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Conformational behaviour of dinuclear Rh(I) complexes of the open-chain tetrapyrrolic ligand 2,2′-bidipyrrin (H_2BDP)

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Abstract

The reaction of 2,2′-bidipyrrins H_2BDP with the Rh^I complexes $[Rh(COD)(\mu\text{-OMe})]_2$ and $[Rh(CO)_2(\mu\text{-Cl})]_2$ yields the neutral species $[\{Rh(COD)\}_2BDP]$ (**7**, **8**) and $[\{Rh(CO)_2\}_2BDP]$ (**2**, **9**), respectively. Treatment of the COD complexes with carbon monoxide results in the exchange of all COD ligands against CO. Ligand exchange studies on the carbonyl complexes **2** and **9** with different phosphane donors reveal the regioselective exchange of one CO per metal ion. In most cases, the reaction is accompanied by a large conformational change of the tetrapyrrole from a *syn* to an *anti* conformation. This conformational change was resolved by a combination of NMR spectroscopy and X-ray diffraction studies.

Keywords: Oligopyrroles; Conformational control; Rhodium

1. Introduction

$Rh(CO)_2$-fragments have been of frequent use in the chemistry of oligopyrrolic macrocycles. They were first introduced by Ogoshi in 1972, when the mechanism of porphyrin metalation was in question [1]. So-called sitting-atop (SAT) intermediates [2] were proposed to be vital in this respect, and Ogoshi's compounds were the first structurally characterized species, for which this particular feature was observed [3]. Later on rhodium(I) complexes of especially porphyrin and corrole derivatives were much studied with respect to the analogy with vitamin B_{12} [4], the ability of anion sensing [5], and the finding of CH-activation processes [6].

In more recent years, the complexation of non-natural cyclic oligopyrroles with the planar $Rh(CO)_2$- or $Rh(CO)(PR_3)$-fragment was employed in order to obtain crystalline derivatives and therefore the structural proof for a new macrocycle [7]. Some important examples are given in Scheme 1. Besides the rather large number of macrocyclic compounds only one report about rhodium complexes of open-chain tetrapyrroles has been published so far [8]. This is surprising, since structural information on open-chain oligopyrroles is still rare, and, in addition, special reactivity schemes of these complexes can be deduced from the redox properties of open-chain oligopyrroles and group 9 cations [9].

Our first attempts to fill this gap made use of the artificial open-chain tetrapyrrole 2,2′-bidipyrrin (H_2BDP) [10] and produced the puzzling result, that either mono- or dinuclear Rh(I) complexes **3** and **2** of the H_2BDP ligand **1**, or mononuclear Rh(III) complexes **4** of a macrocycle related to the corrin are formed, depending on the Rh(I) precursor used (Scheme 2) [11]. From a simple sterical argument it could be deduced, that dinuclear Rh(I) species are in

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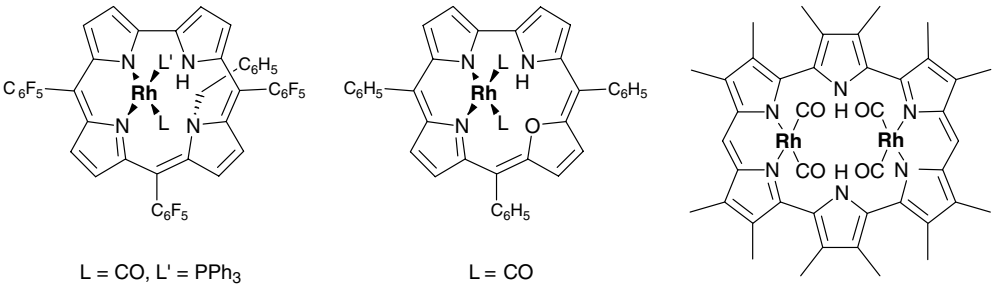
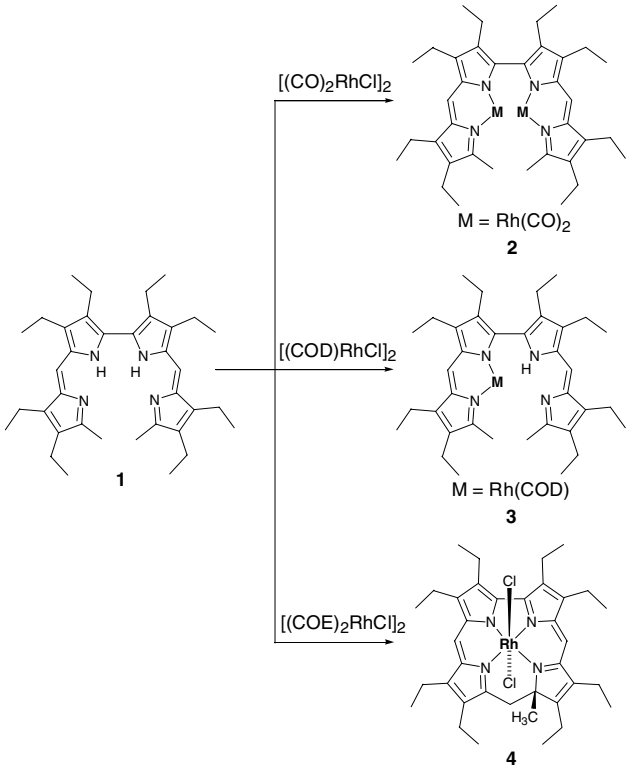
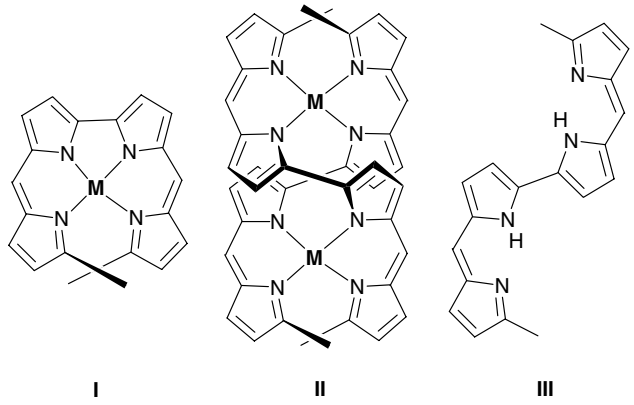


Scheme 1. Selected oligopyrrolic macrocycles characterized via Rh(CO)L derivatives.



Scheme 2. Visitor ligand-dependent metalation reactions of 2,2′-bidipyrrins.

a sterical dilemma, in that the visitor ligands of the Rh(I) centres of each dipyrrin fragment are in close contact with the methyl termini, and with the respective other metalated dipyrrin fragment of the complex. Non-planar species residing in one of two limiting conformations, a pseudomacrocyclic *syn* conformation and a stretched *anti* conformation (similar to **I** and **III** in Scheme 3), can therefore be expected. Since the barrier of interconversion between the *syn* and *anti* form is presumably high, we expected an influence of the respective conformation on the ability to form macrocycles like **4**. This paper summarizes our results on the conformational features of dinuclear Rh(I) complexes of 2,2′-bidipyrrin ligands.



Scheme 3. Prominent conformations of 2,2′-bidipyrrin and metal chelates.

2. Results and discussion

2.1. Crystallographic analysis of a H_2BDP ligand

The most prominent coordination modes found in BDP complexes of four coordinate metal ions are the distorted square **I** and the distorted tetrahedron **II** (Scheme 3) [12]. The tetrapyrrolic ligand therefore adopts either a conjugated pseudomacrocyclic *syn* conformation as in **I** or a non-conjugated conformation with orthogonal dipyrrin subunits as in **II**. In contrast to this, the ligand H_2BDP itself usually resides in a planar and conjugated *anti* conformation **III**. This was deduced for the solution from 2D NMR experiments [10b] and has now been proven for the solid state by an X-ray diffraction study on the 3,3′,4,4′-tetraethyl-8,8′,9,9′,10,10′-hexamethyl-derivative **5** [10b].

Suitable crystals from **5** were obtained by slow evaporation from dichloromethane under argon. Complex **5** forms green cubes with a metallic luster, space group $P\bar{1}$, $a = 4.6919(6)$ Å, $b = 10.5834(13)$ Å, $c = 14.281(2)$ Å, $\alpha = 75.849(15)°$, $\beta = 83.730(16)°$, $\gamma = 83.427(15)°$, $Z = 1$. Fig. 1 shows the molecular structure and Table 1 gives selected bond lengths and distances. Complex **5** crystallizes with two identical dipyrrin subunits. The most prominent structural finding is the proof for the planar

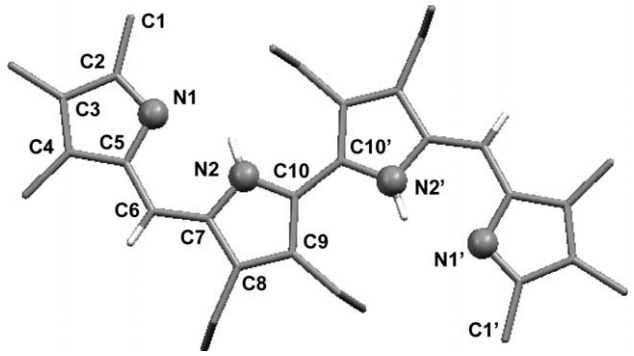


Fig. 1. Molecular structure of 3,3′,4,4′-tetraethyl-8,8′,9,9′,10,10′-hexamethyl-2,2′-bidipyrrin (**5**) (numbering scheme deviating from the nomenclature).

Table 1
Selected bond lengths (Å) and bond angles (°) for **5**, **2** (mean values) and **18**

Complex	**5**	**2**	**18**
Bond lengths (Å)			
M–N1		2.094(3)	2.093(7)
M–N2		2.078(3)	2.100(6)
M–C_{CO}1		1.843(5)	1.748(11)
M–C_{CO}2		1.859(4)	
M–P			2.280(3)
M···M		3.1985	6.288
C2–N1	1.3312(18)	1.341(5)	1.348(10)
N1–C5	1.398(2)	1.403(4)	1.427(10)
C5–C6	1.378(2)	1.372(5)	1.367(11)
C6–C7	1.4062(19)	1.402(5)	1.386(10)
C7–N2	1.3784(18)	1.383(4)	1.412(9)
N2–C10	1.3592(16)	1.365(4)	1.372(8)
C10–C10′	1.441(3)	1.459(5)	1.436(13)
Bond angles (°)			
N1–M–N2		87.86(11)	84.7(3)
N1–M–C_{CO}1		94.35(15)	88.4(5)
N1–M–C_{CO}2		171.14(15)	
N1–M–P			168.9(2)
N2–M–C_{CO}1		176.61(17)	172.9(5)
N2–M–C_{CO}2		92.42(14)	
N2–M–P			98.6(2)
C_{CO}1–M–C_{CO}2		85.05(17)	
C_{CO}1–M–P			87.9(4)
Torsion angles (°)			
N2–C10–C10′–N2′	180.00	47.31	57.59
C2–C10–C10′–C2′	180.00	17.98	64.89
P–C*x*–C*x*′–P′			67.07

and stretched *anti* conformation of free base 2,2′-bidipyrrins in the solid state. A similar conformation was reported earlier for a related hexapyrrole [13]. The linear conformation is apparently not capable of binding metal ions in the classical fashion due to the fact, that both chelating NH···N units are blocked by one of the ethyl substituents (on C9, C9′) of the opposite dipyrrin subunit. Deprotonated H_2BDPs will therefore act as two-compartment ligands for monocationic metal complex fragments, yielding dinuclear complexes with six-membered chelate rings. The alternative binding of metal ions via a N2,N2′-chelate, on the other hand, appears to be conformationally disfavoured.

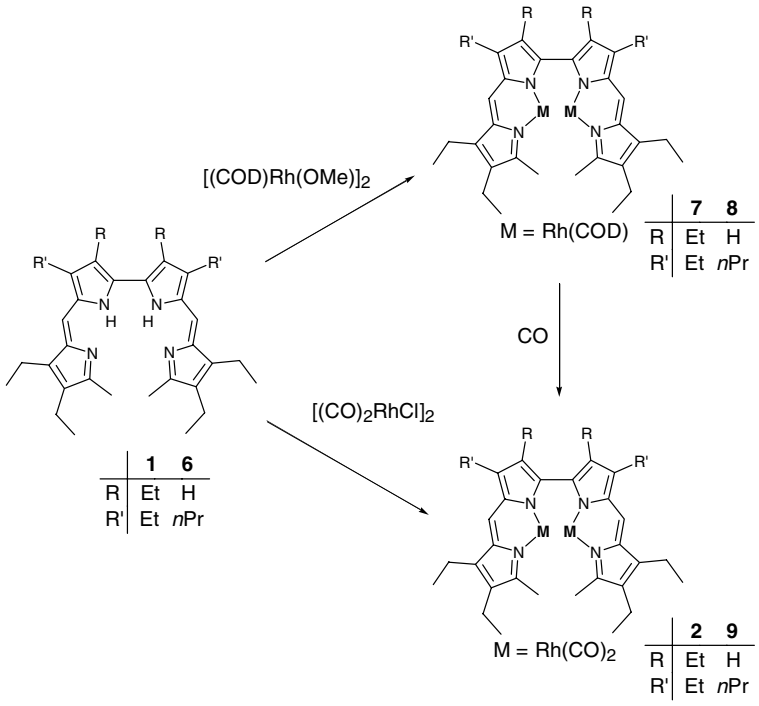
2.2. Metalation reactions of **1** and **6** with Rh(I) precursors and crystallographic analysis of the neutral [{Rh(CO)$_2$}$_2$BDP] complex **2**

For the complexation studies the two known H_2BDP derivatives **1** and **6** were chosen [10b]. The octaethyl dimethyl derivative **1** is sterically similar to **5** and serves as the working horse in all of our bidipyrrin studies, while the dipropyl tetraethyl dimethyl derivative **6** was introduced as a ligand with reduced steric hindrance in the *anti* conformation (Scheme 4). The preparation of [{Rh(CO)$_2$}$_2$BDP]complexes of ligands **1** and **6** was successfully carried out in two different ways, either starting from [Rh(COD)(μ-OMe)]$_2$ and successive treatment of the isolated COD complexes **7** and **8** with CO, or directly using [Rh(CO)$_2$(μ-Cl)]$_2$ as the precursor (Scheme 4). The new compounds [{Rh(COD)}$_2$BDP] (**7** and **8**) as well as [{Rh(CO)$_2$}$_2$BDP] (**2** and **9**) were obtained in 70–95% yield as dark green-brown crystals with a metallic sheen and could be fully characterized by NMR, IR and mass spectroscopy. By a temperature dependent ^{1}H NMR spectroscopic analysis we were able to show, that all isolated complexes display a stable, non-dynamic conformation in solution up to 80 °C.

Additional attempts were undertaken in order to prepare mononuclear Rh(I) complexes of 2,2′-bidipyrrins by the use of stoichiometric amounts of Rh(I) precursors. These experiments were not successfull, and the desired mononuclear species were obtained only as tlc detectable short-lived constituents of mixtures. The high propensity of all mononuclear species to undergo fast hydrolytic cleavage prevented their isolation and spectroscopic characterization.

Also unsuccessfull were attempts to transform the dinuclear Rh(I) complexes **2**, **7**, **8** and **9** into pseudomacrocyclic mononuclear Rh(III) species by means of iodine oxidation or photooxidation with CCl_4 [14]. These procedures represent standard protocols in porphyrinoid rhodium chemistry, but lead to decomposed material only when applied to bidipyrrin chemistry.

Single crystals of the carbonyl complex **2** were obtained from dichloromethane by slow evaporation under argon. **2** forms a dichloromethane solvate as dark blue-green cubes with a metallic luster, space group $P2_1/c$, $a = 12.1400(9)$ Å, $b = 39.025(4)$ Å, $c = 9.1365(7)$ Å, $\beta = 104.915(9)°$, $Z = 4$. Fig. 2 shows the molecular structure and Table 1 gives selected bond lengths and distances. Due to the presence of one molecule of dichloromethane per formula, the two [Rh(CO)$_2$dipyrrin] fragments of **2** differ slightly in their molecular structure. Mean values for bond lengths and bond angles are therefore used in the discussion.



Scheme 4. Preparation of dinuclear carbonyl and COD complexes.

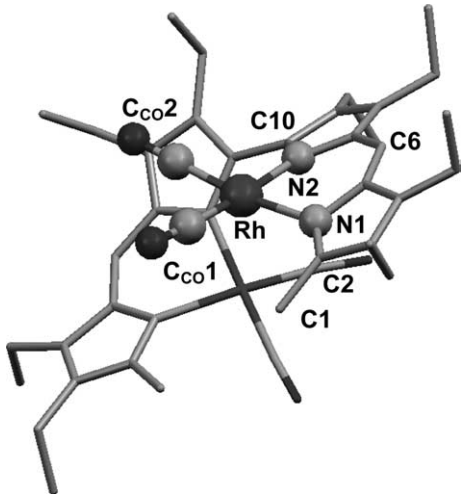


Fig. 2. Molecular structure of [{Rh(CO)$_2$}$_2$BDP] (**2**) (numbering scheme deviating from the nomenclature).

The rhodium(I) ion is unsymmetrically coordinated by two nitrogen donors at 2.078 and 2.094 Å, and by two carbonyl ligands at 1.843 and 1.859 Å, respectively. These values and the angles at Rh, which generally deviate less than 5° from the ideal 90°, fit well into the expectations for porphyrinoid rhodium(I) complexes and therefore bear no surprise. The same is true for the C–C and C–N bond lengths within the tetrapyrrole ligand backbone of **2**, which displays the same pattern with the central pyrrole type C_4N rings and the terminal pyrrolenin substructures as was seen for the free base **5**.

The *syn* conformation of complex **2** is achieved in the way, that both metalated dipyrrin subunits are bent in a contra-rotating wing-like fashion, so that the torsion angle at the central bipyrrole N2–C10–C10′–N2′ is as high as 47.31°, but the torsion angle C2–C10–C10′–C2′, which describes the overall tilt much better, is as low as 17.98°. In this arrangement the Rh(CO)$_2$ fragments of **2** organize above and below the mean tetrapyrrole plane and escape most of the steric encumbrance of the constrained centre of the molecule.

The special geometry of complex **2** causes a short Rh···Rh contact of 3.1985 Å, posing the question, whether an attractive metal–metal interaction between the rhodium atoms directs the *syn* conformation energetically. Theoretical work done on related square planar d^8 systems suggest, that attractive metal metal interactions can be found only for ML$_4$ fragments eclipsed towards each other [15]. For **2** a mean torsion angle L–Rh–Rh′–L′ of ca. 65° is found, pointing against an attractive interaction in this case. The same conclusion can be drawn from the finding of only two IR absorptions for the Rh(CO)$_2$ fragments of **2** at 2060 and 1996 cm^{-1}. Within the scenario of a Rh–Rh bond a strongly coupled system of all four CO stretches should be expected. For these reasons we believe, that the observation of the *syn* conformation of **2** is solely based on sterical interactions between the different ligands and does not indicate any attractive dispersion interaction between the two metal centres.

2.3. Ligand exchange reactions with phosphane donors

Ligand exchange reactions were carried out for the four CO and COD complexes **2**, **7**, **8** and **9** with monophosphanes PR_3 of different size (R = Ph, Me, *i*-Pr) as well as with diphosphanes $Ph_2P–(CH_2)_n–PPh_2$ ($n = 1$, 2). All attempts with the COD complexes **7** and **8** failed due to immediate demetalation. The same was observed, if a large excess of phosphane was reacted with the CO complexes **2** and **9**. Additionally, the reactions of monophosphanes with the di-*n*-propyl derivative **9** yielded very impure products and will therefore not be discussed further.

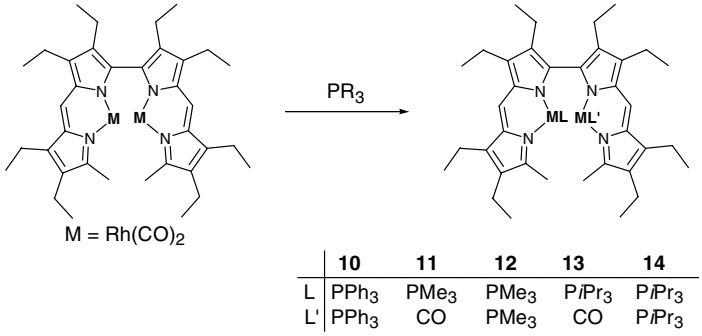
The treatment of $[\{Rh(CO)_2\}_2BDP]$ (**2**) with 2 equiv of PPh_3 at elevated temperature resulted in a single product **10**, in which one of the two CO ligands of each $Rh(CO)_2$ fragment is stereoselectively exchanged. The action of the more reactive alkyl phosphanes PR_3 (R = Me, *i*-Pr) on **2** was found to proceed with diminished selectivity even at 0 °C. In both cases mixtures of products with one and two exchanged CO ligands, $[\{Rh(CO)(PR_3)\}\{Rh(CO)_2\}BDP]$ (**11**) (R = Me) or (**13**) (R = *i*-Pr) and $[\{Rh(CO)(PR_3)\}_2BDP]$ (**12**) (R = Me) or (**14**) (R = *i*-Pr) were obtained in addition to decomposed material. Using 1 or 2 equiv of phosphane allows to enrich the mixtures with either the non-symmetric complexes **11** and **13** or the symmetric species **12** and **14**, so that a ^1H and ^{31}P NMR spectroscopic characterization became possible.

In contrast to the monophosphanes, the reactions of the CO complexes **2** and **9** with stoichiometric amounts of the diphosphanes dppm and dppe proceed very slowly in all cases. Of the four new compounds **15**, **16**, **17** and **18**, only **15** and **18** could be isolated and fully characterized. The complexes **16** and **17** were characterized as mixtures with the respective starting material **9** or **2** by ^1H and ^{31}P NMR. All ligand exchange reactions are summarized in Scheme 5.

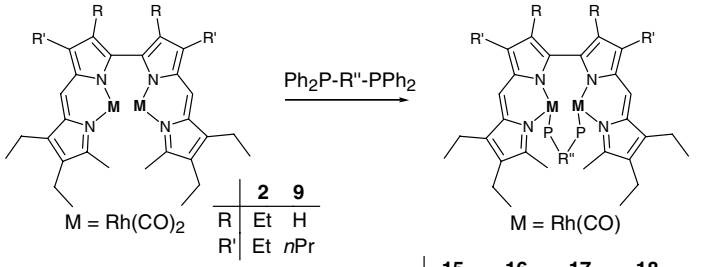
Single crystals suitable for X-ray diffraction were obtained from compound **18** by slow diffusion of pentane into a dichloromethane solution at −30 °C **18** forms brown blocks, space group *I2/a*, $a = 23.186(3)$ Å, $b = 10.2310(8)$ Å, $c = 25.752(3)$ Å, $\beta = 111.955(14)°$, $Z = 4$. Fig. 3 presents two different views of the molecular structure and Table 1 gives selected bond lengths and distances.

The rhodium atoms in **18** are unsymmetrically surrounded with one CO ligand at 1.748 Å, two N donors at 2.093 (N1) and 2.100 Å (N2), and one P donor at 2.280 Å. While these bond lengths and the found angles are within the limits of normal Rh(I) complexes, the fact, that the P donor in **18** has replaced the inner CO of **9**, and therefore now occupies the sterically more unfavourable position, was not expected.

The bond lengths pattern of the tetrapyrrole ligand backbone of **18** differs remarkably from those found for **2** or **5**. Other than in these cases, the C_4N rings of **18** appear electronically reorganized in the way, that



	10	11	12	13	14
L	PPh_3	PMe_3	PMe_3	P*i*Pr$_3$	P*i*Pr$_3$
L'	PPh_3	CO	PMe_3	CO	P*i*Pr$_3$



	2	9
R	Et	H
R'	Et	*n*Pr

	15	16	17	18
R	Et	H	Et	H
R'	Et	*n*Pr	Et	*n*Pr
R''	CH_2	CH_2	$(CH_2)_2$	$(CH_2)_2$

Scheme 5. Overview of ligand exchange reactions of this study.

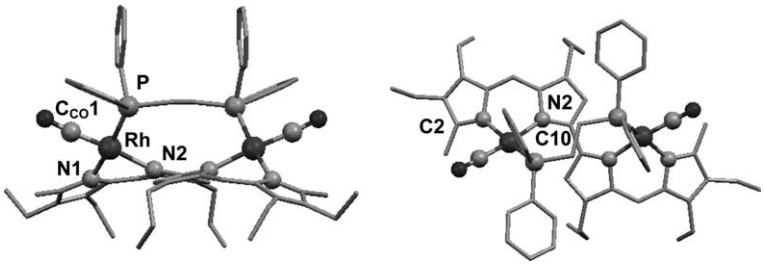


Fig. 3. Molecular structure of [{Rh(CO)}$_2$(μ-dppe)BDP] (**18**). Left side: view along the bipyrrole axis C10–C10′; right side: view along the crystallographic *b*-axis (numbering scheme deviating from the nomenclature).

the former differences between the pyrrole type and the pyrrolenine type substructure are mainly evened out.

The most prominent detail of the molecular structure of **18** ist the *anti* conformation, in which the bidipyrrin ligand binds to the rhodium ions. This conformation is again achieved by a wing-like distortion of both metallodipyrrin subunits. In contrast to **2**, however, the two subunits of **18** are distorted in a con-rotating way, resulting in similar torsion angles N2–C10–C10′–N2′ and C2–C10–C10′–C2′ of 57.59° and 64.89°, respectively. In order to allow the bridging diphosphane to bind in an intramolecular fashion, both Rh(CO)P fragments are situated at the same side of the tetrapyrrole. As a result, the Rh···Rh distance of 6.288 Å is rather large.

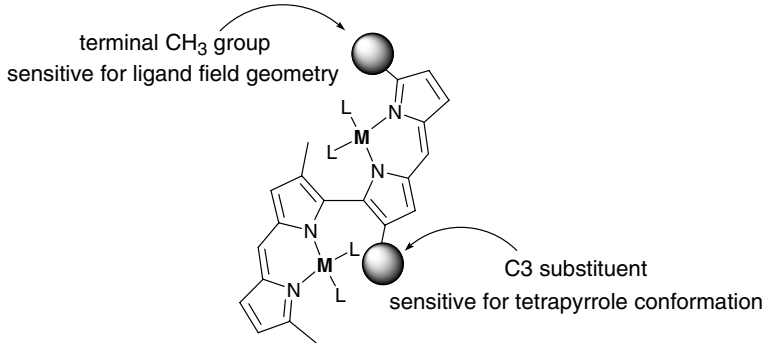
2.4. ^{1}H NMR analyses of ligand field geometries and molecular conformations

The peripheral alkyl substituents of the BDP complexes described in this work can in principle be used as spectroscopic probes in order to analyse the geometry of the ligand sphere, i.e., the site, to which the phosphane ligand binds, and the conformation of the tetrapyrrole. Two molecular positions can be of importance in this regard (Scheme 6).

The site of ligand substitution is presumably best reflected by the shift of the signal of the protons of the nearby methyl termini, while a tetrapyrrole conformational change should influence the substituents at the positions 3 and 3′ most significantly. The latter should be particularly true for all complexes derived from ligand **1**, in which diastereotopic splittings $\Delta\delta_{A,B}$ of differing strengths should be observed for the proton resonances of the methylene groups at C3, C3′. Table 2 summarizes all relevant NMR parameters of the complexes described herein.

Table 2 shows that the agreement between the diastereotopic splitting of the 3,3′-situated methylene protons $\Delta\delta_{A,B}$ and the tetrapyrrole conformation is particularly convincing. Apparently, only those complexes bearing the smallest ligands, i.e., CO and PMe_3, as well as the half substituted species **13** are capable to take the *syn* conformation, while all other compounds prefer the stretched *anti* conformation. The analysis of further data, however, is not so straightforward, and conclusions could not be drawn. The privileged low-field position of the $\delta_{CH3\,term}$ values of all PMe_3 containing complexes, however, seems to indicate, that PMe_3 occupies the outer position close to the methyl termini, while all other P donor ligands are bound to the inner position. For a detailed analysis of the latter point further reference material will be necessary.

The question remains, how the conformational change from one stable conformation to the other occurs during ligand exchange. We believe, that this process is initiated by the association of the second donor to the second rhodium centre, and that the dynamic rearrangement of the coordination sphere of the metal is directly coupled to the conformational dynamic of



Scheme 6. Schematic view on efficient spectroscopic probes for coordination geometry and tetrapyrrole conformation.

Table 2
Selected ^{1}H NMR data for the complexes of this work (see text)

Compound	$\delta_{CH3\,term}$	$\delta_{H\text{-}3}$	$\Delta\delta_{A,B}$
[{Rh(CO)$_2$}$_2$BDP] (**2**)	2.73	–	0.16
[{Rh(COD)}$_2$BDP] (**7**)	2.36	–	2.57
[{Rh(CO)(PPh$_3$)}$_2$BDP] (**10**)	2.27	–	1.43
[{Rh(CO)(PMe$_3$)}{Rh(CO)$_2$}BDP] (**11**)	3.12/3.10	–	ca. 0.10
[{Rh(CO)(PMe$_3$)}$_2$BDP] (**12**)	3.28	–	0.09
[{Rh(CO)(P*i*-Pr$_3$)}{Rh(CO)$_2$}BDP] (**13**)	2.48/2.37	–	ca. 0.15
[{Rh(CO)(P*i*-Pr$_3$)}$_2$BDP] (**14**)	2.43	–	1.56
[{Rh(CO)}$_2$(μ-dppm)BDP] ((**15**)	2.58	–	2.09
[{Rh(CO)}$_2$(μ-dppe)BDP] (**17**)	2.56	–	2.95
[{Rh(CO)$_2$}$_2$BDP] (**9**)	2.95	6.89	–
[{Rh(COD)}$_2$BDP] (**8**)	2.77	6.70	–
[{Rh(CO)}$_2$(μ-dppm)BDP] (**16**)	2.50	6.95	–
[{Rh(CO)}$_2$(μ-dppe)BDP] (**18**)	2.42	7.36	–

the tetrapyrrole. In other words this means, that the sterical condition of the (unknown) transition state is responsible for the respective conformation and the positionally selective product formation. Theoretical work will be necessary to further elucidate this point.

From this study, however, it becomes apparent, why dinuclear Rh(I) BDP complexes, other then the porphyrins, decay under oxidising conditions and do not form mononuclear Rh(III) compounds. In dinuclear Rh(I) porphyrins the strained and non-planar macrocycle has a strong tendency to planarize, and therefore to tear one of the metal ions inside the N_4 cavity, with concomitant loss of the other ion. In dinuclear BDP complexes this strain is directed outwards, so that the ligand escapes into a stretched conformation as soon as the metal ions start to react. The formation of a pseudomacrocyclic Rh(III) complex is therefore rather improbable. In order to explain the observation, that under particular conditions a macrocyclic Rh(III) complex **4** is formed from a H_2BDP ligand and a Rh(I) source, we assume, that a metal template directed ligand centered oxidation process and ring closure reaction must occur prior to the oxidation of the metal ion. This hypothesis is currently under investigation.

3. Experimental

3.1. General details

NMR spectra (^{1}H, ^{13}C, ^{31}P) were recorded in C_6D_6 at ambient temperature on the following spectrometer (Bruker): ARX 300, ARX 200, and DRX 400. Chemical shifts are given in ppm relative to the residual proton resonance of the solvent. Mass spectra (MALDI-TOF) were recorded on a Bruker Biflex IV, using *trans*-3,5-dimethoxy-4-hydroxycinnamic acid as matrix. HRMS analyses were obtained using ESI-MS on a QStarPulsar i.

All reactions were performed in an inert atmosphere of either nitrogen or argon by using standard Schlenk techniques and vacuum-line methods. Solvents were dried and distilled under nitrogen prior to use. Column chromatography was carried out under nitrogen using either silica gel (particle size 0.063–0.200 nm) or alumina (neutral) as stationary phase. Most chemicals were used directly without prior purification.

3.2. Crystal structure determination

Data of **2**, **5** and **18** were collected at −90 °C on an IPDS-I diffractometer using monochromated Mo Kα radiation. Data were corrected for Lorenz polarization effects and for absorption. The structures were solved by direct methods (**5**) or by the Patterson method (**2**, **18**), using SHELXS [16], and refined by full-matrix least-squares techniques against F^2 (SHELXL) [17]. The hydrogen atoms of the structures were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. Crystal data and other experimental procedures and refinement parameters are given in Table 3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary material publication nos. CCDC-262833 (**2**), CCDC-262835 (**5**) and CCDC-262834 (**18**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [fax: (internal) +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk].

3.3. Syntheses of complexes

3.3.1. Metalation of H_2BDP ligands with Rh(I) – general procedure

A THF solution (15 ml) of H_2BDP (**1** or **6**) (0.6 mmol) is treated with the rhodium precursor [Rh(CO)$_2$Cl]$_2$ or [Rh(COD)(OMe)]$_2$ (0.61 mmol) and stirred at ambient temperature. After 20 h all volatiles are removed in vacuo, and the residue is washed repeatedly with small aliquots of ice-cold methanol. After drying in vacuo the products are obtained as dark to olive green powders.

*3.3.1.1. [{Rh(CO)$_2$}$_2$BDP] (**2**).* Yield: 95%. Anal. Calc. for $C_{40}H_{48}N_4O_4Rh_2$: C, 56.21; H, 5.66; N, 6.55. Found: C, 56.33; H, 5.62; N, 6.29%. ^{1}H NMR (C_6D_6, 295 K): 7.22 (s, 2H), 2.98 (m, 2H), 2.82 (m, 2H), 2.73 (s, 6H), 2.69 (q, 4H), 2.44 (q, 4H), 2.21 (m, 4H), 1.21, 1.09, 1.05, 0.95 (4 × t, 24H). ^{13}C NMR (C_6D_6, 295 K): 186.5 (d, J_{RhC} = 65 Hz), 182.1 (d, J_{RhC} = 67 Hz), 163.3, 152.1, 145.2, 142.2, 134.7, 132.4, 131.6, 131.3, 121.1, 18.7, 18.6, 17.6, 17.5, 16.5, 16.3, 14.5, 14.1. IR (KBr): ν (cm^{-1}) = 2056, 1992. MS (MALDI): 854 (M^+).

3.3.1.2. [{Rh(COD)}$_2$BDP] (7). Yield: 71%. HRMS calc. for $C_{52}H_{72}N_4Rh_2$: 958.38667. Obs.: 958.38693;

Table 3
Crystal data, collection and refinement details for **2**, **5** and **18**

Complex	**2**	**5**	**18**
Empirical formula	$C_{32}H_{42}N_4$	$C_{41}H_{50}Cl_2N_4O_4Rh_2$	$C_{62}H_{68}N_4O_2P_2Rh_2$
Formula weight	482.70	939.57	1168.96
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$I2/a$
Unit cell dimensions			
a (Å)	4.6919(6)	12.1400(9)	23.186(3)
b (Å)	10.5834(13)	39.025(4)	10.2310(8)
c (Å)	14.281(2)	9.1365(7)	25.752(3)
α (°)	75.849(15)		
β (°)	83.730(16)	104.915(9)	111.955(14)
γ (°)	83.427(15)		
V (Å^3)	680.68(15)	4182.7(6)	5665.7(11)
Z	1	4	4
D_{calc} (Mg/m^3)	1.178	1.492	1.370
Absorption coefficient (mm^{-1})	0.069	0.961	0.685
$F(000)$	262	1920	2416
θ Range (°)	2.18–25.33	1.74–26.08	2.17–25.35
Reflections collected	6405	32294	22341
Independant reflections	2335	8052	4967
Data/restraints/parameters	2335/0/172	8052/0/488	4967/0/330
Goodness-of-fit on F^2	1.033	0.988	0.874
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0396$, $wR_2 = 0.1072$	$R_1 = 0.0447$, $wR_2 = 0.1129$	$R_1 = 0.0661$, $wR_2 = 0.1545$
R indices (all data)	$R_1 = 0.0504$, $wR_2 = 0.1122$	$R_1 = 0.0548$, $wR_2 = 0.1190$	$R_1 = 0.1224$, $wR_2 = 0.1770$

$\Delta = 0.26$ mmu. ^{1}H NMR (C_6D_6, 293 K): 7.31 (s, 2H), 5.79 (m, 2H), 4.96–3.85 (m, 8H), 3.22 (m, 2H), 3.04–1.83 (m, 28H), 2.36 (s, 6H), 1.42, 1.28, 1.22, 1.17 (4 × t, 24H). ^{13}C NMR (C_6D_6, 293 K): 160.9, 151.4, 143.3, 141.2, 136.4, 135.6, 133.4, 131.4, 123.8, 80.3 (2 × d, $J_{Rh-C} = 9$ Hz), 79.2 (d, $J_{Rh-C} = 12$ Hz), 75.7 (d, $J_{Rh-C} = 11$ Hz), 31.7, 31.0, 29.9, 29.5, 20.4, 18.3, 18.1, 17.8, 17.4, 17.3, 16.3, 15.2, 14.7. MS (MALDI): 958 (M^+).

*3.3.1.3. [{Rh(COD)}$_2$BDP] (**8**).* Yield: 85%. HRMS calc. for $C_{50}H_{68}N_4Rh_2$: 930.35537. Obs.: 930.35505; $\Delta = -0.32$ mmu. ^{1}H NMR (C_6D_6, 300 K): 7.31 (s, 2H), 6.70 (s, 2H), 4.97–3.62 (m, 8H), 2.90–1.77 (m, 16H), 2.77 (s, 6H), 2.70 (q, 4H), 2.66 (q, 4H), 2.42 (m, 4H), 1.69 (m, 4H), 1.26 (t, 6H), 1.13 (t, 6H), 0.94 (t, 6H). ^{13}C NMR (C_6D_6, 300 K): 160.0, 153.3, 144.0, 143.6, 138.7, 137.2, 131.7, 123.5, 118.65, 82.2 (d, $^1J_{RhC} = 15$ Hz), 80.3 (2 × d, $^1J_{RhC} = 15$ Hz), 73.9 (d, $^1J_{RhC} = 13$ Hz), 29.7, 29.0, 24.7,18.9, 18.8, 18.0, 17.4, 15.8, 14.2. MS (MALDI): 930 (M^+).

*3.3.1.4. [{Rh(CO$_2$)}$_2$BDP] (**9**).* Yield: 87%. HRMS calc. for $C_{38}H_{44}N_4O_4Rh_2$: 826.14724. Obs.: 826.14727; $\Delta = 0.03$ mmu. ^{1}H NMR (C_6D_6, 300 K): 7.25 (s, 2H), 6.89 (s, 2H), 2.95 (s, 6H), 2.67 (m, 4H), 2.50 (q, 4H), 2.24 (m, 4H), 1.67 (q, 4H),1.10 (m, 6H), 0.99 (t, 6H), 0.92 (t, 6H). ^{13}C NMR (C_6D_6, 300 K): 188.7 (d, $^1J_{RhC} = 66$ Hz, CO), 184.4 (d, $^1J_{RhC} = 66$ Hz, CO), 163.2, 154.1, 145.7, 144.9, 136.6, 136.4, 132.1, 121.4, 118.5, 28.9, 24.8, 19.5, 18.7, 18.6,17.4, 15.3, 14.0. IR (KBr): ν (cm^{-1}) = 2054.3, 1998.5. MS (MALDI): 826 (M^+).

3.3.2. Ligand exchange reactions – general procedure

A solution of the carbonyl complex **2** or **9** (0.1 mmol) in dichloromethane (10 ml) is cooled in an ice bath and treated with 1 or 2 equiv of the respective phosphane or diphosphane. The solution is stirred for 3 h at reflux (for **10**), for 12 h at ambient temperature (for all diphosphane complexes), or for 30 min at 0 °C (for all alkyl phosphanes). After this time the solvent is removed in vacuo and the residue is washed repeatedly with ice cold pentane to leave the product as a green-to-brownish solid.

*3.3.2.1. [{Rh(CO)(PPh$_3$)}$_2$BDP] (**10**).* Yield: 90%. HRMS calc. for $C_{74}H_{78}N_4O_2P_2Rh_2$: 1322.37098. Obs.: 1322.37159; $\Delta = 0.61$ mmu. ^{1}H NMR (C_6D_6, 293 K): 8.11 (m, 12H), 7.48 (m, 6H), 7.39 (s, 2H), 7.36 (m, 12H), 4.85 (m, 2H), 3.42 (m, 2H), 3.15 (m, 4H), 2.73 (q, 4H), 2.42 (m, 4H), 2.27 (s, 6H), 1.73, 1.63, 1.39, 1.14 (4 × t, 24H). ^{13}C NMR (C_6D_6, 293 K): 189.0 (dd, $J_{Rh-C} = 69$ Hz, $J_{P-C} = 24$ Hz), 159.7, 156.9, 143.6, 142.0, 135.3, 134.3, 133.5, 132.4, 132.3, 131.5, 129.4, 128.3, 123.1, 20.5, 18.7, 18.5, 18.4, 18.2, 17.4, 17.3, 16.6, 14.9. ^{31}P NMR (C_6D_6, 293 K): 45.20 (d, $J_{Rh-P} = 164$ Hz). IR (CH_2Cl_2): ν (cm^{-1}) = 1978. MS (MALDI): 1322 (M^+).

*3.3.2.2. [{Rh(CO)(PMe$_3$)}{Rh(CO)$_2$}BDP] (**11**).* ^{1}H NMR (C_6D_6, 300 K): 7.34, 7.18 (2 × s, 2H), 3.12, 3.10

(2 × s, 6H), 2.79 (m, 4H), 2.72 (m, 4H), 2.56 (m, 4H), 2.29 (m, 4H), 1.27 (m, 3H), 1.26 (m, 3H), 1.20 (t, 3H), 1.16 (t, 3H), 1.13 (t, 3H), 1.06 (t, 3H), 1.02 (m, 3H), 1.01 (m, 3H), 0.52 (m, 9H). ^{31}P NMR (C_6D_6, 300 K): −1.42 (d, $^1J_{RhP}$ = 155 Hz).

*3.3.2.3. [{Rh(CO)(PMe$_3$)}$_2$BDP] (**12**).* ^{1}H NMR (C_6D_6, 300 K): 7.24 (s, 2H), 3.28 (s, 6H), 2.85 (m, 4H), 2.75 (m, 2H), 2.66 (m, 2H) 2.61 (m, 4H), 2.35 (m, 4H), 1.33, 1.28, 1.16, 1.06 (4 × t, 24H), 0.50 (m, 18H). ^{31}P NMR (C_6D_6, 300 K): −3.6 (d, $^1J_{RhP}$ = 158 Hz).

*3.3.2.4. [{Rh(CO)(Pi-Pr$_3$)}{Rh(CO)$_2$}BDP] (**13**).* ^{1}H NMR (C_6D_6, 300 K): 7.21, 7.09 (2 × s, 2H), 4.08 (m, 2H), 3.93 (m, 2H), 2.48, 2.37 (2 × s, 6H), 0.56 (m, 6H). Further signals between 3.1 and 0.7 ppm could not be assigned. ^{31}P NMR (C_6D_6, 300 K): 56.0 (d, $^1J_{RhP}$ = 158 Hz).

*3.3.2.5. [{Rh(CO)(Pi-Pr$_3$)}$_2$BDP] (**14**).* ^{1}H NMR (C_6D_6, 300 K): 7.05 (s, 2H), 4.59 (m, 2H), 3.03 (m, 2H), 2.80 (m, 4H), 2.50 (m, 4H), 2.43 (s, 6H), 2.05 (m, 4H), 1.69 (m, 1H), 1.23, 1.18, 1.06, 0.96 (4 × t, 24H), 0.78 (m, 12 H). ^{31}P NMR (C_6D_6, 300 K): 56.6 (d, $^1J_{RhP}$ = 158 Hz).

*3.3.2.6. [{Rh(CO)}$_2$(μ-dppm)BDP] (**15**).* HRMS calc. for $C_{63}H_{70}N_4O_2P_2Rh_2$: 1182.30838. Obs.: 1182.30857; Δ = 0.19 mmu. ^{1}H NMR (C_6D_6, 300 K): 7.83 (m, 4H), 7.08 (m, 8H), 7.05 (s, 2H), 6.99 (m, 2H), 6.71 (m, 2H), 6.51 (m, 4H), 4.77 (m, 2H), 3.50 (m, 2H), 2.68 (m, 2H), 2.58 (s, 6H), 2.54 (q, 4H), 2.47 (m, 4H), 2.29 (m, 4H), 1.18, 1.16, 1.00, 0.99 (4 × t, 24H). ^{13}C NMR (C_6D_6, 300 K): 191.3 (dd, $^1J_{RhC}$ = 69 Hz, $^2J_{PC}$ = 23 Hz), 163.3, 144.1, 141.3, 137.7, 136.6, 134.9 2 ·, 134.1, 132.9, 131.3, 129.6, 129.1, 128.0, 127.8, 122.9, 32.7, 20.5, 19.2, 19.1, 18.8, 18.7, 18.1, 17.5, 15.6, 14.3. ^{31}P NMR (C_6D_6, 300 K): 38.6 (dvt, $^1N_{PRh}$ = 161.8 Hz, $^2N_{PP}$ = 30.5 Hz, $^3N_{PRh}$ = 2.9 Hz, $^4N_{RhRh}$ = 0.0 Hz, AA′XX′). IR (KBr): ν (cm^{-1}): 1969. MS (MALDI): 1182 (M^+).

*3.3.2.7. [{Rh(CO)}$_2$(μ-dppm)BDP] (**16**).* ^{1}H NMR (C_6D_6, 300 K): 7.84 (m, 4H), 7.34 (m, 4H), 7.12 (s, 2H), 7.08 (m, 4H), 6.98 (m, 2H), 6.95 (s, 2H), 6.77 (m, 2H), 6.60 (m, 4H), 3.29 (q, 4H), 3.16 (m, 2H), 2.55 (m, 4H), CH_2CH$_3$, 2.50 (s, 6H), 2.26 (m, 4H), 1.50 (m, 4H), 1.16, 0.99, 0.87, 0.79 (3 × t, 18H). ^{31}P NMR (C_6D_6, 300 K): 40.1 (dvt, $^1N_{PRh}$ = 164.5 Hz, $^2N_{PP}$ = 29.5 Hz, $^3N_{PRh}$ = 2.6 Hz, $^4N_{RhRh}$ = 0.0 Hz, AA′XX′).

*3.3.2.8. [{Rh(CO)}$_2$(μ-dppe)BDP] (**17**).* ^{1}H NMR (C_6D_6, 300 K): 7.73 (m, 4H), 7.57 (m, 4H), 7.34 (s, 2H), 7.08 (m, 2H), 6.99 (m, 4H), 6.78 (m, 2H), 6.65 (m, 4H), 5.57 (m, 2H), 2.62 (m, 2H), 2.56 (s, 6H), 2.32 (m, 4H), 2.01 (br.s, 2H), 1.50 (br.s, 2H), 1.19, 1.18, 1.04, 1.02 (4 × t, 24H). The signals for two of the ethyl methylene groups could not be assigned. ^{31}P NMR (C_6D_6, 300 K): 39.0 (dvt, $^1N_{PRh}$ = 161.3 Hz, $^3N_{PP}$ = 59.8 Hz, $^4N_{PRh}$ = −0.35 Hz, $^5N_{RhRh}$ = 0.0 Hz, AA′XX′).

*3.3.2.9. [{Rh(CO)}$_2$(μ-dppe)BDP] (**18**).* HRMS calc. for $C_{62}H_{68}N_4O_2P_2Rh_2$: 1168.29273. Obs.: 1168.29251; Δ = −0.22 mmu. ^{1}H NMR (C_6D_6, 300 K): 7.93 (s, 2H), 7.87 (m, 4H), 7.63 (m, 4H), 7.36 (s, 2H), 7.08 (m, 4H), 7.01 (m, 2H), 6.79 (m, 2H), 6.69 (m, 4H), 2.79 (m, 4H), 2.60 (m, 4H), 2.42 (s, 6H), 2.26 (m, 4H), 2.06 (br.s, 2H), 1.58 (m, 4H), 1.44 (br.s, 2H), 1.21, 0.97, 0.81 (3 × t, 18H). ^{13}C NMR (C_6D_6, 300 K): 191.4 (dd, $^1J_{RhC}$ = 67 Hz, $^2J_{PC}$ = 23 Hz), 164.4, 153.8, 144.9, 142.6, 138.5, 138.0, 134.9, 131.7, 132.0, 130.3, 129.4, 128.3, 127.8, 122.4, 119.5, 29.3, 25.5, 19.4, 18.8, 18.6, 17.5, 15.3, 14.3. ^{31}P NMR (C_6D_6, 300 K): 35.2 (dvt, $^1N_{PRh}$ = 162.2 Hz, $^1N_{PP}$ = 51.3 Hz, $^4N_{PRh}$ = −0.28 Hz, $^5N_{RhRh}$ = 0.0 Hz, AA′XX′). IR (KBr): ν (cm^{-1}): 1967. MS (MALDI): 1168 (M^+).

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