Synthesis and X-ray Structure of Metalated Rhodium(II) Catalysts with a Chiral Phospholane

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Dedicated to Professor R. Uson on the occasion of his 75th birthday

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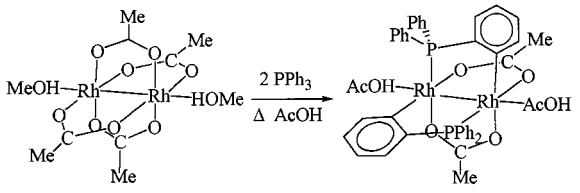
The reaction of $Rh_2(O_2CR)_4$ (R = CH_3, CF_3) with the chiral phosphane (2*S*,5*S*)-2,5-dimethyl-1-phenylphospholane (PC* H), results in the formation of two diastereoisomers of $Rh_2(O_2CCR)_2(PC^*)_2$, with (*P*) and (*M*) configuration. These can easily be isolated by chromatographic methods to obtain enantiomerically pure Rh^{II} compounds. Preliminary catalytic studies have shown that they induce moderate asymmetry in the cyclization of 5-aryl-1-diazo-2-pentanones and 1-diazo-5-hexen-2-one. X-ray analysis of the (*M*) diastereoisomer with formula $Rh_2(O_2CCCH_3)_2(PC^*)_2$ is reported. The crystallographic parameters are as follows: space group $P2_12_12$ (orthorhombic) with *a* = 12.1347(11) Å, *b* = 14.5870(13) Å, *c* = 9.8171(9) Å.

Introduction

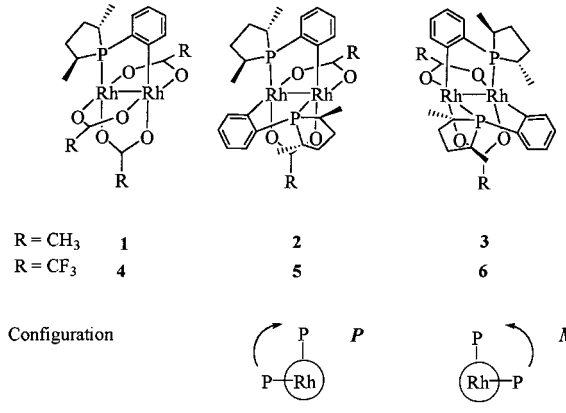
After the first report that the reaction of rhodium acetate and triphenylphosphane readily forms the bis(cyclometalated) compound $Rh_2(O_2CCH_3)_2[(C_6H_4)PPh_2]_2$,[1] it has been confirmed that this reaction can be extended to other rhodium carboxylates and to other arylphosphanes,[2−4] yielding the homologous metalated compounds $Rh_2(O_2CR)_2(PC)_2$, (PC = metalated phosphane; R = CH_3, CF_3; Scheme 1). Kinetic studies confirmed that the cyclometalation reaction was catalysed by protic acids.[5]



Scheme 1. *ortho*-Metalation reactions in binuclear dirhodium compounds

Different transition-metal compounds have been used as catalysts in the transformation of α-diazocarbonyl compounds, but the compounds of rhodium(II) have shown general utility.[6] We have reported that the bis(cyclometalated) complexes $Rh_2(O_2CR)_2(PC)_2$, exhibit excellent chemoselectivity in the catalytic intramolecular C−H insertion reactions of α-diazo compounds, where this reaction is competing with aromatic substitution.[7] In these compounds, the presence of two different ligands, the metalated phosphane and the carboxylate, allowed for a modulation of the electronic and steric properties of the catalyst which influence the activity and selectivity of the catalytic reactions.

Many efforts have been devoted to obtain chiral rhodium(II) complexes suitable for asymmetric induction in carbene transfer reactions. In this context, great success has been achieved by using rhodium(II) compounds having four chiral carboxylates[8] or amidate groups[9] as bridging ligands. As the bis(cyclometalated) complexes $Rh_2(O_2CR)_2(PC)_2$ with head-to-tail arrangement are inherently chiral, we have recently reported the isolation of the pure enantiomers [see (*P*) and (*M*) notation in Scheme 2]



Scheme 2. Structures of compounds $Rh_2(O_2CCR)_3(PC^*)$ and $Rh_2(O_2CCR)_2(PC^*)_2$ [(*P*) and (*M*) isomers]

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resulting from the metalation of PPh_3.[10] These enantiomers induced identical enantiomeric control, but with opposite *ee* values (36% *ee*; 70% yield), in the C−H insertion reaction of 1-diazo-5-phenyl-2-pentanone.

An alternative and previously unused approach to the preparation of chiral bis(cyclometalated) rhodium(II) compounds, is by the reaction of rhodium(II) carboxylates with a chiral $PhPR_2$* phosphane. Owing to the inherent chirality of $Rh_2(O_2CR)_2(PC)_2$ dimers,[10] this process would result in the formation of two diastereoisomers, which could be isolated to perform catalytic assays. Furthermore, since bis(cyclometalated) compounds having basic phosphanes have proved to be reactive and selective in carbene transfer reactions,[7] our primary objective was the generation of new, enantiomerically pure, cyclometalated rhodium(II) derivatives with chiral, electron-rich phospholanes[5] as ligands.

We describe in this paper the synthesis of several cyclometalated rhodium(II) compounds resulting from the reaction of rhodium acetate or rhodium trifluoroacetate and (2*S*,5*S*)-2,5-dimethyl-1-phenylphospholane (PC*H). The crystal structure of one of the isolated diastereoisomers of formula $Rh_2(O_2CCH_3)_2(PC^*)_2 \cdot 2\,CH_3CO_2H$ is also reported. Their utility in asymmetric induction has been studied in C−H insertion and cyclopropanation reactions of model diazo ketones. The observed enantioselectivities, though moderate, compare favourably with those obtained for other types of chiral rhodium(II) complexes[11,12] and reveal the great potential of these compounds in asymmetric catalysis.

Results and Discussion

Rhodium(II) acetate and (2*S*,5*S*)-2,5-dimethyl-1-phenylphospholane (molar ratio 1:2.2) were heated at reflux in a mixture of toluene and acetic acid (3:1). The reaction was considerably slow and did not go to completion even after 33 h. From this reaction mixture, three new compounds were isolated by column chromatography: the monometalated compound $Rh_2(O_2CCH_3)_3(PC^*)$ (**1**) (43%) and the two diastereoisomers $Rh_2(O_2CCH_3)_2(PC^*)_2$ [(*P*) isomer] (**2**) (23%) and $Rh_2(O_2CCH_3)_2(PC^*)_2$ [(*M*) isomer] (**3**) (13%).

These compounds exchange the carboxylate groups upon treatment with trifluoroacetic acid, to form the corresponding trifluoroacetate derivatives $Rh_2(O_2CCF_3)_3(PC^*)$ (**4**), $Rh_2(O_2CCF_3)_2(PC^*)_2$ [(*P*) isomer] (**5**), and $Rh_2(O_2CCF_3)_2(PC^*)_2$ [(*M*) isomer] (**6**) (Scheme 2).

The reaction of rhodium(II) trifluoroacetate and the phospholane was considerably faster and, after 16 h at room temperature in CH_2Cl_2 solution, the two bismetalated compounds **5** (32%) and **6** (14%) were formed. Under these conditions, the monometalated compound **4** was not detected in solution.

Crystal Structure of 3

A schematic drawing of the structure of compound **3** together with selected bond lengths and angles, is presented in Figure 1. In the dinuclear complex **3**, the two rhodium atoms are bridged by two acetate groups and by two phospholane molecules metalated at the phenyl ring; two oxygen atoms of two acetic acid molecules occupying the axial positions, complete the slightly distorted octahedral coordination (bond angles in the range 83.00−93.90 Å) around the metal centres. As observed in all the related compounds, each of these acetic acid molecules undergoes an O···H−O interaction with one oxygen atom of each bridging acetate group. The value of the Rh−Rh bond length 2.5036(6) Å falls within the range reported for dirhodium compounds of comparable structure.[13]

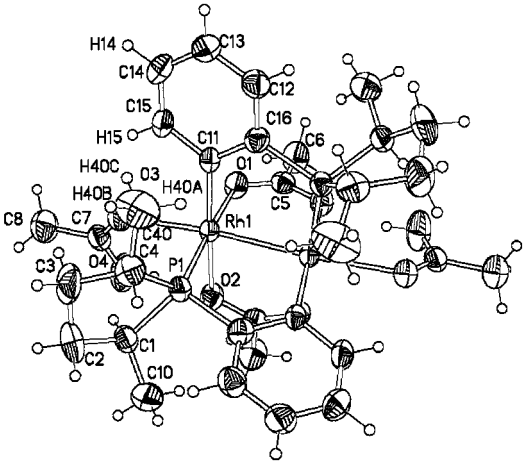
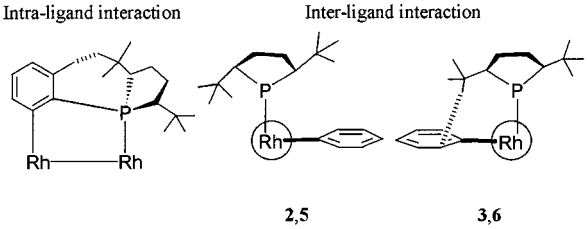


Figure 1. ORTEP diagram of the complex (*M*)-**3**·$(HO_2CCH_3)_2$; selected bond lengths [A] and angles [°]: Rh1−Rh1A 2.5036(6), Rh1−C16 1.992(4), Rh1−O2 2.196(2), Rh1−O3 2.370(3), Rh1−O1 2.139(2), Rh1−P1 2.2187(10); C16−Rh1−O1 89.45(12), O1−Rh1−O2 83.00(10), O1−Rh1−P1 175.15(8), C16−Rh1−O3 94.59(12), C16−Rh1−O2 172.43(12), P1−Rh1−O3 93.90(7)

The crystal structure determination confirmed that compound **3** has the (*M*) configuration. Consequently, compound **6** will have the same configuration while compounds **2** and **5** must have the (*P*) configuration (Scheme 2). An interesting feature in compound **3** is that the methyl group attached to C1 of the phospholane ring is oriented toward the metalated phenyl ring of the same phosphane ligand (intra-ligand interaction), while the methyl group attached to C4 points towards the metalated phenyl ring of the other phosphane (inter-ligand interaction). A simple molecular model built for compound **2** (or **5**) shows that for the (*P*) configuration only the intra-ligand interaction can be generated as is shown in Scheme 3.



Scheme 3. Model of inter- and intra-ligand interactions in compounds **2**, **3**, **5**, **6**

Spectroscopic Data

All the new compounds were characterised by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum of

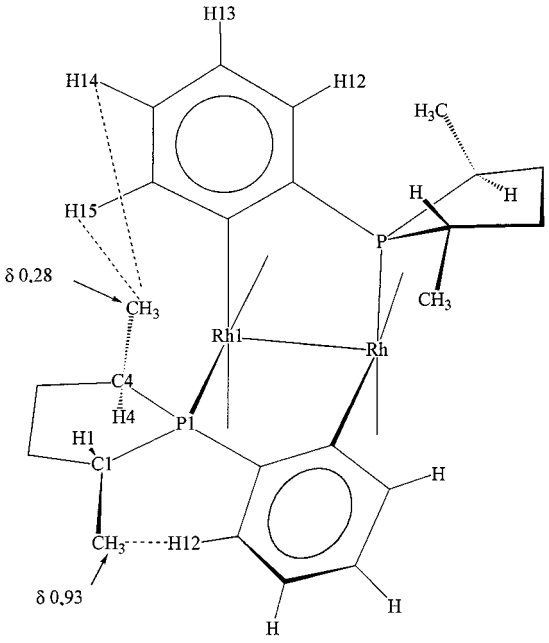
compound **1**, with only one metalated phosphane ligand, displays a characteristic doublet of doublets due to the coupling to both rhodium nuclei ($\delta = 35.9$; $^1J_{RhP} = 152$ Hz, $^2J_{RhP} = 3$ Hz). In contrast, the bis(cyclometalated) compounds show a multiplet corresponding to the AA′ part of an AA′XX′ system at lower chemical shift values ($\delta = 27.4$ and 28.3). As expected, the three acetate groups of compound **1** are magnetically different and this is reflected in the ^{1}H and ^{13}C NMR spectroscopic data.

The molecules of compound **3** have a crystallographic C_2 symmetry axis. This symmetry is apparently retained in solution as the four methyl groups of the phospholane ligands are equivalent in the ^{1}H NMR spectrum in a pairwise manner. These two signals are of equal intensity and integrate as 6 H each. They appear as doublets of doublets, showing coupling to one proton and to the phosphorus atom. The other three bis(cyclometalated) compounds show a similar pattern of signals for the phospholane ligands. The difference in chemical shift values for the methyl groups of the phospholane ligands is relatively small ($\delta \approx 0.6$) for compounds **2** and **5** but it is larger for complexes **3** and **6** ($\delta \approx 1.2$). This can be attributed to the different environments of the methyl groups in the (*P*) and (*M*) configurations and also to the possible H···H interactions (Scheme 3).

A careful NMR spectroscopy study carried out for compounds **5** and **6** confirmed that the supposed H···H interactions (see above) also occur in solution. The ^{1}H NMR spectrum of **6** displays three multiplet signals in the aromatic region which, based on COSY experiments, were assigned as following: $\delta = 6.85$ (H^{12}), 6.95 (H^{13} and H^{14}), and 7.56 (H^{15}). The signals at $\delta = 0.28$ and 0.93 were assigned to the methyl groups of the phospholane and appeared as very characteristic doublets of doublets owing to the coupling to the phosphorus atom and to the H^1 and H^4 protons whose signals appeared as multiplets at $\delta = 2.86$ and 2.33 , respectively. The assignment of these signals was made with an NOE experiment.

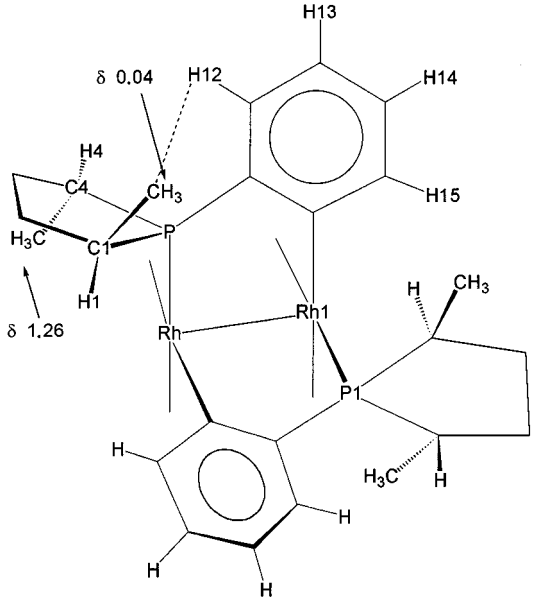
Irradiation of the methyl resonance at $\delta = 0.93$ led to an enhancement of the signal at $\delta = 2.86$, assigned to H^1, and also of the signal at $\delta = 6.85$ (Scheme 4). This is in agreement with an intra-ligand interaction between H^{12} and the protons of the methyl group attached to C^1. Irradiation of the methyl signal at $\delta = 0.28$ resulted in an enhancement of the intensity of the signal at $\delta = 2.33$, assigned to H^4, and also of the signals at $\delta = 6.95$ and 7.56. This result supports the interaction between the protons of the methyl group attached to C^4 and two aromatic protons, H^{15} and probably H^{14}.

Different results were obtained when this experiment was performed with isomer **5**. The ^{1}H NMR spectrum of **5** displays four signals in the aromatic region which, based on COSY experiments, were assigned as follows: $\delta = 6.74$ (H^{12}), 6.86 (H^{13}), 6.98 (H^{14}), 7.57 (H^{15}). We use the same labelling scheme as in compound **6** to identify the hydrogen atoms in compound **5**. The signals at $\delta = 0.04$ and 1.26 were assigned to the methyl groups of the phospholane and appeared again doublets of doublets. The protons H^1 and H^4 gave rise to a broad signal at $\delta = 2.37$.



Scheme 4. NOE experiment for compound **6**

In an NOE experiment (Scheme 5), irradiation of the methyl signal at $\delta = 0.04$ led to an enhancement of the intensity of the signal at $\delta = 2.37$, due to an interaction with H^1, and to that of the signal at $\delta = 6.74$. This result is indicative of an interaction between the protons of the methyl group attached to C^1 and the aromatic proton H^{12}. Irradiation of the methyl resonance at $\delta = 1.26$ gave only an enhancement of the signal at $\delta = 2.37$, due to an interaction with H^4, but not of any other signal in the aromatic region. These results support the *P*-configuration of compound **5**.



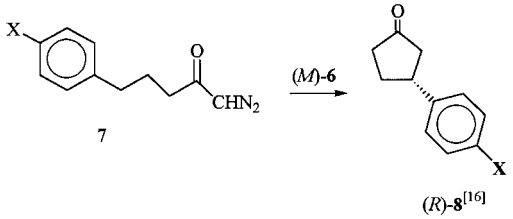
Scheme 5. NOE experiment for compound **5**

Exploratory Catalytic Studies

1-Diazo-2-alkanones were prepared from the corresponding acid by reaction with ethyl chloroformate, followed by treatment with freshly prepared diazomethane.

Catalytic reactions were performed by the addition of the rhodium(II) complex (1 mol-%) to an anhydrous dichloromethane solution containing the diazo compound; the reaction mixture was heated at reflux for 1 h. After cooling, the solution was filtered through a short plug of silica gel to remove the catalyst, and the solvent was evaporated under reduced pressure. The residue was analysed by ^1H and ^{13}C NMR spectroscopy.

We mainly studied the ability of the diastereoisomers (*P*)-**5** and (*M*)-**6** to induce a C−H insertion reaction of diazo compounds **7** (Scheme 6). Complex (*M*)-**6** catalysed the cyclisation of **7** with high yield but only a small variation in enantiomeric control was observed by the introduction of electron-withdrawing or electron-donating groups on the benzene ring of the organic substrate (Scheme 6). It is worth mentioning that although the enantiomeric control offered by these rhodium(II) compounds was modest, complexes containing chiral carboxamidates catalyse intramolecular aliphatic C−H insertion of 1-diazo-2-alkanones with practically no asymmetric induction.[11] Surprisingly, in the case of (*P*)-**5**, the diazo compounds **7** were recovered unchanged after several hours of heating in the presence of the rhodium catalyst.

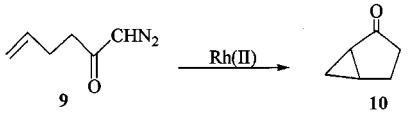


7 (*R*)-**8**[16]

	Yield (%)	% ee[15]
X = H	85	39
X = Cl	93	33
X = OCH_3	80	37

Scheme 6. C−H insertion of 1-diazo-5-aryl-2-pentanones

Both diastereoisomers (*M*)-**6** and (*P*)-**5** were able to transform the 1-diazo ketone **9** in high yield, but the sense and extent of the enantiotopic selection were different (Scheme 7). It is interesting to note that low enantiomeric control has been achieved in the intramolecular cyclopropanation of this type of diazo compound catalysed by chiral rhodium(II) carboxamides.[14] In particular, the cyclisation of the diazo ketone **9** using those catalysts have only provided levels of enantiomeric control in the 3−23% *ee* range.[12]



9 10

	Yield (%)	% ee[15]	
(*P*)-**5**	84	52	(1*S*,5*R*)[17]
(*M*)-**6**	90	22	(1*R*,5*S*)
Rh_2(carboxamidates)$_4$[12]	50-94	3-23	

Scheme 7. Cyclopropanation of 1-diazo-5-hexen-2-one

Conclusion

In summary, we explored the synthesis of chiral bis(cyclometalated) rhodium(II) compounds based on the use of a chiral phosphane. The reaction of dirhodium carboxylates with (2*S*,5*S*)-2,5-dimethyl-1-phenylphospholane led to two types of dimers with different environments around the Rh centre. Diastereoisomers were easily isolated by chromatographic methods. Preliminary catalytic studies showed their different efficiencies in inducing asymmetry in the cyclisation of model 1-diazo carbonyl compounds. The level of enantiomeric control, although moderate, is promising since other rhodium(II) catalysts have shown less selectivity in the transformation of this type of diazo compound. The availability of other chiral 2,5-disubstituted phospholanes[18] can allow further studies to determine the influence of the electronic and steric effects of the phosphane ligand on the reactivity and selectivity of these new chiral rhodium(II) catalysts.

Experimental Section

All reactions were carried out under argon, using standard Schlenk techniques. $Rh_2(O_2CCF_3)_4$ was prepared by literature procedures.[19] Other starting materials (besides the phospholane) were commercially available and used as received. Solvents were degassed and used without further purification. − NMR spectra were recorded with Bruker AC-200 and Varian Unity-300 spectrometers. Chemical shifts (δ values) are given relative to TMS (^1H, ^{13}C), and to 85% H_3PO_4 aqueous solution (^{31}P). Coupling constants (*J*) are given in Hertz.

Preparation of (2*S*,5*S*)-2,5-Dimethyl-1-phenylphospholane: This ligand was prepared according to literature procedures.[18]

Synthesis of Acetate Complexes 1−3: $Rh_2(O_2CCH_3)_4$ (206 mg, 0.433 mmol) and (2*S*,5*S*)-2,5-dimethyl-1-phenylphospholane (183 mg, 0.952 mmol) were heated at reflux in a mixture of toluene/acetic acid (6 mL, 3:1) for 33 h. After cooling, the solvent was evaporated under reduced pressure and the resulting violet solid was dissolved in CH_2Cl_2.The solution was purified by chromatography on silica gel. Elution with CH_2Cl_2/ether/acetone (50:10:1) separated a dark blue band from a green band. The blue band was collected and the solvent was evaporated. Crystallisation of the residue from acetone/hexane gave $Rh_2(O_2CCH_3)_3$(PC) (**1**) as a dark blue solid. Yield 115 mg (43%). − ^1H NMR ($CDCl_3$): δ = 0.63 (dd, J_{PH} = 13.8, J_{HH} = 6.8, 3 H, CH_3 ring), 1.03 (dd, J_{PH} = 15.6, J_{HH} = 6.9, 3 H, CH_3 ring), 1.71 (s, 3 H, CH_3 *cis*), 1.78 (s, 3 H, CH_3 *cis*), 2.11 (s, 3 H, CH_3 *trans*), 1.20−2.90 (m, 6 H, CH_2, CH ring), 6.60−9.00 (m, 4 H, C_6H_4). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 35.9 (dd, $^1J_{RhP}$ = 152, $^2J_{RhP}$ = 3). − The green band was redissolved in CH_2Cl_2.The solution was chromatographed on silica gel. Elution with CH_2Cl_2/acetone (5:1) led to a separation into two green bands. The green solutions were concentrated to dryness and dissolved in acetone. Addition of hexane precipitated green solids, which were dried in vacuum.

Fraction 1: Compound **2** [(*P*) isomer], 75 mg (23%). − ^1H NMR ($CDCl_3$): δ = 0.04 (dd, J_{PH} = 14.3, J_{HH} = 7.0, 6 H, CH_3 ring), 1.21 (dd, J_{PH} = 15.5, J_{HH} = 7.0, 6 H, CH_3 ring), 1.40−3.00 (m, 12 H, CH_2, CH ring), 2.15−2.25 (s, 6 H, CH_3COO) 6.70−7.52 (m, 8 H, C_6H_4). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 27.9 (AA′XX′ system).

Fraction 2: Compound **3** [(*M*) isomer], 41 mg (13%). – ^{1}H NMR ($CDCl_3$): δ = 0.33 (dd, J_{PH} = 15.1, J_{HH} = 7.1, 6 H, CH_3 ring), 0.97 (dd, J_{PH} = 13.6, J_{HH} = 6.9, 6 H, CH_3 ring), 1.40−3.00 (m, 12 H, CH_2, CH ring), 2.07−2.2 (s, 6 H, CH_3CO_2) 6.80−7.00 (m, 6 H, C_6H_4), 7.58 (dd J = 5.2, J = 2.7 2 H, C_6H_4). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 27.4 (AA′XX′ system).

Synthesis of Trifluoroacetate Derivative 4: $Rh_2(O_2CCH_3)_3(PC)$ (**1**) (58 mg, 0.1 mmol) was dissolved in CH_2Cl_2 and after trifluoroacetic acid (0.77 mL, 10 mmol) was added, the solution was stirred for 2 h. The solvent was removed under vacuum and the crude solid was dissolved in CH_2Cl_2 (1 mL).The solution was purified by chromatography on silica gel. Elution with CH_2Cl_2 gave a blue band from which a blue solid was obtained after evaporation of the solvent. – ^{1}H NMR ($CDCl_3$): δ = 0.60 (dd, J_{PH} = 15.8, J_{HH} = 6.6, 3 H, CH_3 ring), 1.22 (dd, J_{PH} = 16.6, J_{HH} = 6.9, 3 H, CH_3 ring), 0.94−2.80 (m, 6 H, CH_2, CH ring), 6.98−8.53 (m, 4 H, C_6H_4). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 36.3 (dd, $^1J_{RhP}$ = 141, $^2J_{RhP}$ = 4).

Synthesis of Trifluoroacetate Derivatives 5 and 6: $Rh_2(O_2CCF_3)_4$ (100 mg, 0.21 mmol) and (2*S*,5*S*)-2,5-dimethyl-1-phenylphospholane (188 mg, 0.46 mmol) were stirred in CH_2Cl_2 (6 mL) for 16 h. The solvent was evaporated under reduced pressure and the resulting violet solid was worked up as described for the acetate derivatives **2** and **3**.

Compound 5 [(*P*) Isomer]: 116 mg (32%). – ^{1}H NMR ($CDCl_3$): δ = 0.04 (dd, J_{PH} = 15.5, J_{HH} = 7.0, 6 H, CH_3 ring), 1.26 (dd, J_{PH} = 16.0, J_{HH} = 6.2, 6 H, CH_3 ring), 0.80−2.50 (m, 12 H, CH_2, CH ring), 6.74 (t, J = 7.7, 2 H, C_6H_4), 6.86 (t, J = 7.4, 2 H, C_6H_4), 6.98 (t, J = 7.5, 2 H, C_6H_4), 7.58 (dd J = 7.9, J = 3.6, 2 H, C_6H_4). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 29.1 (AA′XX′ system).

Compound 6 [(*M*] Isomer]: 48 mg (14%). – $[\alpha]_D$ = +423 (c = 0.04, $CHCl_3$). – ^{1}H NMR ($CDCl_3$): δ = 0.28 (dd, J_{PH} = 15.4, J_{HH} = 7.2, 6 H, CH_3 ring), 0.93 (dd, J_{PH} = 15.5, J_{HH} = 8.5, 6 H, CH_3 ring), 1.4−3.00 (m, 12 H, CH_2, CH ring), 6.85 (m, 2 H, aromatic H), 6.95 (m, 4 H, aromatic H), 7.56 (m, 2 H, aromatic H). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 27.4 (AA′XX′ system).

Crystallographic Data Collection and Refinement of the Structure: A Siemens SMART CCD diffractometer was used for data collection on crystals of the compound. Unit-cell dimensions were determined by a least fit of 50 reflections, ($2.07° < \theta < 23.32°$) The crystal structure determination was done by direct methods, using SHELXTL V 5.05;[20] the refinement on F^2 was done using all reflections. The positions of all non-hydrogen atoms were deduced from difference Fourier maps and were refined anisotropically. Hydrogen atoms were placed in their geometrically generated positions and were refined riding on the carbon atom to which they are attached. Green single crystals were grown in CH_2Cl_2/hexane. $C_{32}H_{46}O_8P_2Rh_2$: crystal size 0.3 × 0.25 × 0.3 mm, M = 826.45, orthorhombic, space group $P2_12_12$ with a = 12.1347(11), b = 14.5870(13), c = 9.8171(9) Å, V = 1737.7(3) Å^3 and Z = 2 ($\rho_{calcd.}$ = 1.579 g cm^{-3}), μ (Mo-K_α) = 1.088 mm^{-1}. 3932 reflections measured, 2174 unique (R_{int} = 0.0212), which were used in all calculations. Data/parameters 2174:205. The final R value was 0.0187 ($wR2$ = 0.042). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-142404. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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