Pergamon

Tetrahedron: *Asymmetry* 9 (1998) 475–482

TETRAHEDRON: *ASYMMETRY*

Chiral discrimination at the η^3-allyl units of rhodium(I) η^3-cyclooctenyl complexes containing chiral bidentate phosphanes

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Received 26 November 1997; accepted 8 December 1997

Abstract

A three step synthesis of rhodium(I) η^3-cyclooctenyl complexes $[(P_2{*})Rh(\eta^3\text{-}C_8H_{13})]$ (P_2*=chiral bidentate phosphane) starting from commercially available $[\{(cod)Rh(\mu\text{-}Cl)\}_2]$ is described. Examination of these complexes by multinuclear NMR-spectroscopy reveals a distinct stereochemical differentiation of the terminal positions of the η^3-allyl unit. Preliminary results on the reactivity of these compounds towards various electrophiles are reported.

1. Introduction

η^3-Allyl transition metal complexes containing chiral phosphane ligands are an important class of organometallic compounds[1] which have found increasing interest as key intermediates in stoichiometric and catalytic asymmetric syntheses. For example, the enantioselective isomerization of allylamines to enamines involving a chiral rhodium(III) allyl intermediate is conducted on an industrial scale in the Takasago process.[2] The synthetically most useful application of chiral η^3-allyl transition metal complexes is probably the nucleophilic allylic substitution, which is of great interest in the asymmetric formation of C–C as well as C–X bonds.[3] Asymmetric allylation reactions have been reported for a broad range of substrates using chiral palladium complexes and very high levels of enantiocontrol can be achieved by the choice of suitable phosphorus ligands. Asymmetric allylic substitution reactions using complexes of transition metals other than palladium have been studied to a much lesser extent. A notable exception is the enantioselective allylic substitution of allylic phosphates catalyzed by tungsten complexes containing (phosphinoaryl)oxazoline ligands,[4] but it appears that this reaction does not proceed via a η^3-allyl intermediate.

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0957-4166/98/$19.00
PII: S0957-4166(97)00628-9

Allyl rhodium(I) complexes containing phosphane ligands are known to react with both nucleophiles[5] and electrophiles.[6] Whereas η^1-allyl intermediates are discussed in the first case, there is spectroscopic evidence for a η^3 binding mode during attack of electrophiles. Regardless of the mechanistic details, rhodium(I) allyl complexes have found surprisingly little attention as potential reagents or catalysts in asymmetric C–C or C–X bond formation. Even more unexpected is the apparent lack of data on the properties of chiral bisphosphane rhodium(I) η^3-allyl complexes.[7] Fryzuk briefly reported a complex where an η^3-allyl rhodium(I) fragment is coordinated with a chiral bidentate phosphane ligand, but there is no information on the influence of the chirality of the ligand on the properties of the η^3-allyl unit.[7a] In this paper we report the synthesis of new chiral complexes of type $[(P_2{*})Rh(\eta^3\text{-}C_8H_{13})]$ and on their full stereochemical analysis by multinuclear NMR-spectroscopy. Preliminary results on the reactivity of these compounds towards various electrophiles are also presented.

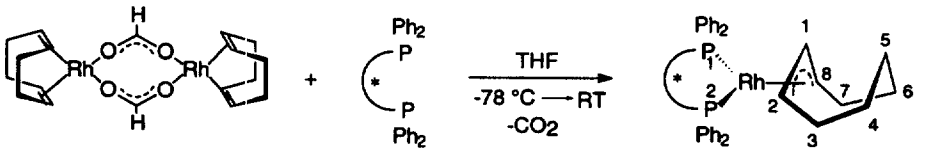
2. Results and discussion

We reported recently that achiral complexes of general formula $[(P_2)Rh(\eta^3\text{-cyclooctenyl})]$ **5** (P_2=$Ph_2P(CH_2)_nPPh_2$, n=3,4) are readily accessible in three steps from commercially available $[\{(cod)Rh(\mu\text{-}Cl)\}_2]$ **1** (cod=1,5-cyclooctadiene) via the intermediates $[\{(cod)Rh(\mu\text{-}X)\}_2]$ (X=OH, **2**; X=κ^2-O,O′–O_2CH, **3**).[8,9] The formation of the η^3-cyclooctenyl fragment occurs via decarboxylation of the bridging formate unit in **3** and subsequent hydride transfer from rhodium to coordinated 1,5-cyclooctadiene.[10] To optimize this synthetic procedure, we intended to convert **1** directly into **3** in analogy to the successful synthesis of the acetate complex $[\{(cod)Rh(\mu\text{-}\kappa^2O,O'\text{–}O_2CCH_3)\}_2]$ reported by Werner et al.[11] However, attempts to replace the bridging chloride with HCO_2^- by reacting **1** with KO_2CH in various solvents (acetone, THF, ether, benzene) resulted only in recovery of the starting material. Deliberate addition of small amounts of H_2O to enhance the solubility of the formate led mainly to formation of rhodium metal. Treatment of **1** with KOH and formic acid in ether at room temperature yielded a bright yellow solid which — unlike **3** — was insoluble in conventional organic solvents. The yellow solid decomposed slowly at room temperature with the apparent formation of rhodium metal even under an argon atmosphere and was therefore not characterized further.[12]

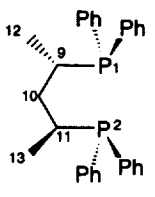
$$\underset{\mathbf{1}}{[\{(cod)Rh(\mu\text{-}Cl)\}_2]} \xrightarrow[TEBAC]{C_6H_6/KOH_{aq}} \underset{\mathbf{2}}{[\{(cod)Rh(\mu\text{-}OH)\}_2]} \xrightarrow[Et_2O]{HCO_2H} \underset{\mathbf{3}}{[\{(cod)Rh(\mu,\kappa2\text{-}O,O'\text{-}O_2CH)\}_2]} \quad (1)$$

Although direct conversion of **1** to **3** was not feasible, we were able to improve the synthesis of **3** considerably by preparing **2** from **1** using a two phase reaction mixture C_6H_6/aqueous KOH and benzyl triethylammonium chloride (TEBAC) as a phase transfer catalyst (Eq. (1)).[13] This allows much shorter reaction times than the previously employed procedure. The product **2** can be isolated in pure form from the reaction mixture by simple filtration and then converted to **3** following the established protocol.[8] Addition of the chiral phosphanes **4a–c** to **3** in THF leads smoothly to the formation of the chiral η^3-cyclooctenyl complexes **5a–c** as the major products in all cases, as indicated by ^{31}P-NMR spectroscopic control (Scheme 1, Table 1).

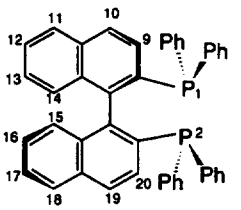
Complexes **5a–c** were unambiguously characterized by multinuclear NMR spectroscopy and mass spectroscopy (**5a**, **5c**). Analytically pure samples were obtained for **5c** and **5c′** by precipitation from Et_2O. We were unable to purify the initial product isolated from the reaction of **3** with **4b** (**5b**, 78% (^{31}P-NMR)) using similar procedures. Characteristic spectroscopic data of **5a–5c** are summarized in Scheme 1 and Table 1. The ^{13}C chemical shift of C-5 in **5c** (23.6 ppm) is characteristic for the η^3-cyclooctenyl



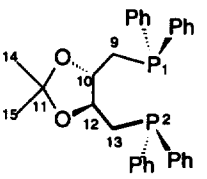
3 4a-c 5a-c



4a (-)-bdpp



4b (-)-binap



4c (-)-diop (4c' (+)-diop)

	δ_{H_1}	δ_{H_2}	δ_{H_8}	$\delta_{H_5}^{endo}$	$\delta_{H_5}^{exo}$
5a	5.41	3.95	3.54	1.35	2.36
5b	5.51	4.19	3.73		
5c	5.28	3.71	3.35	1.22	2.15

Scheme 1. Synthesis and selected ^{1}H-NMR data (C_6D_6) of chiral η^3-cyclo-octenyl complexes **5a–5c**

Table 1
^{31}P-NMR and ^{103}Rh-NMR data of **5a–c** (solvent: C_6D_6)

	T [K]	δ_{Rh}	δ_{P_1}	δ_{P_2}	$^1J_{RhP_1}$ [Hz]	$^1J_{RhP_2}$ [Hz]	$^1J_{PP}$ [Hz]
5a	298	-1002	39.9	39.9	192	192	
5b	298		42.0	43.1	199	201	31
5c	298	-1015	27.9	25.8	199.6	199.9	24.1
	313		27.6	25.8			
	333		27.4	26.0			
	353		27.3	26.1			

ligand adopting a boat-like conformation,[14] as is also observed in achiral complexes of type **5**.[8] The large chemical shift difference (approx. 1 ppm) between the *endo* and *exo* hydrogens at position 5, which is observed for complexes **5a** and **5c**, is also consistent with this conformation. The chemical shifts of the ^{103}Rh nuclei in complexes **5a** and **5c** are almost identical despite the chelate ring sizes of the rhodium phosphane moiety being different.[8]

Simultaneous coordination of a prochiral η^3-allyl moiety and a chiral C_2 symmetric chelating phosphane like **4a–c** at a 16e rhodium(I) center results in two diastereotopic phosphorus and terminal carbon sites. The different stereochemical environment may lead to differences in the chemical shifts of the respective nuclei, as has also been observed for related Pd(II)-complexes.[15] For the ^{31}P nuclei of complexes **5a–c** (Table 1), this differentiation is most strongly pronounced with the ligand diop (**4c**). The 81 MHz ^{31}P{^{1}H}-NMR spectrum of **5c** exhibits a line pattern characteristic of a AMX spin system (A,M=^{31}P, X=^{103}Rh) with a chemical shift difference $\Delta\delta(^{31}P)$=2.1. Under identical conditions, binap (**4b**) leads to an ABX spin system in **5b** ($\Delta\delta$=1.1), whereas for **5a** containing bdpp (**4a**) an apparent A_2X

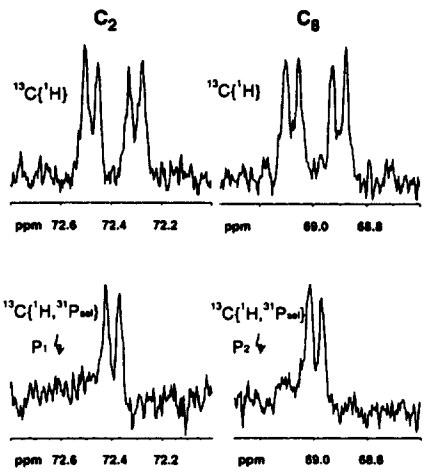


Fig. 1. $^{13}C\{^1H\}$-NMR spectrum (top trace) and simultaneously ^1H and selective ^{31}P decoupled ^{13}C-NMR spectrum (bottom trace) of the terminal allyl carbon atoms of **5c**

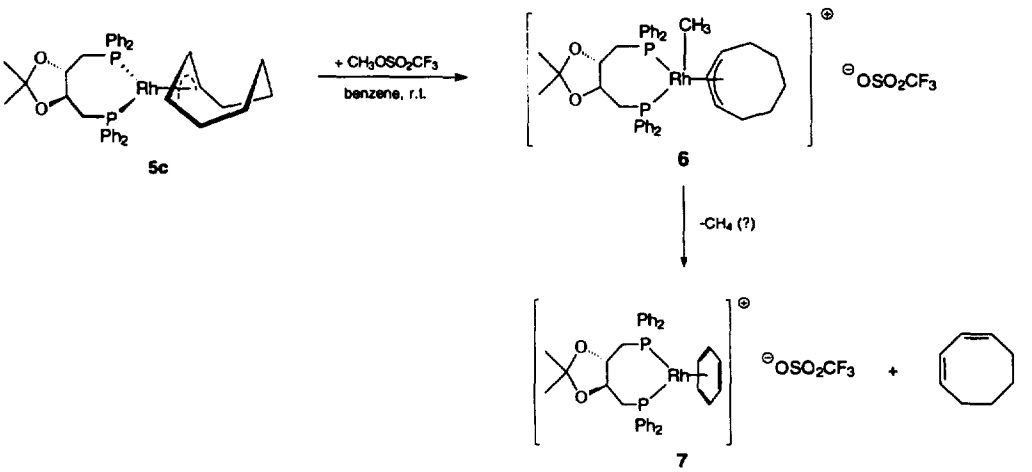
pattern results. The latter observation is in accordance with Fryzuk's findings for [(**4a**)Rh(η^3-C_3H_5)] and suggests that **4a** is not an effective ligand for chiral discrimination in rhodium(I) η^3-allyl complexes.

A detailed analysis of the ^1H- and ^{13}C-NMR spectroscopic data of **5c** reveals that the chirality of ligand **4c** leads also to a distinct differentiation of the terminal allylic positions of the η^3-cyclooctenyl ring. The complete connectivity of the hydrocarbon skeleton of the C_8H_{13} ring and the phosphane backbone was established by two dimensional $^1H,^1H$ and $^{13}C,^1H$ correlation spectra. The η^3-allyl moiety of **5c** is part of an eight membered ring and hence locked in an *anti,anti* arrangement. The allylic *syn*-protons at the terminal position of the η^3-allyl moiety exhibit characteristic and significantly distinct multiplets at 3.71 and 3.35 ppm, respectively. Each of the corresponding carbon atoms C-2 and C-8 appears as a doublet of doublets in the $^{13}C\{^1H\}$-NMR spectrum and the two signals are separated by 3.5 ppm. For both carbon atoms the coupling constants $^1J_{RhC}$ have a magnitude of 7.5 Hz and $^2J_{PtransC}$ is approximately 26 Hz. The coupling constants between the terminal allyl carbon atoms and the *cis*-phosphorus are very small and not resolved in the spectrum. A selective decoupling experiment was conducted to determine the position of the terminal allyl carbon atoms in relation to the two phosphorus atoms. As shown in Fig. 1, the signal of C_2 collapsed to a doublet by selective decoupling of P_1 demonstrating that C_2 is *trans* to P_1. Analogous changes are observed for the signal of C_8 upon selective irradiation of P_2.

Allyl rotation is known to be slow on the NMR time scale at room temperature for complexes of type **5** and for [(P_2)Rh(η^3-allyl)] complexes in general.[7,8] In the case of **5c**, this rigidity is evident because the coupling constants $^2J_{PC}$ are not averaged (see above). The temperature dependence of the ^1H- and ^{31}P-NMR spectra of **5c** was examined between 298 and 353 K. The experiments could not be extended to higher temperatures because slow darkening of the solution and concomitant formation of cyclooctene indicated that some decomposition was already occurring at 353 K. No evidence for rotation of the allyl moiety was found up to this temperature. The eight line AMX pattern in the $^{31}P\{^1H\}$-NMR spectrum of **5c** varies with temperature, but no significant line broadening is observed. Simulation of the spectra revealed that the spectral changes can be explained solely by temperature dependence of the ^{31}P chemical shifts (Table 1). These shift variations are most likely due to conformational changes in the phosphane backbone.[16]

The reactivity of complexes **5** was examined by treating benzene or THF solutions of **5c** with various electrophiles EX. Reaction of **5c** with Me_3SiCl, Me_3SnCl, $Me_3SiOSO_2CF_3$ or $MeOSO_2CF_3$ resulted in

hydrogen transfer under formation of cyclooctene or cyclooctadiene rather than in C–E bond formation. Control experiments revealed that hydrogenolysis of EX with traces of water can be excluded as a possible explanation for this lack of reactivity. Furthermore, a short lived intermediate was detected by ^{31}P-NMR spectroscopy (P_1: δ=17.0, $^1J_{RhP}$=143 Hz; P_2: δ=17.3, $^1J_{RhP}$=144 Hz, $^2J_{PP}$=8.4 Hz) during cyclooctadiene formation upon reacting a benzene solution of **5c** with $MeOSO_2CF_3$. At low temperature, the new complex had a sufficiently long lifetime to monitor a $^{13}C\{^1H\}$-NMR spectrum in toluene-[d_8], which showed a characteristic doublet (J=27 Hz) of poorly resolved multiplets at 12.0 ppm. The chemical shift and the multiplet structure are in agreement with a methyl group bound directly to a rhodium phosphane center,[17] and the new complex is therefore tentatively assigned as **6**. In benzene solution, complex **6** is rapidly converted to [((−)diop)Rh(C_6H_6)][F_3CSO_3] **7** (^{31}P-NMR: δ=29.7, d, $^1J_{RhP}$=202.5 Hz) and 1,3-cyclooctadiene upon warming to room temperature (Scheme 2). The identity of **7** was confirmed by independent synthesis *via* hydrogenation of [(**4c**)Rh(cod)] in CD_2Cl_2/C_6H_6.



Scheme 2. Reactivity of **5c** towards methyl triflate

In summary we have shown that chiral rhodium(I) phosphane complexes of type [(P_2*)Rh(η^3-C_8H_{13})] **5** are readily accessible from commercially available [{(cod)Rh(μ-Cl)}$_2$] **1** in three steps. The chiral ligand can lead to distinct stereochemical differentation of the terminal sites of the η^3-allyl moiety as revealed by $^{13}C\{^1H, ^{31}P\}$-NMR experiments. Complex **5c** reacts with electrophiles under attack at the metal center, but subsequent hydrogen transfer seems to be preferred over reaction pathways leading to C–E bond formation.

3. Experimental

3.1. General remarks

All manipulations of oxygen- and moisture-sensitive materials were conducted under an argon atmosphere using standard Schlenk techniques. Solvents were degassed and dried by standard methods. The following commercially available phosphane ligands were used without further purification: (−)-diop, (+)-diop (>99%, FLUKA), (−)-binap (97%, STREM), (−)-bdpp (99%, STREM). The complex [{(cod)Rh(μ-κ^2O,O′–O_2CH)}$_2$] **3** was prepared from **2** as described in our earlier publication.[8]

NMR measurements were recorded on a Bruker AC 200 spectrometer operating at 200, 50.3 and 81 MHz and on a Bruker AMX 600 spectrometer operating at 600.2, 150.9 and 243.0 MHz for ^{1}H, ^{13}C, and ^{31}P, respectively. Triple resonance experiments were carried out using a TBX triple resonance probe (^{1}H, ^{13}C, and tunable from ^{31}P to ^{109}Ag) and applying either (a) GARP or (b) selective CW decoupling for ^{31}P. The assignments of the ^{1}H and ^{13}C NMR spectra are based on COSY and 2D $^{1}H,^{13}C$ shift correlated spectra (*via* $^{1}J_{CH}$). $^{1}H,^{13}C$ coupling constants were obtained from gated decoupled ^{13}C NMR spectra and the multiplicities were confirmed by DEPT spectra. Chemical shifts are referenced to TMS for ^{1}H and ^{13}C and to H_3PO_4 for ^{31}P as an external standard, coupling constants are reported in Hertz. ^{103}Rh-NMR shifts were determined from 2D ($^{103}Rh,^{31}P$){^{1}H} experiments on a Bruker AMX 400 spectrometer[18] and chemical shift values are referenced to Ξ(Rh)=3.16 MHz.

3.2. *[{(cod)Rh(μ-OH)}$_2$] 2*

Eighty millilitres of a 0.2 M aqueous KOH solution containing 180 mg TEBAC was added over a period of 10 min under vigorous stirring to a solution of 2.51 g (5.09 mmol) 1 in 100 ml benzene. After stirring the mixture for 15 min the yellow product was filtered off and dried *in vacuo*. The analytical data were identical as described by Fornika et al.[8] Yield: 95%.

3.3. *General procedure for the synthesis of complexes type 5*

A quantity (0.5 mmol) of **3** was suspended in 30 ml THF and cooled to −78°C. A THF solution of 1.0 mmol **4** was added dropwise within 10 min. The reaction mixture was then warmed to room temperature and stirred for another 30 min. Evaporation of the solvent yielded yellow to red–orange solids that were redissolved for spectroscopic analysis and/or further purification.

3.4. *[(−)-(bdpp)Rh(η^3-C$_8$H$_{13}$)] 5a*

The crude yellow product contained more than 90% (^{31}P-NMR) of **5a** and was not purified further. MS m/z: 652 ($M^{\bullet+}$), 543 ($MH^{\bullet+}-C_8H_{12}$), 466 ($M^{\bullet+}-C_8H_{12}-C_6H_6$). ^{1}H-NMR (C_6D_6): δ=1.05 (m, 2H, H12, H13), 1.30 (m, 1H, $H5_{endo}$), 1.50 (m, 4H, H4, H6), 1.85 (m, 2H, H3), 1.93 (m, 2H, H10), 2.05 (m, 2H, H7), 2.36 (m, 1H, $H5_{exo}$), 2.70 (m, 2H, H9, H11), 3.54 (q, 1H, H8, $^{3}J_{HH}$=8), 3.95 (q, 1H, H2, $^{3}J_{HH}$=8), 5.41 (t, 1H, H1, $^{3}J_{HH}$=8), 7.20 (m, 16H, $H_{arom.}$), 7.82 (m, 4H, $H_{arom.}$). ^{31}P-NMR (C_6D_6): δ=39.9 (d, 2P, $^{1}J_{RhP}$=192). ^{103}Rh-NMR (C_6D_6): δ=−1002.

3.5. *[((−)-binap)Rh(η^3-C$_8$H$_{13}$)] 5b*

The crude red–orange product contained 78% **5b** according to ^{31}P-NMR data. Attempts to purify this material by standard purification methods were hampered by partial decomposition of **5b** in solution. ^{1}H-NMR (C_6D_6) δ=1.3–2.5 (m, 10H, H3-7), 3.73 (m, 1H, H8), 4.19 (m, 1H, H2), 5.51 (t, 1H, H1, $^{3}J_{HH}$=8), 6.4–8.5 (m, 32H, $H_{arom.}$). ^{31}P-NMR (C_6D_6) δ=42.0 (ABX, 1P, P1, $^{1}J_{RhP}$=199, $^{2}J_{PP}$=31), 43.1 (ABX, 1P, P2, $^{1}J_{RhP}$=201, $^{2}J_{PP}$=31).

3.6. *[((−)-diop)Rh(η^3-C$_8$H$_{13}$)] 5c, [((+)-diop)Rh(η^3-C$_8$H$_{13}$)] 5c′*

The crude material was recrystallised from ether affording pure **5c** (**5c′**) as a yellow solid. Yield: 83%. MS m/z: 710 ($M^{\bullet+}$), 602 ($MH^{\bullet+}-C_8H_{12}$), 524 ($M^{\bullet+}-C_8H_{12}-C_6H_6$). Anal. calc. for $C_{39}H_{45}P_2O_2Rh_1$

(710.64): C, 65.92; H, 6.38; P, 8.72; found **5c**: C, 65.74; H, 6.33; P, 8.69. ^{1}H-NMR (C_6D_6) δ=1.16 (s, 3H, H15), 1.24 (m, 1H, H4b), 1.26 (s, 3H, H14), 1.27 (m, 1H, H6b), 1.22 (m, 1H, $H5_{endo}$), 1.33 (m, 1H, H3b), 1.36 (m, 1H, H6a), 1.38 (m, 1H, H4a), 1.58 (m, 1H, H3a), 1.69 (m, 1H, H7b), 1.85 (m, 1H, H7a), 2.15 (m, 1H, $H5_{exo}$), 2.54 (dd, 1H, H9b, $^2J_{9b,9a}$=13, $^3J_{9b,10}$=9.6), 2.56 (dd, 1H, H13b, $^2J_{13b,13a}$=13, $^3J_{13b,11}$=9.7), 3.22 (t, 1H, H9a, $^2J_{9a,9b}$=13, $^2J_{9a,P1}$=13), 3.26 (t, 1H, H13a, $^2J_{13a,13b}$=13, $^2J_{13a,P2}$=13), 3.35 (m, 1H, H8, $^3J_{HH}$=8), 3.71 (m, 1H, H2, $^3J_{HH}$=8), 4.03 (m, 1H, H10), 4.04 (m, 1H, H12), 5.28 (t, 1H, H1, $^3J_{HH}$=8), 7.01 (m, 1H, $H_{p\text{-arom.}}$), 7.04 (m, 1H, $H_{p\text{-arom.}}$), 7.07 (m, 1H, $H_{m\text{-arom.}}$), 7.08 (m, 2H, $H_{m\text{-arom.}}$, $H_{p\text{-arom.}}$), 7.11 (m, 1H, $H_{m\text{-arom.}}$), 7.13 (m, 1H, $H_{p\text{-arom.}}$), 7.17 (m, 1H, $H_{m\text{-arom.}}$), 7.40 (dd, 1H, $H_{o\text{-arom.}}$, $^3J_{PH}$=9.5, $^3J_{HH}$=7.5), 7.47 (dd, 1H, $H_{o\text{-arom.}}$, $^3J_{PH}$=9.5, $^3J_{HH}$=7.5), 7.84 (dd, 1H, $H_{o\text{-arom.}}$, $^3J_{PH}$=10.0, $^3J_{HH}$=7.5), 7.98 (dd, 1H, $H_{o\text{-arom.}}$, $^3J_{PH}$=10.0, $^3J_{HH}$=7.5), ^{13}C{^{1}H}-NMR (C_6D_6) δ=23.6 (s, 1C, C5), 27.1 (s, 1C, C15), 27.3 (s, 1C, C14), 30.0 (dd, 1C, C6, $^4J_{CP2}$=4.2, $^4J_{CP1}$=1.6), 30.4 (dd, 1C, C4, $^4J_{P1C}$=3.9, $^4J_{P2C}$=1.4), 32.2 (d, 1C, C7, $^2J_{P2C}$=3.3), 33.0 (d, 1C, C3, $^2J_{P1C}$=3.0), 36.2 (m, 1C, C9), 36.3 (m, 1C, C13), 68.9 (dd, 1C, C8, $^1J_{RhC}$=7.5, $^2J_{P2C}$=26.0), 72.4 (dd, 1C, C2, $^1J_{RhC}$=7.5, $^2J_{P1C}$=26.5), 79.0 (dd, 1C, C10, $^2J_{P1C}$=14.6, $^3J_{P2C}$=0.7), 80.1 (d, 1C, C12, $^2J_{P2C}$=11.1), 104.7 (d, 1C, C1, $^1J_{RhC}$=5.3), 107.9 (s, 1C, C11), 127.9 (dd, 2 C, $C_{m\text{-arom.}}$, $C_{p\text{-arom.}}$, $^3J_{P2C}$=8.6, $^4J_{P2C}$=1.2), 128.0 (1C, $C_{p\text{-arom.}}$), 128.1 (dd, 2C, $C_{m\text{-arom.}}$, $^3J_{P1C}$=9.8, $^3J_{P1C}$=8.3), 128.4 (d, 1C, $C_{m\text{-arom.}}$, $^3J_{P2C}$=9.2), 129.7 (d, 1C, $C_{p\text{-arom.}}$, $^4J_{P1C}$=1.8), 129.9 (d, 1C, $C_{p\text{-arom.}}$, $^4J_{P2C}$=1.5), 130.8 (d, 1C, $C_{o\text{-arom.}}$, $^2J_{P2C}$=11.1), 131.3 (d, 1C, $C_{o\text{-arom.}}$, $^2J_{P1C}$=11.1), 134.8 (dd, 1C, $C_{o\text{-arom.}}$, $^2J_{P1C}$=14.3, $^3J_{RhC}$=1.3), 134.9 (d, 1C, $C_{o\text{-arom.}}$, $^2J_{P2C}$=14.9), 138.7 (d, 1C, $C_{i\text{-arom.}}$, $^1J_{P2C}$=29.4), 139.3 (ddd, 1C, $C_{i\text{-arom.}}$, $^1J_{P1C}$=34.0, $^2J_{RhC}$=2.3, $^3J_{P2C}$=0.7), 143.0 (dd, 1C, $C_{i\text{-arom.}}$, $^1J_{P1C}$=33.3, $^3J_{P2C}$=1.7), 145.1 (ddd, 1C, $C_{i\text{-arom.}}$, $^1J_{P2C}$=36.6, $^3J_{P1C}$=3.9, $^2J_{RhC}$=1.4). ^{31}P-NMR (C_6D_6) δ=25.8 (dd, 1P, P2, $^1J_{RhP}$=199.9, $^3J_{PP}$=24.1), 27.9 (dd, 1P, P1, $^1J_{RhP}$=199.6, $^3J_{PP}$=24.1). ^{103}Rh NMR (C_6D_6) δ=−1015.

Acknowledgements

This work was supported by the Max-Planck-Society, the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Dr. W. Baumann, Rostock, for recording the ^{103}Rh-NMR spectra. A generous loan of $RhCl_3 \times nH_2O$ by Degussa AG is gratefully acknowledged.

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