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Synthesis and structural studies of rhodium(I)-catalytic precursors containing two furanoside diphosphines

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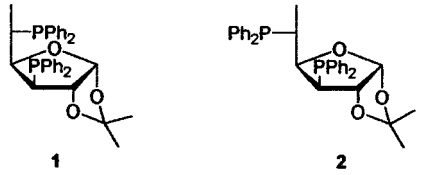
Abstract

We have prepared new rhodium(I) complexes with two furanoside diphosphines, 3,5,6-trideoxy-3,5-bis-diphenylphosphine-1,2-*O*-isopropylidene-β-L-idofuranose (**1**) and 3,5,6-trideoxy-3,5-bis-diphenylphosphine-1,2-*O*-isopropylidene-α-L-glucofuranose (**2**), which form six-membered chelate rings when they coordinate to rhodium. NMR spectroscopy of the Rh complexes and molecular mechanics calculations showed that the configuration of the stereocenter C-5 greatly influences the structure of these complexes, and thus their enantioselectivity. The pre-catalyst [Rh(cod)(**2**)]BF_4, which gives the highest enantioselectivities in the asymmetric hydrogenation of alkenes, adopts the twist-λ conformation. By changing the configuration of the C-5, the complex becomes fluxional at room temperature and enantioselectivity drops considerably.

Keywords: Rhodium complexes; Diphosphine; Sugar derivatives; NMR characterisation

1. Introduction

The enantioselective hydrogenation of prochiral substrates is one of the most important applications of asymmetric catalysis [1]. Diphosphines are among the most efficient chiral ligands in this process [1,2]. Those that form five- or seven-membered chelate rings are the ones that are most often studied and used in organometallic complexes. From the available data, these cycles are superior to six-membered chelate rings [3]. The low enantioselectivity achieved with this type of diphosphines has been attributed to the particular conformational flexibility of six-membered chelate cycles, which allows both chair and twist conformations, although only the twist conformations induce strong enantiomeric discrimination [4]. However, we cannot deduce any general trends from results available so far. For example, in solid-state structures, both conformations have been observed, even with the same chelate ligand. Diphosphine Bdpp ((2*S*,4*S*)-2,4-bis(diphenylphosphanyl)pentane) therefore forms a chelate chair in the catalyst precursor $[Rh(Bdpp)(nbd)]^+$. When the catalyst precursor uses cyclooctadiene (cod) instead of norbornadiene (nbd), however, it has a twist conformation [5]. Even though the chair conformation is possible with this chelate cycle, the enantioselectivities are excellent [5].



Scheme 1.

We recently have synthesised new furanoside diphosphines **1** and **2** (Scheme 1), which form six-membered chelate rings when they coordinate to rhodium, and we have reported their use in the asymmetric hydrogenation of alkenes [6]. Our results showed that the configuration of the carbon atom C-5 strongly influences enantioselectivity. Therefore, enantioselectivities (ee up to 98% *S*) were best when we used the catalytic precursor containing ligand **2** with *R*-configuration in C-5, while ligand **1** produced moderate enantioselectivities (ee up to 53% *S*) [6]. In order to explain the different

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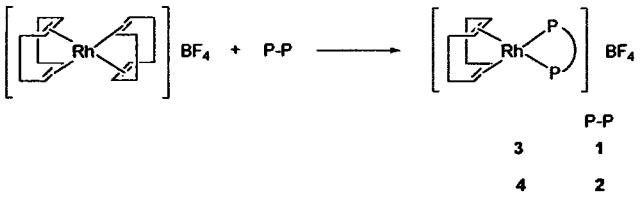


Scheme 2.

enantioselective efficiencies of these catalysts precursors, we report here the synthesis of the new pre-catalysts [Rh(cod)(diphosphine)]BF_4 (diphosphine = **1** and **2**) and their solution structures. We have paid special attention to the conformation of the six-membered chelate rings (which is directly connected with the special orientation of the phenyl groups) since it has been linked with the enantioselective efficiency of the catalysts [1].

2. Results and discussion

2.1. Synthesis and characterisation of Rh(I) complexes

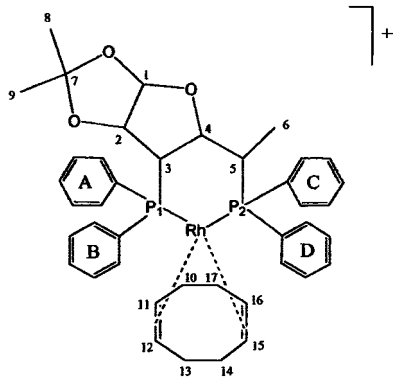
The chiral diphosphines **1** and **2** reacted quickly with [$Rh(cod)_2$]BF_4 in dichloromethane solution. One molecule of the 1,5-cyclooctadiene ligand was displaced to afford the cationic mononuclear complexes [Rh(cod)(diphosphine)]BF_4 **3** and **4** (Scheme 2).

The olefinic complexes **3** and **4** were isolated as moderately air stable yellow powders by adding diethyl ether. Elemental analysis of C and H matched the stoichiometry $[Rh(cod)(diphosphine)]_n(BF_4)_n$. The FAB mass spectra show the highest ions at m/z 752, which corresponds to the cationic mononuclear species. The IR spectra show a strong band between 1090 and 1050 cm^{-1} and a medium band around 450 cm^{-1}. These bands are characteristic of the non-coordinated BF_4^- anion [7].

The structure of the cations [Rh(cod)(diphosphine)]$^+$ (diphosphine = **1** and **2**) was obtained by ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy. The spectral assignments (Tables 1 and 2 and Section 3) were based on information from ^{1}H–^{1}H COSY, ^{13}C–^{1}H and ^{31}P–^{1}H correlation measurements, in combination with the ^{1}H–^{1}H NOESY results.

The expected pattern for the glucofuranoside nucleus was obtained for both complexes (Table 1 and Section 3). Vicinal ^{1}H,^{1}H couplings in the sugar rings were in the normal range (0–7 Hz) for furanoside systems [8]. The coupling constants ^3J(H-1,H-2) were larger than 3.5 Hz, which is consistent with the *cis*-disposition of these protons in both complexes (Table 1) [8]. Carbon atoms C-3 and C-5 appeared as doublets of doublets because each of the carbons couples with both phosphorus atoms (see Section 3).

Table 1
^{1}H NMR (400 MHz) assignments of compounds **3** and **4** in $CDCl_3$ solution (except aromatics)



Atom	**3**		**4**	
	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)
H-1	5.79 (d)	^3J(H-1,H-2) = 4.3	6.05 (d)	^3J(H-1,H-2) = 3.6
H-2	5.35 (dd)	^3J(H-2,P-1) = 2.2	5.54 (dd)	^3J(H-2,P-1) = 4.5
H-3	3.78 (dd)	^3J(H-3,H-4) = 7.6	3.99 (m)	^3J(H-4,H-3) = 4.2
H-4	5.11 (m)	^2J(H-3,P-1) = 5.2	4.75 (dd)	^3J(H-4,H-5) = 6.6
H-5	2.61 (ddd)	^3J(H-5,H-4) = 1.8	3.91 (m)	^3J(H-6,H-5) = 6.8
H-6	1.16 (dd)	^2J(H-5,P-2) = 10.3	1.62 (dd)	^3J(H-6,P-2) = 16.2
H-8	1.42 (s)	^3J(H-5,H-6) = 7.2	1.30 (s)	
H-9	1.59 (s)	^3J(H-6,P-2) = 11.8	1.35 (s)	
H-10	2.40 (m)		2.01 (m)	
H-11	4.69 (m)		4.82 (m)	
H-12	5.11 (m)		5.29 (m)	
H-13	2.53 (m)		2.54 (m)	
H-14	2.40 (m)		2.54 (m)	
H-15	4.92 (m)		5.38 (m)	
H-16	4.46 (m)		5.01 (m)	
H-17	2.40 (m)		2.23 (m)	

The olefinic protons H-11, H-12, H-15 and H-16 of the cyclo-1,5-octadiene appeared in the ^{1}H-NMR as separate broad signals, while the signals of the methylenic protons H-10, H-13, H-14, H-17 were only partially resolved (Table 1). The proton signals of the cod ring were assigned relatively according to the ^{1}H–^{1}H COSY spectrum and assigned absolutely according to the NOESY spectrum. In both complexes, all the cyclooctadiene carbon atoms were well resolved (see Section 3). The olefinic carbon atoms appear as doublets of doublets or triplets due to the ^{13}C–^{31}P and ^{13}C–^{103}Rh couplings.

As expected, the ^{31}P-NMR spectra of complexes **3** and **4** showed the presence of two non-equivalent phosphorus atoms. The signal pattern, which is characteristic of each phosphorus nucleus, consisted of a doublet of doublets with $^1J_{Rh-P} \approx 145$ Hz and $^2J_{P-P} \approx 45$ Hz (see Section 3). At 293 K the ^{31}P{^{1}H}-NMR spectrum of complex **4** showed two sharp doublets of doublets.

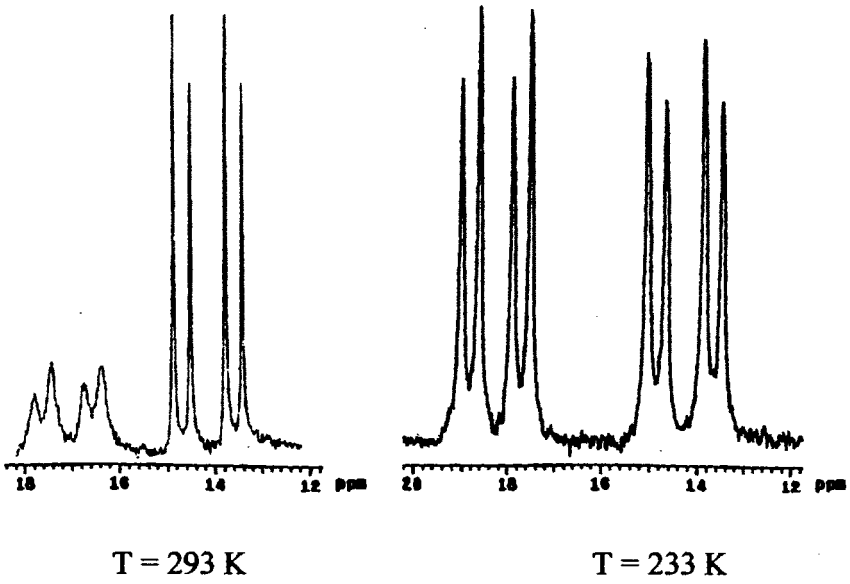


Fig. 1. VT $^{31}P\{^{1}H\}$-NMR spectra of complex **3**.

Table 2
Selected ^{1}H-NMR (400 MHz) data of the aromatic part of compound **3** and **4** in $CDCl_3$ solution

Complex	Phenyl	δ (ppm)			J (Hz)		
		ortho	*meta*	*para*	J(P–H-*o*)	J(H-*o*–H-*m*)	J(H-*o*–H-*p*)
3	A (P_1)	7.50	7.26	7.45	[a]	[a]	[a]
	B (P_1)	7.62	7.45	7.45	6.2	4.3	[a]
	C (P_2)	7.33	7.45	7.45	5.4	4.7	[a]
	D (P_2)	7.56	7.45	7.45	6.5	4.7	[a]
4	A (P_1)	7.40	7.64	7.64	6.4	4.5	2.0
	B (P_1)	8.18	7.80	7.80	6.1	4.7	2.4
	C (P_2)	7.29	7.59	7.59	5.8	4.7	2.4
	D (P_2)	8.04	7.72	7.72	6.4	4.6	2.4

[a] Not reliably determined.

However, the $^{31}P\{^{1}H\}$-NMR spectrum of complex **3** showed that the phosphorus signal at 19.5 ppm was a broad doublet of doublets, and the other phosphorus signals were sharp. This suggests a fluxional process on the ^{31}P-NMR time scale between two different conformers of the six-membered chelate ring (vide infra). This was confirmed by measuring the variable temperature (VT) $^{31}P\{^{1}H\}$- and ^{1}H-NMR spectroscopy.[1] At 233 K, sharp signals ($\Delta w_{1/2}$ around 8 Hz) were observed for both phosphorus atoms and suggested that only one conformer was present at 233 K (Fig. 1).

The signals of phosphorus atoms P-1 and P-2 were assigned by the $^{31}P-^{1}H$ correlation spectra, using the vicinal couplings between P-1/H-3 and P-2/H-5 and the long-range couplings between P-1/H-2 and P-2/H-6.

The $^{31}P-^{1}H$ correlation spectra were used to assign the ^{1}H-NMR signals of the four phenyl groups in pairs to the phosphorus atoms P-1 and P-2 (Table 2). For example, for complex **4** the signals at 7.40 (2H) and 8.18 (2H) ppm were assigned, respectively, to the *ortho*-protons of phenyls A and B attached to P-1; the *ortho*-protons of phenyls C and D attached to P-2 were found at 7.29 (2H) and 8.04 (2H) ppm, respectively.

For complex **4**, an $^{1}H-^{1}H$ COSY experiment helped in assigning the *meta*- and *para*-protons of the corresponding phenyl groups (Table 2). However, for complex **3** the *meta*- and *para*-protons appeared too close together to be reliably determined (Table 2).

We performed the 2D-NOESY experiments to obtain the spatial orientation of phenyl groups A–D and, therefore, the conformation adopted for the six-membered chelate ring. The 2D-NOESY spectrum of complex **3** at room temperature is showed in Fig. 2. Thus, the correlations involving the *ortho*-protons of the

[1] The VT-NMR indicates that the proton spectrum becomes broad at 278 K. At 233 K sharp signals were again obtained giving further support for the presence of only one conformer at low temperature.

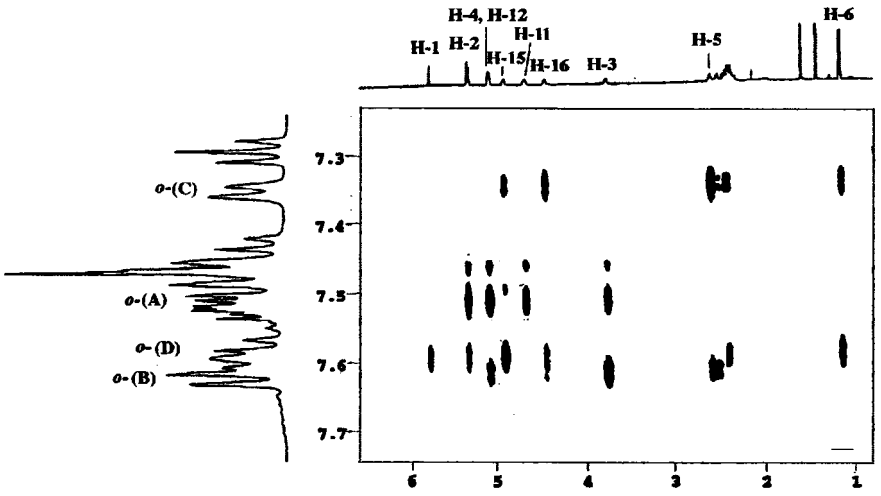


Fig. 2. Section of the 2D-NOESY spectrum of **3** with broadband ^{31}P decoupling.

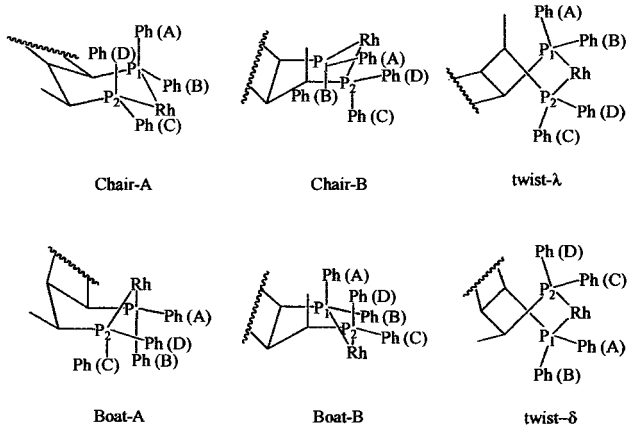
phenyl groups attached to P_1 (A and B) indicate that phenyl groups A and B are in an equatorial and axial position, respectively. The *ortho*-protons at 7.56 (D) showed cross peaks with protons H-1 and H-2, which indicates that this phenyl group is spatially close to the furanoside ring. The fact that the *ortho*-protons of phenyl groups C and D attached to P_2 have cross peaks with both olefinic protons H-15 and H-16 clearly indicates an equatorial–axial exchange, corroborating the dynamic behaviour of **3** observed in the VT-NMR spectra. Moreover, the olefinic proton H-15 correlates with proton H-6, which indicates that H-6 is in an axial position.

Examination of the models of all theoretically possible conformations of six-membered chelate rings (Scheme 3) showed that only the chair-B and the twist-δ conformations were compatible with the NMR data. Twist-λ? and chair-A conformations could be excluded because the phenyl group A (attached to P-1) was in the axial position. Moreover, twist-λ and boat-B conformations were highly inaccessible because of the steric hindrance between the axial phenyl groups and the methyl group (C-6).

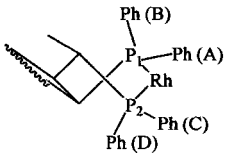
At 223 K, the 2D-NOESY spectrum of **3** showed that furanoside protons H-1 and H-2 had cross peaks with olefinic protons H-12 and H-15. This means that cyclooctadiene is spatially close to the furanoside ring. Olefinic proton H-15 also correlates with proton H-6, which indicates that H-6 is in an axial position. The models (Scheme 3) showed that only the chair-B conformation matched these NMR results.

Molecular mechanics calculations (CERIUS2) showed that chair-B was the most stable conformation. From these results and the spectroscopic study, we can conclude that at room temperature there is a fluxional process involving the chair-B and the twist-δ conformations for complex **3**. During the exchange process, the phosphorus P-1 remains almost unchanged, which could explain the sharp signals in its ^{31}P-NMR at room temperature. At low temperature, fluxionality was completely frozen, and only the most stable chair-B conformer was preferred.

The 2D-NOESY spectrum of **4** showed that there were cross peaks between the *ortho*-protons at 8.04 ppm (D) and the furanoside protons H-3, H-4 and H-6, and with olefinic proton H-16. The *ortho*-protons at 8.18 ppm (B) correlated with protons H-1, H-2, H-5 and H-6. The *ortho*-protons at 7.40 ppm (A) showed cross peaks with olefinic protons H-11 and H-12 and with proton H-2. The *ortho*-proton at 7.19 ppm (C) correlated with olefinic protons H-15 and H-16, and with H-6. From these data, we can conclude that complex **4** adopts a twist-λ conformation for the six-membered chelate ring. In this conformation, phenyl rings B and D are in an axial position, and the phenyl rings A and C and the methyl substituent are in an equatorial position (Scheme 4). The models and molecular mechanics calculations (CERIUS2) showed that the most stable conformer was twist-λ.



Scheme 3.



Twist-λ

Scheme 4.

In both complexes, the phenyl carbon atoms showed well-separated signals except for the quaternary carbon atoms which could not be assigned absolutely. The olefinic carbons appeared as a doublet because of the ^{13}C, ^{31}P couplings with the respective phosphorus atoms. For complex **4**, the geminal couplings $^2J_{P-C-o}$ of the phenyl moieties B and D were greater than those of moieties A and C, which corroborated the axial-spatial arrangement of phenyls B and D [9]. For complex **3**, the coupling value $^2J_{P-C-o}$ of phenyl moiety B was greater than A, while similar coupling values were obtained for phenyl moieties C and D. This further proves that, at room temperature, the twist-δ conformation and the chair-B conformation interchange.

In summary, NMR spectroscopy and molecular mechanics calculations showed that the configuration of the stereocenter C-5 greatly influenced the structure of these complexes and therefore their enantioselectivity. As expected for the structure of catalyst precursor **4**, the (*S*)-enantiomer, of the hydrogenate product, was predominantly formed. For catalyst precursor **3**, which shows a dynamic equilibrium between different conformers (chair-B and twist-δ), we suggest that the chair conformation is mainly responsible for the catalytic activity and, consequently, for the moderate enantiodiscrimination in favour of the (*S*)-enantiomer. This agrees with both the empirical rule that the twist-δ conformer should yield the (*R*)-enantiomer as the major product and the studies of Huttner et al., which show that with chair conformers, both (*S*)- and (*R*)-products can be obtained [4].

3. Experimental

3.1. General remarks

All syntheses were performed by standard Schlenk techniques under N_2 or Ar atmosphere. Complex $[Rh(cod)_2]BF_4$ [7a] and ligands **1** and **2** [6] were prepared by previously described methods. Solvents were purified by standard procedures. All other reagents were used as commercially available. Elemental analyses were performed on a Perkin–Elmer 240 B instrument. ^1H-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectra were recorded on Varian Gemini 300 MHz and 500 MHz spectrometers. Chemical shifts are relative to Me_4Si (^1H and ^{13}C) as internal standard, or H_3PO_4 (^{31}P) as external standard. All assignments in NMR spectra were determined by COSY, $^{31}P-^1H$ and $^{13}C-^1H$ correlation experiments. Standard pulse sequences were employed for the ^1H-2D-NOESY. The phase-sensitive NOESY experiments used mixing times of 1 s. EI mass spectra were obtained on an HP 5989 A spectrometer. VG-Autospect equipment was used for FAB mass spectral analyses. The matrix was *m*-nitrobenzylalcohol. Molecular mechanics calculations were carried out with the program CERIUS2 [10] developed by molecular simulations (MSI) and the force field UFF developed by Rappe and co-workers [11]. The electrostatic interactions were taken into account from the atomic changes generated by the Q_{eq} method [12].

3.2. Synthesis of cationic rhodium complexes

Diphosphane ligand (59.4 mg, 0.11 mmol) was added to a solution of $[Rh(cod)_2]BF_4$ (40.5 mg, 1 mmol) in CH_2Cl_2 (2 ml). After 10 min, the desired products were obtained by precipitation with Et_2O.

3.2.1. [Rh(cod)(**1**)]BF_4 (**3**)

^{31}P-NMR: δ 14.2 (dd, 1P, P-1, $^1J_{P-Rh} = 144.8$ Hz, $^2J_{P-P} = 47.1$ Hz), 16.9 (dd, 1P, P-2, $^1J_{P-Rh} = 139.7$ Hz, $^2J_{P-P} = 47.1$ Hz). ^{13}C-NMR: δ 17.2 (d, C-6, $J_{C-P2} = 3.4$ Hz), 26.9 (CH_3), 27.2 (CH_3), 29.7 (dd, C-5, $J_{C-P1} = 11.4$ Hz, $J_{C-P2} = 25.9$ Hz), 30.2 (CH_2), 30.3 (CH_2), 30.6 (C-13), 31.2 (CH_2), 43.8 (dd, C-3, $J_{C-P1} = 26.3$ Hz, $J_{C-P2} = 5.3$ Hz), 83.4 (m, C-4), 84.0 (d, C-2, $J_{C-P1} = 10.3$ Hz), 98.9 (t, C-12, $J_{C-P2} = J_{C-Rh} = 8.0$ Hz), 99.7 (dd, C-11, $J_{C-P2} = 9.2$ Hz, $J_{C-Rh} = 7.2$ Hz), 102.4 (dd, C-16, $J_{C-P1} = 9.2$ Hz, $J_{C-Rh} = 7.0$ Hz), 102.6 (dd, C-15, $J_{C-P1} = 8.9$ Hz, $J_{C-Rh} = 7.2$ Hz), 104.9 (C-1), 112.8 (C-7), 128.8 (d, C-*m*, $J_{C-P2} = 10.4$ Hz), 129.4 (d, C-*m*, $J_{C-P1} = 9.9$ Hz), 129.6 (d, C-*m*, $J_{C-P1} = 10.3$ Hz), 129.9 (d, C-*m*, $J_{C-P2} = 9.8$ Hz), 131.2 (d, C-*p*, $J_{C-P2} = 2.8$ Hz), 131.6(d, C–*p*, $J_{C-P1} = 2.5$ Hz), 131.7 (d, C-*o* A, $J_{C-P1} = 10.3$ Hz), 131.8 (d, C-*p*, $J_{C-P2} = 2.5$ Hz), 132.0 (d, C-*p*, $J_{C-P1} = 2.7$ Hz), 132.6 (d, C-*o* C, $J_{C-P2} = 11.1$ Hz), 132.9 (d, C-*o* B, $J_{C-P1} = 11.8$ Hz), 135.0 (d, C-*o* D, $J_{C-P2} = 11.2$ Hz). ^{31}P-NMR (223 K): δ 14.3 (dd, 1P, P-1, $^1J_{P-Rh} = 144.1$ Hz, $^2J_{P-P} = 45.8$ Hz), 18.4 (dd, 1P, P-2, $^1J_{P-Rh} = 135.5$ Hz, $^2J_{P-P} = 45.8$ Hz). ^1H-NMR (223 K): δ 1.06 (dd, 3H, H-6, $^3J_{6-5} = 3.0$ Hz, $^3J_{6-P2} = 10.4$ Hz), 1.41 (s, 3H, H-8), 1.61 (s, 3H, H-9), 2.28 (m, 4H, H-10, H-14), 2.46 (m, 4H, H-13, H-17), 2.52 (m, 1H, H-5), 3.98 (m, 1H, H-3), 4.44 (m, 2H, H-11, H-16), 4.87 (m, 1H, H-15), 5.15 (ddd, 1H, H-4, $^3J_{4-5} = 12.1$ Hz, $^3J_{4-3} = 3.9$ Hz, $^3J_{4-P2} = 8.2$ Hz), 5.26 (m, 1H, H-12), 5.34 (m, 1H, H-2), 5.97 (m, 1H, H-1), 7.25 (m, 2H, CH=), 7.41 (m, 16H, CH=), 7.56 (m, 2H, CH=). Anal. Found: C, 58.61; H, 5.61. Calc. for $C_{41}H_{46}BF_4O_3P_2Rh$ (838.4): C, 58.73; H, 5.53%.

*3.2.2. [Rh(cod)(**2**)]BF_4 (**4**)*

^{31}P-NMR: δ 21.0 (dd, 1P, P-1, $^1J_{P-Rh} = 145.5$ Hz, $^2J_{P-P} = 42.9$ Hz), 28.7 (dd, 1P, P-2, $^1J_{P-Rh} = 142.7$ Hz, $^2J_{P-P} = 42.9$ Hz). ^{13}C-NMR: δ 15.7 (d, C-6, $J_{C-P2} = 10.3$ Hz), 26.3 (dd, C-5, $J_{C-P1} = 4.2$ Hz, $J_{C-P2} = 28.6$ Hz), 27.6 (CH_3), 28.5 (CH_3), 33.1 (C-10), 33.4 (CH_2), 33.8 (C-17), 34.6 (CH_2), 45.8 (dd, C-3, $J_{C-P1} = 21.5$ Hz, $J_{C-P2} = 7.5$ Hz), 81.7 (m, C-4), 84.2 (d, C-2, $J_{C-P1} = 4.2$ Hz), 99.0 (t, C-11, $J_{C-P2} = J_{C-Rh} = 7.6$ Hz), 100.1 (dd, C-12, $J_{C-P2} = 9.1$ Hz, $J_{C-Rh} = 7.2$ Hz), 103.7 (C-1), 104.4 (dd, C-16, $J_{C-P1} = 9.4$ Hz, $J_{C-Rh} = 7.3$ Hz), 106.7 (dd, C-15, $J_{C-P1} = 9.3$ Hz, $J_{C-Rh} = 7.2$ Hz), 112.0 (C-7), 130.0 (d, C-*m* A, $J_{C-P1} = 10.5$ Hz), 130.3 (d, C-*m* D, $J_{C-P2} = 10.3$ Hz), 130.4 (d, C-*m* B, $J_{C-P1} = 10.9$ Hz), 130.6 (d, C-*m* C, $J_{C-P2} = 10.6$ Hz), 130.7 (d, C-*o* A, $J_{C-P1} = 11.3$ Hz), 131.9 (d, C-*p* A, $J_{C-P1} = 2.5$ Hz), 133.3 (d, C-*p* D, $J_{C-P2} = 2.7$ Hz), 133.8 (d, C-*p* B, $J_{C-P1} = 2.7$ Hz), 134.0 (d, C-*p* C, $J_{C-P2} = 2.5$ Hz), 135.3 (d, C-*o* C, $J_{C-P2} = 10.8$ Hz), 136.1 (d, C-*o* B, $J_{C-P1} = 13.5$ Hz), 136.8 (d, C-*o* D, $J_{C-P2} = 12.8$ Hz). Anal. Found: C, 58.86; H, 5.55. Calc. for $C_{41}H_{46}BF_4O_3P_2Rh$ (838.4): C, 58.73; H, 5.53%.

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