b]</sup> and Joost N. H. Reek\*<sup>[a]</sup>

**Abstract:** Sulfonamido-phosphoramidites are known to form 6membered ring Rh-P-N-Rh-P-N- dinuclear complexes. Apart from a single X-ray structure, little is known about their three dimensional structure in solution. This study proposes a <sup>31</sup>P, <sup>15</sup>N and <sup>103</sup>Rh NMR investigation of the question, as a well as a DFT study. The AA'MM'XX' 6 spin system of the corresponding <sup>15</sup>N-enriched dinuclear complex is notably described.

#### Introduction

Since the ground-breaking 1865 proposition of Kekulé,<sup>[1,2]</sup> the atomic 6-membered ring structure has been found to be one of the most dominant cyclic arrangements in Nature. This arises from the relative stability of the 6-membered ring versus other ring sizes. In this study, we propose to prove: 1) that sulfonamido-phosphoramidite (METAMORPhos) ligands<sup>[3]</sup> promote a characteristic Rh-P-N-Rh-P-N- 6-membered ring organometallic dinulcear structure,<sup>[4]</sup> 2) that a strong Rh-N bond exists in solution, 3) that <sup>15</sup>N enrichment of this characteristic dinuclear complex leads to a rare AA'MM'XX' 6-spin system including <sup>31</sup>P, <sup>103</sup>Rh, and <sup>15</sup>N nuclei, in which we propose to solve the spin-spin couplings.<sup>[5]</sup> Moreover, we propose to investigate the 3D-geometries of those complexes through computational studies, and thereby investigate the possibility of several conformers/twistamers in solution.

Joining anionic phosphoramidite METAMORPhos ligand (HNEt<sub>3</sub>)(L<sup>1</sup>) together with cationic Rh<sup>1</sup> precursor Rh(nbd)<sub>2</sub>BF<sub>4</sub> leads to dinuclear complex Rh<sub>2</sub>(nbd)<sub>2</sub>(L<sup>1</sup>)<sub>2</sub> (Scheme 1, Figure 1), releasing one equivalent of (HNEt<sub>3</sub>)(BF<sub>4</sub>) salt and one nbd (norbornadiene) per Rh center. This dinuclear complex yields a characteristic AA'XX' 4-spin system in the <sup>31</sup>P NMR profile, which we originally reported in 2009.<sup>[4a]</sup> The 4-spin coupling system can be easily solved with Günther's equations.<sup>[6]</sup> In the case of L<sup>1</sup> (R = *para-n*-butyl-phenyl), J = 261 Hz, J' = -3 Hz,  $J_A = 29$  Hz and  $J_X$  is negligible. Because  $J_{PP'}$  was expected to be significantly superior to  $J_{RhRh'}$ , we originally assigned A-spins to <sup>31</sup>P and X-spins to <sup>103</sup>Rh, thus yielding the following coupling

[a]	F. W. Patureau, J. M. Ernsting, J. N. H. Reek,
	Van't Hoff Institute for Molecular Sciences, University of Amsterdam,
	Science Park 904 1098 XH Amsterdam (The Netherlands)
	E-mail: j.n.h.reek@uva.nl
[b]	F. W. Patureau, J. Groß, C. van Wüllen,
	FB Chemie, TU Kaiserslautern,

Erwin Schrödinger Strasse 52, 67663 Kaiserslautern E-Mail (DFT calculations): vanwullen@chemie.uni-kl.de

[c] Parts of this work were developed in the doctoral thesis of FWP, 2<sup>nd</sup> December 2009, University of Amsterdam, Netherlands. Current affiliation of FWP: TU Kaiserslautern.

NMR spectra, supporting information for this article is given via a link at the end of the document.

attributions:  $J_{RhP}$  = 261 Hz,  $J_{RhP'}$  = - 3 Hz,  $J_{PP'}$  = 29 Hz and  $J_{RhRh'}$  ~ 0 Hz.<sup>[7]</sup>



Scheme 1. Preparation of Rh2(nbd)2(L)2

In the case of  $L^2$  (R = CF<sub>3</sub>), which we will utilize as second METAMORPhos ligand in this study,  $J_{RhP} = 265$  Hz,  $J_{RhP'} = -3$ Hz,  $J_{PP'} = 21$  Hz. These NMR coupling constants confirm the symmetrical dinuclear disposition of Rh<sub>2</sub>(nbd)<sub>2</sub>(L<sup>1 or 2</sup>)<sub>2</sub>, but say little about the coordination mode of the dinuclear core in the organometallic complex. In particular, at this point, neither NMR nor HRMS distinguishes µ-P,N bridging (Structure I) versus P,O bridging mode (Structure II). In 2009, early DFT calculations indicated that the µ-P,N bridging mode should be favored by approximatively 6 kcal/mol.<sup>[4a]</sup> This was confirmed in 2013 when the racemic CF3- analogue of this complex based on (HNEt<sub>3</sub>)(±L<sup>2</sup>) was successfully crystallized and characterized by X-Ray, thus demonstrating the P,N character of the ligand in a cyclic six membered ring Rh-P-N-Rh-P-N- structure.<sup>[8]</sup> This was the first direct experimental evidence for the µ-P,N bridging mode in the solid state. However, in other organometallic complexes based on METAMORPhos ligands, including Rh complexes, the P,O coordination mode was found to take place as well.<sup>[3b-c]</sup> These dinuclear complexes are not always easy to crystallize however, and in addition, solid and solutions states could greatly differ in the assembly of dinuclear complexes. Moreover, the diastereomeric effects arising from the  $C_2$ -chiral binol backbones may have unexpected influence on the dinuclear complexation mode (ie dinuclear structure I or II). We therefore propose here an NMR method in order to characterize

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those organometallic systems in solution, as well as a <sup>103Rh:500.002.2n</sup> computational investigation.



**Figure 1.** Real and simulated <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 202.3 MHz), of **Rh<sub>2</sub>(nbd)<sub>2</sub>(R-L<sup>1</sup>)<sub>2</sub>**, (AA' part),  $J_{RhP} = 261$  Hz,  $J_{RhP'} = -3$  Hz,  $J_{PP'} = 29$  Hz and  $J_{RhRh'} \approx 0$  Hz, top, and of **Rh<sub>2</sub>(nbd)<sub>2</sub>(R-L<sup>2</sup>)<sub>2</sub>**,  $J_{Rh} = 265$  Hz;  $J_{PRh'} = -3.0$  Hz;  $J_{PP'} = 21$  Hz;  $J_{RhRh'} \approx 0$  Hz, beneath, (the CF<sub>3</sub> gives a singlet in <sup>19</sup>F NMR: no significant interference with the AA'XX' 4-spin system).



#### **Results and Discussion**

When we first discovered the dinuclear complex  $Rh_2(nbd)_2(L^1)_2$ in 2009,<sup>[4a]</sup> we originally imagined it as a single most stable regioisomer. The first X-ray structure of such a dinuclear system, published in 2013,<sup>[8]</sup> comforted this idea. However, when we started to look deeper into the <sup>103</sup>Rh NMR of those species in solution, it became clear that this notion needed further investigations. An initial <sup>103</sup>Rh NMR study of dinuclear complex  $Rh_2(nbd)_2(L^1)_2$  was performed, in which we were hoping to find the XX' half spin system corresponding to the AA' part of the <sup>31</sup>P NMR (Figure 1). However, the <sup>1</sup>H-<sup>103</sup>Rh HMQC spectra of  $Rh_2(nbd)_2(L^1)_2$  revealed a more complex situation than anticipated (Figure 2).<sup>[4a, 9]</sup> In particular, it is unclear whether the projection along the <sup>103</sup>Rh axis belongs solely to a second order XX' half spin system (Figure 2), or if some additional lines are present as well.



Figure 2.  $^{1}\text{H-}^{103}\text{Rh}$  HMQC NMR experiment of  $\text{Rh}_2(\text{nbd})_2(\text{L}^1)_2$  (121.5 and 9.4 MHz respectively, top), and projection along  $^{103}\text{Rh}$  axis

Because part of the characterization difficulties in those systems arise from the second order symmetry, we had originally decided that a convenient solution could be to simplify the spin system by performing a scrambling experiment.<sup>[4a]</sup> One of the aims was to suppress the second ordered AA'XX' 4-spin system. Thus, [HNEt<sub>3</sub>][(R)-L<sup>1</sup>] can be united with inequivalent [HNEt<sub>3</sub>][(R)-L<sup>2</sup>] and Rh(nbd)<sub>2</sub>BF<sub>4</sub> in a 1:1:1 ratio. Under those conditions, one obtains an approximatively statistical mixture (~ 25:50:25) of homo1-, hetero-, and homo2- complexes:  $Rh_2(nbd)_2(L^1)_2$ , Rh<sub>2</sub>(nbd)<sub>2</sub>(L<sup>1</sup>)(L<sup>2</sup>), and Rh<sub>2</sub>(nbd)<sub>2</sub>(L<sup>2</sup>)<sub>2</sub> respectively.<sup>[4a]</sup> Therefore, in the case of the combination of (R)-L<sup>1</sup> and (R)-L<sup>2</sup>, the statistical distribution indicates that no significant sorting occurs (Figure 3). As expected, in the *hetero* combination:  $Rh_2(nbd)_2(L^1)(L^2)$ , the second order has completely disappeared and each phosphorous signal now displays a simple first order doublet of doublet ( ${}^{1}J_{P-Rh}$  and  ${}^{3}J_{P1-P2}$ , Figure 3). This interpretation is confirmed by a special <sup>31</sup>P{<sup>103</sup>Rh} NMR experiment of this

mixture, in which the latter signals become simple doublets  $({}^{3}J_{P1})$ P2), while previously second ordered homo1 and homo2 complexes  $Rh_2(nbd)_2(L^1)_2$  and  $Rh_2(nbd)_2(L^2)_2$  become, as expected, singlets. In this particular system,  ${}^{1}J_{P1or2-Rh1or2} = 268$ Hz,  ${}^{1}J_{P2or1-Rh2or1} = 258$  Hz, and finally  ${}^{3}J_{P1-P2} = 25$  Hz. We then performed a <sup>31</sup>P-<sup>103</sup>Rh HMQC experiment of the mixture. Strikingly, the first order  $Rh_2(nbd)_2(L^1)(L^2)$  complex does not display as originally anticipated a single line per Rh atom along the <sup>103</sup>Rh axis (Figure 4). Indeed, each of the two inequivalent Rh atoms in  $Rh_2(nbd)_2(L^1)(L^2)$  is in fact splitted in a least 6 individual lines, lacking any obvious symmetry. Moreover, the most outer lines are distant by at least 119 Hz, which arguably excludes any unexpected NMR coupling. This is supported by the fact that large  $^3J_{\rm Rh-Rh}$  couplings don't fit in our simulation models.  $^{[7]}$  Moreover,  $^1\rm H-^{103}Rh$  NMR couplings arising from the nbd unit are known not to exceed 4 Hz.<sup>[9]</sup> This is in good accordance with the <sup>1</sup>H NMR profiles of our  $Rh_2(nbd)_2(L)_2$ complexes, for which the largest vinylic signals don't exceed 3 to 4 Hz NMR couplings.<sup>[7]</sup>



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Figure 4. Scrambling experiment, <sup>31</sup>P-<sup>103</sup>Rh HMQC NMR experiment (121.5 and 9.4 MHz respectively, top), and zoom in on the top left pattern (beneath)

It thus seems that the <sup>31</sup>P{<sup>1</sup>H} NMR profile of Rh<sub>2</sub>(nbd)<sub>2</sub>(L<sup>1</sup>)(L<sup>2</sup>), displaying one dd for each ligand, could be in fact an average/overlap of several species. In contrast to <sup>31</sup>P, <sup>103</sup>Rh NMR benefits from a considerably larger span of chemical shifts, and is thus more sensitive to minor geometry changes. Likewise, <sup>195</sup>Pt NMR has also been found in previous studies to be very sensitive to minor geometrical changes in the coordination sphere of the metal center.<sup>[10]</sup> In the present case, several *chair*, boat and twist configurations may be envisaged, each potential

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sub-divided configuration further in twistameric and diastereomeric isomerism. Α great number of those configurations might thus potentially co-exist in solution at room temperature. This intriguing possibility, which is reminiscent of the various possible conformers of cyclohexane and its organic derivatives, called for a detailed DFT investigation. The full model minus the butyl chain of complexes  $Rh_2(nbd)_2(L^1)_2$ ,  $Rh_2(nbd)_2(L^1)(L^2)$ , and  $Rh_2(nbd)_2(L^2)_2$  were thus respectively considered, under all imaginable conformer possibility. Only homo-chiral (R)-binaphthol derived dinuclear complexes were investigated. The mixed chiral (R)/(S) case was not considered because of the self-sorting effect (Scheme 1).

All DFT calculations were originally performed in the gas-phase. It was found that the 6-membered Rh-P-N-Rh-P-N- has at least seven optimizable conformers of various energies for each dinuclear complex. Two *boat* conformers were notably found, in which the P-N lines are quasi parallel, and which differ "only" by the arrangement of the binaphhol and sulfone units (B1 and B2). A chair configuration (S) was also identified, as well as four twistamers (Twist a-d, Figure 5). Importantly, in all cases, Twist b dominates all other conformers. For Rh<sub>2</sub>(nbd)<sub>2</sub>(L<sup>2</sup>)<sub>2</sub>, Twist b dominates the next most stable conformer (Twist a) by 25 kJ/mol. In Rh<sub>2</sub>(nbd)<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>, the next most stable conformer is the boat B2, by 44 kJ/mol, and in the hetero complex Rh<sub>2</sub>(nbd)<sub>2</sub>(L<sup>1</sup>)<sub>2</sub> the next most stable conformers is the chair S by 49 kJ/mol. All energies and structures are provided in the SI. Clearly, at room temperature, the equilibrium co-existence of several regioisomers seems excluded by these gas-phase DFT calculations. We then also quantified solvent effects by a series of COSMO calculations (supporting Information, Tables S13-S15). While there is some effect on relative conformer stability, the overall picture remains unchanged, especially that Twist b is by far the most stable conformer. Noteworthy to mention, in all three



Figure 5. The seven conformers: *Boat* B1, B2, *Chair* S, Twistamers a, b, c, and d, all represented for Rh<sub>2</sub>(nbd)<sub>2</sub>(*R*-L<sup>1</sup>)<sub>2</sub>, in the gas phase.

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complexes, the most stable Twist b displays a similar Rh-Rh distance, of 3.34 Å for  $Rh_2(nbd)_2(L^1)_2$ , 3.32 Å for  $Rh_2(nbd)_2(L^2)_2$ , and of 3.31 Å for the mixed complex Rh<sub>2</sub>(nbd)<sub>2</sub>(L<sup>1</sup>)(L<sup>2</sup>). In the solid state X-ray structure of Rh<sub>2</sub>(nbd)<sub>2</sub>(L<sup>2</sup>)<sub>2</sub>, the Rh-Rh distance is 3.1460(4) Å. Again, the apparent deviation may come from comparing gas-phase (DFT) and solid state. In general, surprisingly, the contrasting electronic and steric parameters of L<sup>1</sup> (NTs) versus L<sup>2</sup> (NTf) do not seem to impact much the Rh-Rh distance nor the relative energies and structures of the various conformers (Figure 5). Likewise, the N-Rh bond, which is strategic to maintain the 6-membered ring dinuclear structure of the complex, is remarkably consistent in the most stable Twist b isomer of Rh<sub>2</sub>(nbd)<sub>2</sub>(L<sup>1</sup>)<sub>2</sub> (2.189 Å), of Rh<sub>2</sub>(nbd)<sub>2</sub>(L<sup>2</sup>)<sub>2</sub> (2.206 Å), and the X-ray structure of the latter (2.185(3) Å). For a visual comparison, we have reproduced the known X-Ray structure of Rh2(nbd)2(R-L2)2•Rh2(nbd)2(S-L2)2 and the computated most stable Twist b conformer of Rh<sub>2</sub>(nbd)<sub>2</sub>(R-L<sup>2</sup>)<sub>2</sub> in Figure 6.



Figure 6. ORTEP representation (30% probability) of the known X-ray structure of  $Rh_2(nbd)_2(R-L^2)_2 \cdot Rh_2(nbd)_2(S-L^2)_2$ , the  $Rh_2(nbd)_2(R-L^2)_2$  part is represented (CCDC-931393, top),<sup>[8]</sup> and corresponding computed optimized geometry of  $Rh_2(nbd)_2(R-L^2)_2$  in the most stable conformer *Twist* b (gas phase, bottom picture).

The reality and strength of the N-Rh bond in solution was then looked at with <sup>15</sup>N enrichment. In order to do so, a 99% <sup>15</sup>Nenriched METAMORPhos analogue of L<sup>1</sup> was prepared in two simple steps: (HNEt<sub>3</sub>)(<sup>15</sup>N-L<sup>3</sup>). The latter displays a characteristic <sup>1</sup>J<sub>P-15N</sub> = 70 Hz (Scheme 2). It should be noted that while the <sup>1</sup>J<sub>H-15N</sub> NMR coupling in <sup>15</sup>N-TsNH<sub>2</sub> is quite large, at 80 Hz, no NMR coupling could be detected between the <sup>15</sup>N of (HNEt<sub>3</sub>)(<sup>15</sup>N-L<sup>3</sup>), and the proton of the HNEt<sub>3</sub> cation. This is in good agreement with the ionic character of the phosphoramidite. (HNEt<sub>3</sub>)(<sup>15</sup>N-L<sup>3</sup>) was then united with Rh(nbd)<sub>2</sub>BF<sub>4</sub> to produce the characteristic dinuclear complex Rh<sub>2</sub>(nbd)<sub>2</sub>(<sup>15</sup>N-L<sup>3</sup>)<sub>2</sub>. The resulting <sup>31</sup>P{<sup>1</sup>H} NMR profile is presented in Figure 7, together with its corresponding simulation. By analogy with Rh<sub>2</sub>(nbd)<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>, which is electronically and sterically most similar, the following NMR coupling constants:  $J_{RhP} = 261$  Hz,  $J_{RhP'} = -3$  Hz,  $J_{PP'} = 29$  Hz and  $J_{RhRh'} = 0$  Hz can be considered unchanged. Unfortunately, the strategic <sup>1</sup>J<sub>15N-Rh</sub> does not impact the <sup>31</sup>P{<sup>1</sup>H} NMR simulation of Rh<sub>2</sub>(nbd)<sub>2</sub>(<sup>15</sup>N-L<sup>3</sup>)<sub>2</sub>. Indeed, a small (2Hz) or large value (50 Hz) yields the same profile. In other words, one cannot utilize the <sup>31</sup>P{<sup>1</sup>H} simulation to iteratively determine <sup>1</sup>J<sub>15N-Rh</sub>. On the other hand, <sup>1</sup>J<sub>15N-P</sub> could be approached by iterative <sup>31</sup>P{<sup>1</sup>H} simulations and found to be 88 Hz.



Scheme 2. Synthesis of  $(HNEt_3)({}^{15}N-L^3)$  and  $Rh_2(nbd)_2({}^{15}N-L^3)_2$ .

In order to determine the strategic  ${}^{1}J_{15N-Rh}$  coupling, another  ${}^{31}P^{-103}Rh$  HMQC experiment was conducted on  $Rh_2(nbd)_2({}^{15}N-L^3)_2$ . The resulting 2D profile is presented in Figure 7. Four large doublets are clearly visible along the  ${}^{103}Rh$  axis, each corresponding to one of the four great line packages along the  ${}^{31}P$  axis. Each  ${}^{103}Rh$ -directed doublet displays the same large coupling:  ${}^{1}J_{15N-Rh} = 30$  +/- 1 Hz. Importantly, the projection along the  ${}^{103}Rh$  axis gives approximatively the same pattern which had been observed for  $Rh_2(nbd)_2(L^1)_2$  and  $Rh_2(nbd)_2(L^1)(L^2)$ , only each line doubled by a 30 Hz coupling ( ${}^{1}J_{15N-Rh}$ ). The full spin system is represented in Scheme 3.



Scheme 3. AA'MM'XX' 6 spin system based on  $^{31}$ P,  $^{15}$ N and  $^{103}$ Rh, all none displayed NMR couplings are approximatively 0 Hz.



**Figure 7.** AA' part of AA'MM'XX' 6-spin system of  $Rh_2(nbd)_2({}^{15}N-L^3)_2$  in  ${}^{31}P{}^{1}H$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 202.3 MHz) and corresponding simulation (top), corresponding  ${}^{31}P{}^{-103}Rh$  HMQC NMR experiment (121.5 and 9.4 MHz respectively, middle down), and zoom in of the latter spectrum.

Conversely, it is mildly surprising that the  ${}^{2}J_{15N-P}$  across the Rh atom was found to be very small, less than 1 Hz. It is well known however that small coordination angles (*cis* coordination) can dramatically decrease the NMR coupling between two inequivalent  ${}^{31}P$  spins at a metal center. By extension, the rather short N-Rh-P angle (93.22(7)° in the crystal structure of

**Rh<sub>2</sub>(nbd)<sub>2</sub>(***R***-L<sup>2</sup>)<sub>2</sub>•Rh<sub>2</sub>(nbd)<sub>2</sub>(***S***-L<sup>2</sup>)<sub>2</sub>),<sup>[8]</sup> may account for a similar effect. It should be noted that the <sup>31</sup>P{<sup>1</sup>H} NMR simulation does not accommodate a <sup>2</sup>J<sub>15N-P</sub> larger than 1 Hz, above which the simulated <sup>31</sup>P{<sup>1</sup>H} profile becomes significantly more complex (more lines) than reality. In order to illustrate this point, simulations at <sup>2</sup>J<sub>15N-P</sub> = 0, 1, 2, and 5 Hz are provided in supplementary information.<sup>[7]</sup> Finally, it should be noted that <sup>2</sup>J<sub>Rh-R</sub> = 30 +/- 1 Hz. However, its value does not affect the <sup>31</sup>P{<sup>1</sup>H} NMR simulation, rendering iterative estimation impossible. The <sup>103</sup>Rh axis projections are moreover too broad for direct determination. In contrast, we can however safely say that <sup>3</sup>J<sub>15N-15N'</sub> ~ 0 Hz, as any other value significantly alters the <sup>31</sup>P{<sup>1</sup>H} NMR simulation compared to reality.** 

#### Conclusions

In conclusion, we reported here the first AA'MM'XX' 6-spin system based on <sup>31</sup>P, <sup>15</sup>N and <sup>103</sup>Rh. It is as far as we know also the first such AA'MM'XX' 6-spin system to involve a transition metal. <sup>15</sup>N-enrichment of METAMORPhos has allowed the NMR characterization of the Rh-N bond in the 6-membered ring  $Rh_2(nbd)_2(L)_2$  complex, in solution. The  ${}^1J_{15N-Rh}$  was found to be 30 Hz, which is as far as we know also one of the largest ever reported NMR coupling between <sup>15</sup>N and <sup>103</sup>Rh.<sup>[11]</sup> This relatively high value suggests the existence of a strong N-Rh bond in the <sup>103</sup>Rh NMR dinuclear complex in solution. Moreover, characterization and computational studies revealed that several conformers/twistamers are conceivable, even if Twistamer b seems to have a significant advantage over the other conformers according to those DFT studies. The interpretation of the multiple <sup>103</sup>Rh NMR lines observed for these complexes remains therefore open. In general, the characteristic dinuclear disposition of these complexes could have an impact on the development of future cooperative catalysis applications, such as asymmetric hydrogenation reactions. We hope that this study will also inspire characterization and computational solutions for other organometallic coordination problems, particularly those based on cooperative dinuclear complexes.

### **Experimental Section**

Synthetic procedures and selected characterization (for spectra, see SI). All reactions were carried out in dry glassware under argon or nitrogen atmosphere. Every solution addition or transfer was performed with syringes. All solvents were dried and distilled with standard procedures. Chromatographic purifications were performed by flash chromatography on silica gel 60-200 µm, 60 Å. Nuclear Magnetic Resonance experiments were performed either on a Varian Inova500 spectrometer (<sup>1</sup>H: 500 MHz, <sup>31</sup>P: 202.3 MHz, <sup>13</sup>C: 125.7 MHz), Varian Mercury300 (<sup>1</sup>H: 300.1 MHz, <sup>19</sup>F: 282.4 MHz, <sup>31</sup>P: 121.5 MHz), or Bruker DRX300 (<sup>1</sup>H: 300 MHz, <sup>31</sup>P: 121.5 MHz, <sup>103</sup>Rh: 9.4 MHz). All available spectra can be found in the SI.

**Rh<sub>2</sub>(nbd)<sub>2</sub>(***R***-L<sup>1</sup>)<sub>2</sub> was partly described in a previous publication.<sup>[4a]</sup> <sup>31</sup>P{<sup>1</sup>H} NMR (202.3 MHz, CDCI<sub>3</sub>, rt) δ (ppm): 95.869 (<u>AA</u>'XX' half spin system, <sup>1</sup>***J***<sub>P-Rh</sub> = 260.7 Hz; <sup>2</sup>***J***<sub>P-Rh</sub> = -2.6 Hz; <sup>3</sup>***J***<sub>P-P</sub> = 28.7 Hz; <sup>3</sup>***J***<sub>Rh-Rh</sub> ≈ 0** 

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Hz). MS (FAB<sup>+</sup>): m/z calcd. for  $C_{74}H_{66}N_2O_8P_2Rh_2S_2$  ([M]<sup>+</sup>): 1442.18; obsd.: 1442.2. <sup>31</sup>P-<sup>103</sup>Rh HMQC (121.5 and 9.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>):



**Rh<sub>2</sub>(nbd)<sub>2</sub>(***R***-L<sup>2</sup>)<sub>2</sub> was partly described in a previous publication.<sup>[4a]</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, rt) δ (ppm): <sup>31</sup>P{<sup>1</sup>H} NMR (202.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>, rt) δ (ppm):103.487 (<u>AA</u>'XX' half spin system: <sup>1</sup>J<sub>P-Rh</sub> = 264.8 Hz; <sup>2</sup>J<sub>P-Rh</sub> = -3.0 Hz; <sup>3</sup>J<sub>P-P</sub> = 21.2 Hz; <sup>3</sup>J<sub>Rh-Rh</sub> ≈ 0 Hz). <sup>19</sup>F NMR (282.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>, r.t.) δ (ppm): -75.969 (s, CF<sub>3</sub>), -148.734 (s, Et<sub>3</sub>NHBF<sub>4</sub>). MS (FAB<sup>+</sup>): m/z calcd. for C<sub>56</sub>H<sub>40</sub>F<sub>6</sub>N<sub>2</sub>O<sub>8</sub>P<sub>2</sub>Rh<sub>2</sub>S<sub>2</sub> ([M]<sup>+</sup>): 1313.97; obsd.: 1313.9. <sup>31</sup>P-<sup>103</sup>Rh HMQC (121.5 and 9.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>):** 



 $Rh_2(nbd)_2(R-L^2)_2 Rh_2(nbd)_2(S-L^2)_2$  was described in a previous publication.<sup>[8]</sup>

Rh2(nbd)2(R-L1)(R-L2): was partly described in a previous publication.[4a] ligand (R)-[Et<sub>3</sub>NH][1] (0.013 mmol, 1eq.) and (R)-[Et<sub>3</sub>NH][2] (0.013 mmol, 1eq.) were united with Rh(nbd)<sub>2</sub>BF<sub>4</sub> (0.026 mmol, 2 eq.) and dissolved in 0.6 mL of CD<sub>2</sub>Cl<sub>2</sub>, resulting in a very dark purple solution.  $^{31}\text{P}$  NMR yield: quantitative, as a statistical mixture: Rh<sub>2</sub>(nbd)<sub>2</sub>(R-L<sup>1</sup>)(R-L<sup>2</sup>)  $Rh_2(cod)_2(R-L^1)_2$  /  $Rh_2(nbd)_2(R-L^2)_2$  (50:25:25). <sup>31</sup>P{<sup>1</sup>H} NMR (202.3) MHz, 107 mM in CD<sub>2</sub>Cl<sub>2</sub>, rt) δ (ppm): Rh<sub>2</sub>(nbd)<sub>2</sub>(R-L<sup>1</sup>)(R-L<sup>2</sup>): 103.78 (dd,  ${}^{1}J_{P2-Rh2} = 268 \text{ Hz}, {}^{3}J_{P2-P1} = 25 \text{ Hz}, P^{2} \text{ of } L^{2}$ ; 93.65 (dd,  ${}^{1}J_{P1-Rh1} = 258 \text{ Hz}, {}^{3}J_{P1-P2} = 25 \text{ Hz}, P^{1} \text{ of } L^{1}$ ).  ${}^{31}P\{^{1}H, {}^{103}Rh\}$  NMR (121.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>, r.t.)  $\delta$ (ppm):  $Rh_2(nbd)_2(R-L^1)(R-L^2)$ : 103.78 (d,  ${}^{3}J_{P2-P1} = 25$  Hz), 93.65 (d, <sup>3</sup>J⊵1.  $_{P1}$  = 25 Hz), the following data had not been reported before:  $^{31}P^{-103}Rh$ HMQC (121.5 and 9.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>): main <sup>103</sup>Rh lines (9.4 MHz) of Rh<sub>2</sub>(nbd)<sub>2</sub>(R-L<sup>1</sup>)(R-L<sup>2</sup>): δ (ppm/(relative intensity)): 432.25 (0.4), 433.64 (0.35), 435.23 (0.57), 438.01 (0.72), 441.72 (0.25), 444.9 (0.12), 473.16 (0.37), 474.36 (0.32), 476.18 (0.52), 478.99 (0.76), 482.71 (0.30), 485.59 (0.14), see also Figure 4. MS (FAB<sup>+</sup>): m/z calcd. for  $C_{65}H_{53}F_3N_2O_8P_2Rh_2S_2$  ([M]<sup>+</sup>): 1378.08; obsd.: 1378.1.

Ligand (HNEt<sub>3</sub>)(<sup>15</sup>N-L<sup>3</sup>): commercially available <sup>15</sup>NH<sub>4</sub>Cl (>98%, 9.2 mmol) was exposed to 200 mL CH<sub>2</sub>Cl<sub>2</sub> together with Ts-Cl (9.2 mmol). Et<sub>3</sub>N (23 mmol) was added to it under strong magnetic stirring. The

suspension was stirred at r.t. for 1h. The solvent was evaporated. The product was dissolved in THF, filtered and evaporated. Finally the product was crystallized from CH<sub>2</sub>Cl<sub>2</sub> / Hexanes (2:3). Isolated yield: 17.5 %, white crystals: Ts- $^{15}$ NH<sub>2</sub>. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K)  $\delta$ (ppm): 7.823 (broad d  $\approx$  small second order,  ${}^{3}J = 8$  Hz, 2 aromatic H), 7.375 (broad d  $\approx$  small second order, <sup>3</sup>J = 8 Hz, 2 aromatic H), 4.933 (d,  ${}^{1}J_{H-15N} = 80$  Hz, Ts- ${}^{15}NH_{2}$ ), 2.469 (s, CH<sub>3</sub> of Ts moiety).  ${}^{13}C{}^{1}H$  NMR (125.7 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  (ppm): 144.301 (s, C<sub>quat.</sub>, CH<sub>3</sub>-<u>C</u>), 139.885 (d,  ${}^{2}J_{C-15N} = 4$  Hz,  $C_{quat}$ , <u>C</u>-SO<sub>2</sub>.<sup>15</sup>NH<sub>2</sub>), 130.262 (s, CH), 126.832 (s, CH), 21.798 (s, <u>C</u>H<sub>3</sub> of Ts- ${}^{15}$ NH<sub>2</sub>). 1.6 mmol of this compound was then dissolved in 12 mL THF and Et<sub>3</sub>N (4 mmol). A 5 mL THF solution of R-(+)-1,1'-Bi-2-naphthol-PCI (7.0 mmol, 1eq.) was added dropwise under strong magnetic stirring, leading to a suspension, which was stirred at rt overnight. The solution was then filtered and evaporated. The product was submitted to 10 mL Et<sub>2</sub>O and subsequently evaporated. The process was repeated twice. The product was then washed with 10 mL Et<sub>2</sub>O. The product was obtained as a white powder with a close to quantitative yield. <sup>31</sup>P{<sup>1</sup>H} NMR (202.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) δ (ppm): +171.9 (very broad m). <sup>31</sup>P{<sup>1</sup>H} NMR (121.5 MHz, THF unlocked, rt) approx. 174 ppm (sharp d.,  ${}^{1}J_{P-15N}$  = 70 Hz).  ${}^{1}H$  NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K)  $\delta$  (ppm): 10.2 (broad. s, NH), 8.017-6.925 (aromatic area), 2.788 (dq, q: <sup>3</sup>J<sub>Ha-CH3</sub> = 7 Hz, d: <sup>2</sup>J<sub>Ha-</sub> <sub>Hb</sub> = 14 Hz, H<sup>a</sup> of CH<sub>3</sub>-CH<sup>a</sup>H<sup>b</sup>-N), 2.498 (s, CH<sub>3</sub>-Ar) 2.482 (broad m, H<sup>b</sup> of  $CH_3-CH^aH^b-N$ , 0.827 (t,  ${}^{3}J = 7$  Hz,  $CH_3-CH^aH^b-N$ ).  ${}^{13}C{}^{1}H$  NMR (125.7) MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) δ (ppm): note: some lines are missing or overlapped, main lines: 133.37 (C<sub>quat</sub>), 131.89 (C<sub>quat</sub>), 131.19 (C<sub>quat</sub>), 130.58 (CH), 129.53 (2CH), 129.41 (CH), 129.23 (CH), 128.90 (CH), 128.69 (CH), 127.15 (CH), 126.75 (CH), 126.59 (CH), 126.47 (2CH), 125.20 (CH), 124.97 (CH), 124.57 (CH), 122.80 (CH), 45.52 (CH2 of Et<sub>3</sub>NH+), 21.70 (CH<sub>3</sub>), 8.46 (CH<sub>3</sub> of Et<sub>3</sub>NH+).

Rh2(nbd)2(15N-L3)2: ligand (HNEt3)(15N-L3) (0.10 mmol, 1eq.) was united with Rh(nbd)<sub>2</sub>BF<sub>4</sub> (0.10 mmol, 1 eq.) and dissolved in 0.6 mL of CD<sub>2</sub>Cl<sub>2</sub>, resulting in a very dark blue solution. <sup>31</sup>P NMR yield: quantitative. <sup>31</sup>P NMR characterization: see scheme 3 and Figure 6. MS (FAB<sup>+</sup>): m/z calcd. for  $C_{68}H_{54}^{15}N_2O_8P_2Rh_2S_2$ : [M]<sup>+</sup>): 1360.08; obsd.: 1360.1007. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) δ (ppm): 8.22 (d, J = 8.8 Hz, 1H), 8.10 (d, J = 8.3 Hz, 1H), 8.01 (d, J = 8.3 Hz, 1H), 7.96 (d, J = 8.8 Hz, 1H), 7.91 (d, J = 8.5 Hz, 1H), 7.8-7.1 (aromatic area), 6.78 (broad s, ~ 4H, free nbd), 6.74 (d, J = 8.1 Hz, 2H), 6.30 (~q, J ~ 3.7 Hz, 1H), 5.95 (~q, J ~ 3.7 Hz, 1H), 4.66 (s, 1H), 4.02 (s, 1H), 3.61 (s, 2H, free nbd), 3.43 (s, 1H), 3.17 (dq, <sup>3</sup>J = 7.4 Hz, <sup>3</sup>J = 5.2 Hz, 6H, CH<sub>3</sub>-C<u>H</u><sub>2</sub>-NH<sup>+</sup>), 2.58 (s, 1H), 2.20 (s, 3H, CH<sub>3</sub>-Ar), 2.00 (s, ~2H, ~free nbd), 1.50-1.30 (aliphatic area), 1.36 (t,  ${}^{3}J = 7.5$ Hz, ~9H, CH<sub>3</sub>-CH<sub>2</sub>-NH<sup>+</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.7 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) δ (ppm): note: due to the large number of lines, NMR couplings were not systematically solved, only the visible lines are given: 150.45 (Cquat), 150.33 (Cquat), 148.95 (Cquat), 142.46 (Cquat), 142.23 (Cquat), 132.87 (Cquat), 132.76 (C<sub>quat</sub>), 132.34 (C<sub>quat</sub>), 131.51 (C<sub>quat</sub>), 130.79 (CH), 130.08 (CH), 129.70 (CH), 129.52 (CH), 129.11 (2CH), 128.74 (CH), 127.42 (2CH), 127.23 (CH), 126.68 (CH), 126.53 (CH), 126.13 (CH), 125.89 (CH), 125.47 (CH), 124.19 (CH), 123.85 (C\_{quat}), 123.42 (CH), 121.83 (C\_{quat}), 97.44 (d,  ${}^{1}J_{13C-103Rh}$  = 11.0 Hz, CH), 92.14 (d,  ${}^{1}J_{13C-103Rh}$  = 14.8 Hz, CH), 65.36 (CH<sub>2</sub>, free nbd), 60.21 (d,  ${}^{1}J_{13C-103Rh}$  = 9.3 Hz, CH), 57.65 (d,  ${}^{1}J_{13C-103Rh}$ 103Rh = 8.4 Hz, CH), 52.61 (CH), 52.35 (CH), 47.65 (CH<sub>2</sub> of Et<sub>3</sub>NH<sup>+</sup>), 46-8 (aliphatic area), including: 21.6 (CH<sub>3</sub>-Ar), 9.07 (CH<sub>3</sub> of Et3NH<sup>+</sup>).

**Quantum chemical calculations:** All DFT calculations were performed in the gas-phase using the B3LYP functional<sup>[12]</sup> and the def2-TZVP<sup>[13]</sup> basis for all atoms. The rhodium atom carries a quasirelativistic effective core potential (def2-ecp) <sup>[14]</sup> replacing 28 core electrons. The D3 correction by Stefan Grimme<sup>[15]</sup> was used to account for dispersion interaction. For the sake of completeness, the dispersion contribution to relative conformer energies is documented in the supporting Information, Tables **S7-S9**. All calculations were performed with TURBOMOLE.<sup>[16]</sup> For geometry optimization steps the Berny algorithm<sup>[17]</sup> as implemented in

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Gaussian 09<sup>[18]</sup> was used, using the "external" interface of that program. This means, all energies, gradients, and force constants are calculated with TURBOMOLE, and the Gaussian program decides on which steps to take on the potential energy surface. Except in a single case (see supporting Information, Table **S6**), all minima were characterised by frequency calculations having no negative Hessian eigenvalue. To asses the importance of solvent effects on relative conformer energies, geometry optimizations have also been performed with the COSMO model <sup>[19]</sup> (see supporting Information, Tables **S13-S15**). While solvation somewhat affects the relative stability, it does not change the overall trend.

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**Keywords:** METAMORPhos • Rh dinuclear complex • cooperative catalysis • AA'MM'XX' 6 spin system • <sup>103</sup>Rh NMR

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#### Entry for the Table of Contents (Please choose one layout)

Layout 1:

# FULL PAPER

Sulfonamido-phosphoramidites are known to form 6-membered ring Rh-P-N-Rh-P-N- dinuclear complexes. Apart from a single X-ray structure, little is known about their three dimensional structure in solution. This study proposes a <sup>31</sup>P, <sup>15</sup>N and <sup>103</sup>Rh NMR investigation of the question, as a well as a DFT study. The AA'MM'XX' 6 spin system of the corresponding <sup>15</sup>Nenriched dinuclear complex is notably described.



#### **Dinuclear Complexes\***

F. W. Patureau, J. Groß, J. M. Ernsting, C. van Wüllen,\* J. N. H. Reek\*

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P-N bridged dinuclear Rh-METAMORPhos complexes: NMR and computational studies