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Dinuclear Complexes

P-N Bridged Dinuclear Rh-METAMORPhos Complexes: NMR and Computational Studies

Frederic W. Patureau,[a,b][‡] Jessica Groß,[b] Jan Meine Ernsting,[a] Christoph van Wülffen,*[b] and Joost N. H. Reek*[a]

Abstract: Sulfonamido-phosphoramidites are known to form six-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 31P, 15N and 103Rh NMR investigation of the question, as well as a DFT study. The AA′MM′XX′ 6-spin system of the corresponding 15N-enriched dinuclear complex is notably described.

Introduction

Since the ground-breaking 1865 proposition of Kekulé,[1,2] the atomic six-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 six-membered ring vs. other ring sizes. In this study, we propose to prove: 1) that sulfonamido-phosphoramidite (METAMORPhos)[3] ligands[4] promote a characteristic Rh-P-N-Rh-P-N- six-membered ring organometallic dinuclear structure,[4] 2) that a strong Rh–N bond exists in solution, 3) that 15N enrichment of this characteristic dinuclear complex leads to a rare AA′MM′XX′ 6-spin system including 31P, 103Rh, and 15N nuclei, in which we propose to solve the spin-spin couplings.[5] 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 (HNEt3)(L1) together with cationic RhI precursor Rh(nbd)2BF4 leads to dinuclear complex Rh2(nbd)2(L1)2 (Scheme 1, Figure 1), releasing one equivalent of (HNEt3)(BF4) salt and one nbd (norbornadiene) per Rh center. This dinuclear complex yields a characteristic AA′MM′XX′ 4-spin system in the 31P NMR profile, which we originally reported in 2009.[4a] The 4-spin coupling system can be easily solved with Günther’s equations.[6] In the case of L1 (R = para-n-butyl-phenyl), \( J_{RhP} = 261 \text{ Hz} \), \( J_{RhP′} = -3 \text{ Hz} \), \( J_{PP′} = 29 \text{ Hz} \) and \( J_{XX′} \) is negligible. Because \( J_{PP′} \) was expected to be significantly superior to \( J_{RhRh′} \), we originally assigned A-spins to 31P and X-spins to 103Rh, thus yielding the following coupling attributions: \( J_{RhP} = 261 \text{ Hz} \), \( J_{RhP′} = -3 \text{ Hz} \), \( J_{PP′} = 29 \text{ Hz} \) and \( J_{RhRh′} \) ca. 0 Hz.[7]

Scheme 1. Preparation of Rh2(nbd)2(L1)2.

In the case of \( L^2 \) (R = CF3), which we will utilize as second METAMORPhos ligand in this study, \( J_{RhP} = 265 \text{ Hz} \), \( J_{RhP′} = -3 \text{ Hz} \), \( J_{PP′} = 21 \text{ Hz} \). These NMR coupling constants confirm the symmetrical dinuclear disposition of \( \text{Rh}_{2}\text{nbd}_{2}(L^1 \text{ or } L^2)_{2} \), 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) vs. P,O bridging mode (Structure II). In 2009, early DFT calculations indicated that the μ-P,N bridging mode should be favored by approximately 6 kcal/mol.[4a] This was confirmed in 2013 when the racemic CF3-analogue of this complex based on \( \text{(HNEt}_{3})_{(±L^2)} \) 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. 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. 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 C₂-chiral binol backbones may have unexpected influence on the dinuclear complexation mode (i.e., dinuclear structure I or II). We therefore propose here an NMR method in order to characterize those organometallic systems in solution, as well as a computational investigation.

Results and Discussion

When we first discovered the dinuclear complex Rh₂(nbd)₂(L₁)₂ in 2009,[4a] we originally imagined it as a single most stable regioisomer. The first X-ray structure of such a dinuclear system, published in 2013,[8] comforted this idea. However, when we started to look deeper into the ¹⁰³Rh NMR of those species in solution, it became clear that this notion needed further investigations. An initial ¹⁰³Rh NMR study of dinuclear complex Rh₂(nbd)₂(L₁)₂ was performed, in which we were hoping to find the XX’ half spin system corresponding to the AA’ part of the ³¹P NMR (Figure 1). However, the ¹H-¹⁰³Rh HMQC spectra of Rh₂(nbd)₂(L₁)₂ revealed a more complex situation than anticipated (Figure 2).[4a,9] In particular, it is unclear whether the projection along the ¹⁰³Rh axis belongs solely to a second order XX’ half spin system (Figure 2), or if some additional lines are present as well.

Because parts 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.[4a] One of the aims was to suppress the second ordered AA’XX’4-spin system. Thus, [HNEt₃][R)-L₁] can be united with inequivalent [HNEt₃][R)-L₂] and Rh(nbd)₂BF₄ in a 1:1:1 ratio. Under those conditions, one obtains an approximately statistical mixture (ca. 25:50:25) of homo₁-, hetero-, and homo₂- complexes: Rh₂(nbd)₂(L₁)₂, Rh₂(nbd)₂(L₁)(L₂), and Rh₂(nbd)₂(L₂)₂ respectively.[4a] Therefore, in the case of the combination of (R)-L₁ and (R)-L₂, the statistical distribution indicates that no significant sorting occurs (Figure 3). As expected, in the hetero combination: Rh₂(nbd)₂(L₁)(L₂), the second order has completely disappeared and each phosphorus signal now displays a simple first order doublet of doublet (J₁P-Rh and J₂P₁-P₂, Figure 3). This interpretation is confirmed by a special ³¹P{¹⁰³Rh} NMR experiment of this mixture, in which the latter signals become simple dou-
blets ($^3J_{P1-P2}$), while previously second ordered homol and homor complexes $\text{Rh}_2(\text{nbd})_2(L^1)_2$ and $\text{Rh}_2(\text{nbd})_2(L^2)_2$ become, as expected, singlets. In this particular system, $^3J_{P1or2-Rh1or2} = 268 \text{ Hz}$, $^3J_{P2or1-Rh2or1} = 258 \text{ Hz}$, and finally $^3J_{P1-P2} = 25 \text{ Hz}$. We then performed a $^{31}\text{P}-^{103}\text{Rh}$ HMQC experiment of the mixture. Strikingly, the first order $\text{Rh}_2(\text{nbd})_2(L^1)(L^2)$ complex does not display as originally anticipated a single line per Rh atom along the $^{103}\text{Rh}$ axis (Figure 4). Indeed, each of the two inequivalent Rh atoms in $\text{Rh}_2(\text{nbd})_2(L^1)(L^2)$ is in fact split 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 $^3J_{\text{Rh-Rh}}$ couplings do not fit in our simulation models.[7] Moreover, $^1\text{H}-^{103}\text{Rh}$ NMR couplings arising from the nbd unit are known not to exceed 4 Hz.[9] This is in good accordance with the $^1\text{H}$ NMR profiles of our $\text{Rh}_2(\text{nbd})_2(L^2)$ complexes, for which the largest vinylic signals do not exceed 3 to 4 Hz NMR couplings.[7]

It thus seems that the $^{31}\text{P}^1(1\text{H})$ NMR profile of $\text{Rh}_2(\text{nbd})_2(L^1)(L^2)$, displaying one dd for each ligand, could be in fact an average/overlap of several species. In contrast to $^{31}\text{P}$, $^{103}\text{Rh}$ NMR benefits from a considerably larger span of chemical shifts, and is thus more sensitive to minor geometry changes. Likewise, $^{195}\text{Pt}$ NMR has also been found in previous studies to be very sensitive to minor geometrical changes in the coordination sphere of the metal center.[10] In the present case, several chair, boat and twist configurations may be envisaged, each potential configuration further sub-divided in twistameric and diastereomeric isomerism. A 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 $\text{Rh}_2(nbd)_2(L^1)_2$, $\text{Rh}_2(nbd)_2(L^1)(L^2)$, and $\text{Rh}_2(nbd)_2(L^2)_2$ 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 six-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 binaphthol and sulfone units ($\text{B}_1$ and $\text{B}_2$). A chair configuration ($\text{S}$) was also identified, as well as four twistamers ($\text{Twist a-d}$, Figure 5). Importantly, in all cases, Twist b dominates all other conformers. For $\text{Rh}_2(nbd)_2(L^1)_2$, Twist b dominates the next most stable conformer (Twist a) by 25 kJ/mol. In $\text{Rh}_2(nbd)_2(L^1)_2$, the next most stable conformer is the boat $\text{B}_2$, by 44 kJ/mol, and in the hetero complex $\text{Rh}_2(nbd)_2(L^1)_2$ the next most stable conformers is the chair $\text{S}$ by 49 kJ/mol. All energies and structures are provided in the SI. Clearly, at room temperature, the equilibrium co-existence of several regio-isomers 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 complexes, the most stable Twist b displays a similar Rh–Rh distance, of 3.34 Å for $\text{Rh}_2(nbd)_2(L^1)_2$.
Figure 6. ORTEP representation (30 % probability) of the known X-ray structure of \( \text{Rh}_2(\text{nbd})_2(\text{R-L}_2)_2 \cdot \text{Rh}_2(\text{nbd})_2(\text{S-L}_2)_2 \), the \( \text{Rh}_2(\text{nbd})_2(\text{R-L}_2)_2 \) part is represented (CCDC-931393, top),\(^8\) and corresponding computed optimized geometry of \( \text{Rh}_2(\text{nbd})_2(\text{R-L}_2)_2 \) in the most stable conformer \textit{Twist b} (gas phase, bottom picture).

Scheme 2. Synthesis of \((\text{HNEt}_3)(^{15}\text{N-L}_3)^\text{a}\) and \(\text{Rh}_2(\text{nbd})_2(^{15}\text{N-L}_2)_2\).
3.32 Å for Rh₂(nbd)L²₂, and of 3.31 Å for the mixed complex Rh₂(nbd)L₁(L²)₂. In the solid state X-ray structure of Rh₂(nbd)L²₂, 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 L₁ (NTs) vs. L² (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 six-membered ring dinuclear structure of the complex, is remarkably consistent in the most stable Twist b isomer of Rh₂(nbd)L₁(L²)₂ (2.189 Å), of Rh₂(nbd)L²₂ (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)(R–L²)₂·Rh₂(nbd)(S–L²)₂ and the computated most stable Twist b conformer of Rh₂(nbd)(R–L²)₂ in Figure 6.

The reality and strength of the N–Rh bond in solution was then looked at with ¹⁵N enrichment. In order to do so, a 99 % ¹⁵N-enriched METAMORPhos analogue of L₁ was prepared in two simple steps: (HNEt₃)(¹⁵N-L₃). The latter displays a characteristic ¹⁵N-1³¹P = 70 Hz (Scheme 2). It should be noted that while the ¹⁵N-TsNH₂ NMR coupling in ¹⁵N-TsNH₂ is quite large, at 80 Hz, no NMR coupling could be detected between the ¹⁵N of (HNEt₃)(¹⁵N-L₃) and the proton of the HNEt₃ cation. This is in good agreement with the ionic character of the phosphoramidite. (HNEt₃)(¹⁵N-L₃) was then united with Rh(nbd)₂BF₄ to produce the characteristic dinuclear complex Rh₂(nbd)(¹⁵N-L₃)₂. The resulting ³¹P{¹H} NMR profile is presented in Figure 7, together with its corresponding simulation. By analogy with Rh₂(nbd)L₁(L²)₂, which is electronically and sterically most similar, the following NMR coupling constants: ⁴J₁₃¹P⁻¹⁵N = 261 Hz, ⁴J₁₃¹P⁻¹³¹Rh = -3 Hz, ⁴J₁₃¹P⁻¹³¹Rh = 29 Hz and ⁴J₁₃¹P⁻¹³¹Rh = 0 Hz can be considered unchanged. Unfortunately, the strategic ⁴J₁₃¹N⁻¹₃¹Rh does not impact the ³¹P{¹H} NMR simulation of Rh₂(nbd)(¹⁵N-L₃)₂. Indeed, a small (2 Hz) or large value (50 Hz) yields the same profile. In other words, one cannot utilize the ³¹P{¹H} simulation to iteratively determine ⁴J₁₃¹N⁻¹₃¹Rh. On the other hand, ⁴J₁₃¹N⁻¹⁵N could be approached by iterative ³¹P{¹H} simulations and found to be 88 Hz.

In order to determine the strategic ⁴J₁₃¹N⁻¹₃¹Rh coupling, another ³¹P–¹³¹Rh HMQC experiment was conducted on Rh₂(nbd)₂⁻¹⁵N(L₁)₂. The resulting 2D profile is presented in Figure 7. Four large doublets are clearly visible along the ¹³¹Rh axis, each corresponding to one of the four great line packages along the ³¹P axis. Each ¹³¹Rh-directed doublet displays the same large coupling: ⁴J₁₃¹N⁻¹₃¹Rh = 30 +/- 1 Hz. Importantly, the projection along the ¹³¹Rh axis gives approximately the same pattern which had been observed for Rh₂(nbd)(L₁)₂ and Rh₂(nbd)(L²)₂ only each line doubled by a 30 Hz coupling (⁴J₁₃¹N⁻¹₃¹Rh). The full spin system is represented in Scheme 3.

Conversely, it is mildly surprising that the ⁴J₁₃¹N⁻¹⁵N 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 ³¹P spins at a metal center. By extension, the rather short N–Rh–P angle [93.22(7)° in the crystal structure of Rh₂(nbd)(L₁)₂·Rh₂(nbd)(S–L²)₂], may account for a similar
effect. It should be noted that the $^{31}\text{P}^{(1)}\text{H}$ NMR simulation does not accommodate a $J_{1\text{SN-P}}$ larger than 1 Hz, above which the simulated $^{31}\text{P}^{(1)}\text{H}$ profile becomes significantly more complex (more lines) than reality. In order to illustrate this point, simulations at $J_{1\text{SN-P}} = 0, 1, 2,$ and 5 Hz are provided in supplementary information. Finally, it should be noted that $J_{1\text{SN-Rh}}$ is probably small, certainly much smaller than the $J_{1\text{SN-Rh}} = 30 \pm /–1$ Hz. However, its value does not affect the $^{31}\text{P}^{(1)}\text{H}$ NMR simulation, rendering iterative estimation impossible. The $^{103}\text{Rh}$ axis projections are moreover too broad for direct determination. In contrast, we can however safely say that $J_{1\text{SN-15N}}$ ca. 0 Hz, as any other value significantly alters the $^{31}\text{P}^{(1)}\text{H}$ NMR simulation compared to reality.

Conclusions

In conclusion, we reported here the first AA’MM’XX’ 6-spin system based on $^{31}\text{P},^{15}\text{N}$ and $^{103}\text{Rh}$. It is as far as we know also the first such AA’MM’XX’ 6-spin system to involve a transition metal. $^{15}\text{N}$-enrichment of METAMORPhos has allowed the NMR characterization of the Rh–N bond in the six-membered ring Rh$_2$(nbd)$_2$(L)$_2$ complex, in solution. The $J_{1\text{SN-Rh}}$ was found to be 30 Hz, which is for the best of our knowledge also one of the largest ever reported NMR coupling between $^{15}\text{N}$ and $^{103}\text{Rh}$.[11] This relatively high value suggests the existence of a strong N–Rh bond in the dinuclear complex in solution. Moreover, $^{103}\text{Rh}$ NMR 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 $^{103}\text{Rh}$ 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 ($^{1}\text{H}$: 500 MHz, $^{31}\text{P}$: 202.3 MHz, $^{13}\text{C}$: 125.7 MHz), Varian Mercury300 ($^{1}\text{H}$: 300.1 MHz, $^{19}\text{F}$: 282.4 MHz, $^{31}\text{P}$: 121.5 MHz), or Bruker DRX300 ($^{1}\text{H}$: 300 MHz, $^{31}\text{P}$: 121.5 MHz, $^{103}\text{Rh}$: 9.4 MHz). All available spectra can be found in the SI.

Rh$_2$(nbd)$_2$(L)$_2$ The synthesis was partly described in a previous publication,[8] $^{31}\text{P}^{(1)}\text{H}$ NMR (202.3 MHz, CDCl$_3$, room temp.): $\delta = 95.869$ (AA’XX’ half spin system, $^{3}J_{P-Rh} = 280.7$, $^{3}J_{P-Rh} = –2.6$ Hz, $^{1}J_{P-P} = 28.7$, $^{3}J_{P-P} \approx 0$ Hz) ppm. MS (FAB$^+$): $m/z$ calcd. for C$_{20}$H$_{60}$N$_{4}$O$_{3}$P$_{2}$Rh$_2$S$_2$ ([M$^+$]): 1442.18; obsd.: 1442.2. $^{31}\text{P}^{(103}\text{Rh}$ HMOC (121.5 and 9.4 MHz, CD$_2$Cl$_2$):

Rh$_2$(nbd)$_2$(L)$_2$ The synthesis was partly described in a previous publication.[6] $^{31}\text{P}^{(1)}\text{H}$ NMR (500 MHz, CDCl$_3$, room temp.): $\delta = 31\text{P}^{(1)}\text{H}$ NMR (202.3 MHz, CD$_2$Cl$_2$, room temp.): $\delta = 103.487$ (AA’XX’ half spin system: $^{3}J_{P-Rh} = 264.8$ Hz, $^{3}J_{P-Rh} = –3.0$ Hz, $^{1}J_{P-P} = 21.2$ Hz, $^{3}J_{P-P} \approx 0$ Hz) ppm. $^{13}\text{C}$ NMR (282.4 MHz, CD$_2$Cl$_2$, room temp.): $\delta = –75.969$ (s, CF$_3$), –148.734 (s, Et$_3$NHBF$_4$) ppm. MS (FAB$^+$): $m/z$ calcd. for C$_{65}$H$_{53}$F$_3$N$_2$O$_8$P$_2$Rh$_2$S$_2$ ([M$^+$]): 1313.97; obsd.: 1313.9. $^{31}\text{P}^{(103}\text{Rh}$ HMOC (121.5 and 9.4 MHz, CD$_2$Cl$_2$):

Rh$_2$(nbd)$_2$(L)$_2$ The synthesis was partly described in a previous publication.[9] $^{31}\text{P}^{(1)}\text{H}$ NMR yield: quantitative, as a statistical mixture: $^{3}J_{P-Rh}$ ca. 0 Hz, as any other value significantly alters the $^{31}\text{P}^{(1)}\text{H}$ NMR simulation compared to reality.
(9.2 mmol), Et3N (23 mmol) was added to it under strong magnetic stirring. The suspension was stirred at room temp. for 1 h. The solvent was evaporated. The product was dissolved in THF, filtered, and the solvents evaporated. Finally, the product was crystallized from CH2Cl2/Hexanes (2:3). Isolated yield: 17.5 %, white crystals: Ts-15NH2.

1H NMR (500 MHz, CD2Cl2, 298 K): δ (ppm): 7.823 (broad d = small second order, J = 8 Hz, 2 aromatic H), 7.375 (broad d = small second order, J = 8 Hz, 2 aromatic H), 4.933 (d, δAr-15N = 80 Hz, Ts-15NH2), 2.469 (s, CH3 of Ts moiety). 13C{1H} NMR (125.7 MHz, CD2Cl2, 298 K): δ: 144.301 (s, Cquat), 139.885 (d, δ2C-15N = 4 Hz, Cquat), C-SO2H15N, 130.262 (s, CH), 126.832 (s, CH), 21.798 (s, CH3 of Ts-15NH2). 16 mmol of this compound was then dissolved in 12 mL of THF and Et3N (4 mmol). A 5 mL of THF solution of Rh2(nbd)2(15N-L3)2 · Density functional calculations · AA

The product was submitted to 10 mL of THF and dissolved in the solvents evaporated. The product was crystallized from CH2Cl2/Hexanes (2:3). Isolated yield: 17.5 %, white crystals: Ts-15NH2.

The solution was then filtered and evaporated. The product was then washed with 10 mL of Et2O and subsequently evaporated. The process was repeated twice.

The product was obtained as a white powder with a close to quantitative yield. 31P{1H} NMR (202.3 MHz, CD2Cl2, 298 K): δ: +171.9 (very broad m).

13C{1H} NMR (125.7 MHz, CD2Cl2, 298 K): δ (ppm): 130.67 (s, Cquat), 130.262 (s, CH), 126.832 (s, CH), 121.83 (CH), 126.75 (CH), 126.59 (CH), 126.47 (2CH), 125.20 (CH), 124.97 (4CH), (CH), 129.41 (CH), 129.23 (CH), 128.90 (CH), 128.69 (CH), 127.15 (5CH), 126.75 (CH), 126.59 (CH), 126.47 (2CH), 125.20 (CH), 124.97 (4CH), 124.57 (CH), 122.80 (CH), 45.72 (CH2 of Et3N+H+), 21.70 (CH3), 8.46 (CH3 of Et3N+).

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[8] F. G. Terrade, M. Lutz, J. N. H. Reek, Chem. Eur. J. 2013, 19, 10458, the X-ray structure of $\text{Rh}_2(\text{nbd})_2(\text{R-L}_2)^2\cdot\text{Rh}_2(\text{nbd})_2(\text{S-L}_2)^2$: CCDC-931393. CCDC 931393 (for $\text{Rh}_2(\text{nbd})_2(\text{R-L}_2)^2\cdot\text{Rh}_2(\text{nbd})_2(\text{S-L}_2)^2$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.


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