Diastereospecific Control in the Synthesis of Enantiomerically Pure Bis-Equatorial Rhodium(II) Catalysts by Chiral Phosphanes

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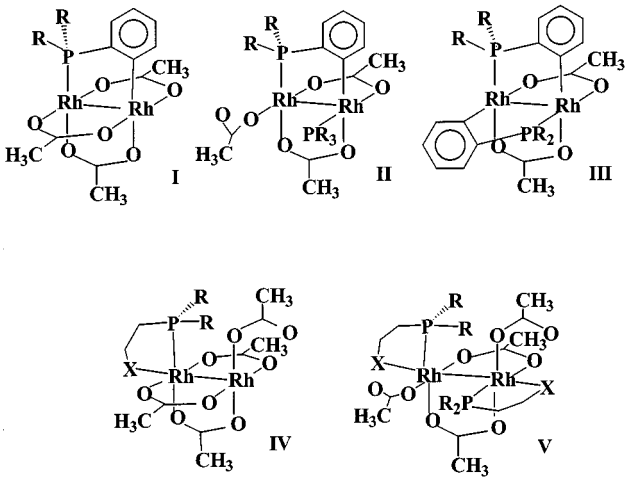
The reaction of $Rh_2(O_2CR)_4$ [R = CH_3, CF_3] with the chiral phosphane (1*S*,2*S*,5*R*)-(2-hydroxy-5-isopropenyl-2-methylcyclohexyl)(diphenyl)phosphane, (+)PPh_2(CH–R*–OH) or its enantiomer (1*R*,2*R*,5*S*)-(2-hydroxy-5-isopropenyl-2-methylcyclohexyl)(diphenyl)phosphane, (–)-PPh_2(CH–R*–OH), results in the specific formation of the products (*P*)-$Rh_2(\mu\text{-}O_2CR)_2(\eta^1\text{-}O_2CR)_2\{\eta^2\text{-}(+)PPh_2(CH–R^*–OH)\}_2$ [**P(+)1**, R = CH_3; **P(+)2** R = CF_3] and (*M*)-$Rh_2(\mu\text{-}O_2CR)_2(\eta^1\text{-}O_2CR)_2\{\eta^2\text{-}(-)PPh_2(CH–R^*–OH)\}_2$ [**M(–)1**, R = CH_3; **M(–)2**, R = CF_3] in a high yield. Their synthesis, characterisation and catalytic behaviour in metal–carbenoid reactions are reported. X-ray analysis of **P(+)2** and **M(–)2** shows, in each case, a Rh_2^{4+} unit supported by two bridging and two monodentate trifluoroacetates; two phosphanes, (+)PPh_2(CH–R*–OH) or (–)PPh_2(CH–R*–OH) respectively, acting as chelating equatorial (P) and axial (O) donor ligands, complete the coordination sphere. These compounds are a pair of enantiomers. The crystallographic parameters are as follow: for **P(+)2**, space group $P3_121$ (trigonal) with $a = b = 13.0366(8)$, $c = 29.756(2)$ Å, $Z = 6$ and $R = 0.0499$; for **M(–)2** space group $P3_2$ (trigonal) with $a = b = 12.9751(9)$, $c = 29.685(3)$ Å, $Z = 3$ and $R = 0.0747$.

Introduction

The current interest in the development of rhodium(II) compounds recently observed[1] is due to their applications in catalytic metal−carbene transformations.[2] Most rhodium(II) compounds are formulated as $[Rh_2(ABC)_4L_2]$ and have the lantern-type structure characteristic of dimetal tetracarboxylate compounds.[1a] Cotton[3] and others[4] have reported that rhodium(II) carboxylate compounds with arylphosphanes afford compounds of the type $[Rh_2(\mu\text{-}O_2CR)_{4-x}(\mu\text{-PC})_x]$ (x = 1,2; R = CH_3 or CF_3; PC = metalated arylphosphane).

The great variety of these structures[3,4] and the possibility of modifying these compounds for specific purposes ensure continued emphasis on synthesis, characterisation and catalytic studies.[5] Cyclometalated rhodium(II) compounds with structures of type **I**−**III** (Scheme 1) have been characterised by X-ray methods,[3a][4a][4b] and some of them have shown chemoselectivity in diazo transformations.[4f]



Scheme 1. Rhodium compounds type **I**−**V**

Related compounds with *ortho*-functionalised phosphanes and structures **IV**[6] and **V**, [5] have also been reported. It should be noted that structures **III** and **V** have C_2 symmetry and consequently are inherently chiral. Compounds with the formula $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2$, with structure **III**, have been isolated as pure enantiomers by conventional resolution methods.[7] The resolved enanti-

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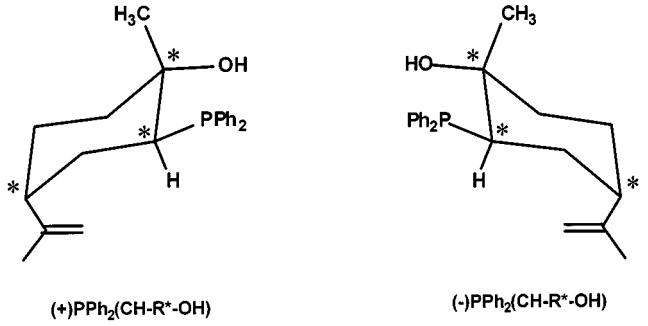
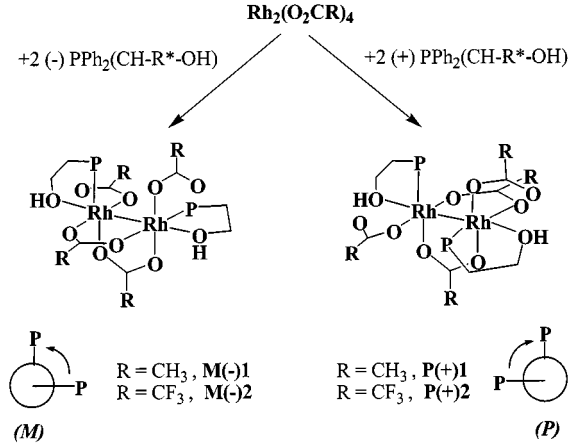
omers induce moderate enantioselectivity in a C−H insertion reaction.

Compounds of type **V**, with acetate groups and X = Cl, OCH_3, have shown catalytic activity in cyclopropanation reactions.[5] Considering the potential interest of these type of compounds as pure enantiomers, we explored their selective synthesis by using the chiral phosphanes (*1S*,2*S*,5*R*)-(2-hydroxy-5-isopropenyl-2-methylcyclohexyl)(diphenyl)-phosphane, (+)-PPh_2(CH−R*−OH)[8] or its enantiomer (1*R*,2*R*,5*S*)-(2-hydroxy-5-isopropenyl-2-methylcyclohexyl)(diphenyl)-phosphane, (−)-PPh_2(CH−R*−OH) (Scheme 2).



Scheme 2. (1*S*,2*S*,5*R*)-(2-hydroxy-5-isopropenyl-2-methylcyclohexyl)(diphenyl)phosphane (+)PPh_2(CH−R*−OH) and its enantiomer, (−)PPh_2(CH−R*−OH)

We describe in this paper the diastereospecific synthesis of compounds **P(+)1** and **P(+)2** from the reaction of (+)-PPh_2(CH−R*−OH) with rhodium acetate or trifluoroacetate (Scheme 3). Similar reactions with the phosphane (−)-PPh_2(CH−R*−OH) produced **M(−)1** and **M(−)2**. We also report on the X-ray structure of the trifluoroacetate derivatives **P(+)2** and **M(−)2**, as well as the catalytic behaviour of several of these compounds.



Scheme 3. Synthesis of bis equatorial rhodium(II) catalysts by reaction of chiral phosphanes with rhodium tetracarboxylates

Results

Synthetic Aspects

Addition of 2 equivalents of (+)-PPh_2(CH−R*−OH) to a solution of $Rh_2(O_2CCH_3)_4$·2MeOH in refluxing toluene/acetic acid (3:1), resulted in the formation of a green solution from which the complex (*P*)-$Rh_2(\mu\text{-}O_2CCH_3)_2(\eta\text{-}O_2CCH_3)_2\{\eta^2\text{-}(+)\text{-}PPh_2(CH-R^*-OH)\}_2$ **[P(+)1]** was easily isolated in a high yield. The same reaction with the phosphane (−)-PPh_2(CH−R*−OH) yielded the corresponding enantiomer (*M*)-$Rh_2(\mu\text{-}O_2CCH_3)_2(\eta\text{-}O_2CCH_3)_2\{\eta^2\text{-}(-)\text{-}PPh_2(CH-R^*-OH)\}_2$ **[M(−)1]**.

Addition of 2 equiv. of (+)-PPh_2(CH−R*−OH) to a solution of $Rh_2(O_2CCF_3)_4$ in diethyl ether at room temperature, yielded the complex (*P*)-$Rh_2(\mu\text{-}O_2CCF_3)_2(\eta\text{-}O_2CCF_3)_2\{\eta^2\text{-}(+)\text{-}PPh_2(CH-R^*-OH)\}_2$ **[P(+)2]** in a high yield. The same reaction with the phosphane (−)-PPh_2(CH−R*−OH) yielded the corresponding enantiomer (*M*)-$Rh_2(\mu\text{-}O_2CCF_3)_2(\eta\text{-}O_2CCF_3)_2\{\eta^2\text{-}(-)\text{-}PPh_2(CH-R^*-OH)\}_2$ **[M(−)2]**.

X-ray Analysis

The crystal structures for compounds **P(+)2** and **M(−)2** have been determined by X-ray procedures. ORTEP diagrams, with the corresponding atom-labelling schemes are shown in Figure 1 and 2 for both the compounds together with selected bond lengths and angles.

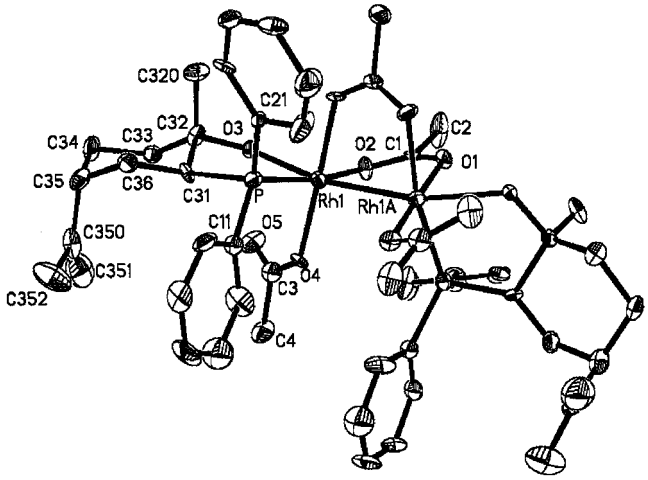


Figure 1. ORTEP diagram of the complex (*P*)-$Rh_2(\mu\text{-}O_2CCF_3)_2(\eta^1\text{-}O_2CCF_3)_2\{\eta^2\text{-}(+)PPh_2(CH-R^*-OH)\}_2$ **[P(+)2]** with the F and H atoms omitted for clarity; selected bond lengths [Å] and angles [°]: Rh1−Rh1A 2.5873(13), Rh1−O3 2.250(5), Rh1−P 2.252(3), Rh1−O2 2.148(8); O1−Rh1−O4 176.4(3), O2−Rh1−P 168.9(2), O3−Rh1−Rh1A 165.8(2), O4−Rh1−P 92.6(2)

The structure of **P(+)2** consists of an Rh_2^{4+} unit supported by two bridging and two monodentate trifluoroacetates; two (+)PPh_2(CH−R*−OH) phosphanes, acting as chelating equatorial (P) and axial (O) donor ligands, complete the coordination sphere around the metal atoms.

The two bridging trifluoroacetate groups are in a *cisoid* configuration and the phosphorous atoms exhibit a (*P*) configuration.

The Rh−Rh bond length, 2.5873(13) Å, is slightly longer than the distance [2.5605(11) Å] found in a structurally related compound with the formula $[Rh_2(\mu\text{-}O_2CCH_3)_2(\eta\text{-}Cl)_2\{\eta^2\text{-}(o\text{-}CH_3OC_6H_4)P(C_6H_5)_2\}_2]$.[5]

One interesting feature of **P(+)2** is that the axial Rh−O bond length, 2.250(5) Å, is shorter than that observed in the analogous $[Rh_2(\mu\text{-}O_2CCH_3)_2(\eta\text{-}Cl)_2\{\eta^2\text{-}(o\text{-}CH_3\text{-}$

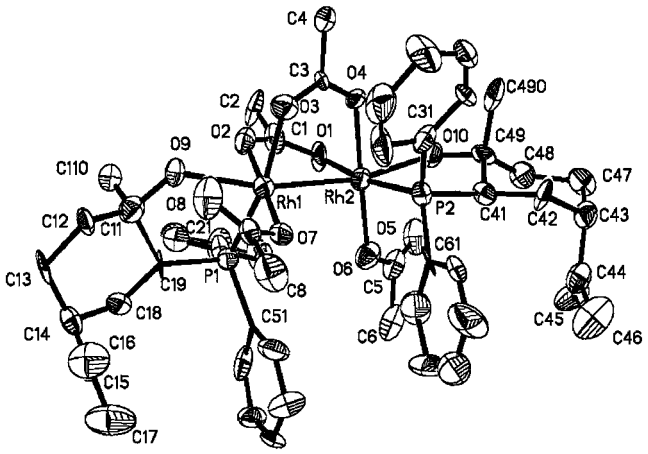


Figure 2. ORTEP diagram of the complex $(Rh_2(\mu\text{-}O_2CCF_3)_2(\eta^1\text{-}O_2CCF_3)_2\ \{\eta^2\text{-}(-)PPh_2(CH-R^*-OH)\}_2$ [**M(−)2**] with the F and H atoms omitted for clarity; selected bond lengths [Å] and angles [°]: Rh1−Rh2 2.6011(18), Rh1−O9 2.255(13), Rh1−P1 2.246(5), Rh1−O3 2.170(12); O2−Rh1−O7 176.0(5), O3−Rh1−P 169.1(4), O9−Rh1−Rh2 166.6(3), O7−Rh1−P 93.0(3)

$OC_6H_4)P(C_6H_5)_2\}_2$, 2.342(7) Å].[5] This distance is also shorter than the average Rh−O distance observed for rhodium(II) bis-adduct complexes with oxygen donor ligands.[1a][3a,4]

Compound **M(−)2** has the same overall structure as **P(+)2**, but has an (*M*) configuration. The Rh−Rh distance of 2.602(8) Å, is typical for such a type of species.

NMR-Spectroscopic Data

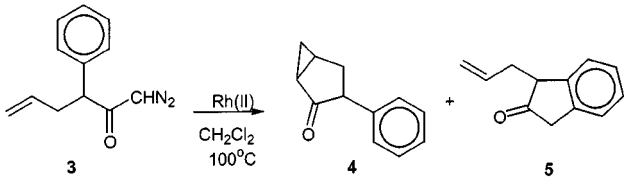
The spectroscopic data recorded for all the isolated compounds, support that the solid-state structure is maintained in solution. The ^{31}P NMR spectra show a second-order signal, with a very similar chemical shift for all the isolated compounds ($\delta \approx 46$), that corresponds to the AA′ part of an AA′XX′ system. This high value of the chemical shift is characteristic of nonmetalated phosphanes in an equatorial coordination.[5] The signals from the protons of the OH groups of the phosphanes appear at a remarkable low field, ($\delta \approx 10-12$), in agreement with the axial Rh−O coordination observed in the X-ray data. In particular, the homonuclear shift correlated 2D NMR spectrum of **P(+)2** confirms the coupling between the proton of the OH group (at 10.1 ppm) with the CH_3 group at $\delta = 1.4$ ppm, and also the coupling between the olefinic protons ($\delta = 4.2$ and 4.6) and the methyl group ($\delta = 1.1$).

The NMR-spectroscopic data also confirms the existence of two different types of carboxylate groups in each compound. Thus, compounds **P(+)2** and **M(−)2**, with trifluoroacetate groups, show two resonance signals in the corresponding ^{19}F NMR spectra. For the corresponding compounds with acetate groups, **P(+)1** and **M(−)1**, the ^1H NMR spectra show four resonance signals of equal intensity; two of these signals, at $\delta = 1.4$ and 1.1, correspond to the phosphane while the others, at $\delta = 1.0$ and 1.2, correspond to the acetate groups.

Catalytic Studies

The X-ray structural analysis provides evidence for the relatively strong coordination of the OH groups of the phosphanes to the axial site of the rhodium centre. This data suggests a low reactivity of these rhodium dimers toward diazo compounds; in order to confirm this assumption, control experiments were performed. Thus, the reaction of ethyl diazoacetate with compound **P(+)2** in dichloromethane, was carried out in a sealed tube at different temperatures in the 45−100 °C temperature range. We only observed a transformation of the diazo compound at temperatures close to 100 °C; at lower temperatures the substrate was recovered unchanged after extensive heating. ^{31}P and ^1H NMR spectra confirm that no decomposition of the rhodium compound occurred during this heating.

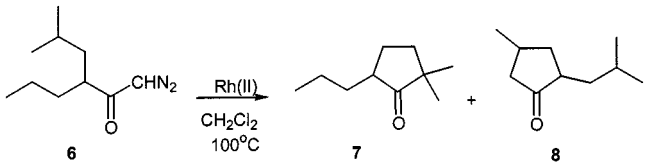
Studies of chemo- and regioselectivity of compounds **P(+)1** and **P(+)2** in diazo compound transformation were performed by using model substrates. Diazo ketone **3**[9] was used to study the competition between the cyclopropanation reaction and aromatic substitution (Scheme 4), while diazo ketone **6**[10] was used for similar studies in tertiary versus secondary C−H insertion reaction (Scheme 5). It is remarkable that these compounds led to a similar selectivity as rhodium acetate. Not surprisingly, these rhodium compounds exhibited poor enantioselectivity in the cyclopropanation of 1-diazo-5-phenyl-2-pentanone[11] (enantiomeric excess less than 6%).



3 **4** **5**

Complex	Yield(%)	4	5
1	75	69	31
2	74	60	40
$Rh_2(O_2CCH_3)_4$	92	63	27

Scheme 4. Cyclopropanation vs. aromatic substitution



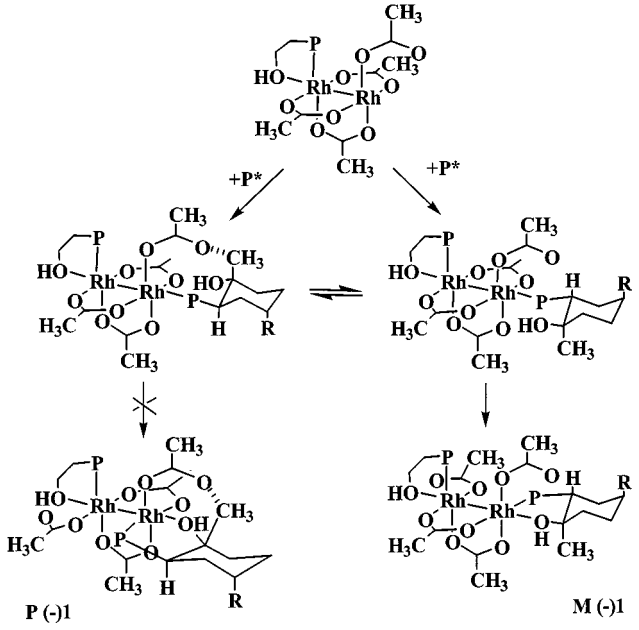
6 **7** **8**

Complex	Yield(%)	7	8
1	85	73	27
2	80	76	24
$Rh_2(O_2CCH_3)_4$	84	79	21

Scheme 5. Aliphatic tertiary vs. secondary C−H insertion

Discussion

The above results confirm that it is possible to induce diastereospecificity in the synthesis of compounds of type **V**, $Rh_2(\mu\text{-}O_2CR)_2(\eta\text{-}O_2CR)_2(\eta\text{-}P{-}X)_2$, using the OH-functionalised chiral phosphanes (+)PPh_2(CH−R*−OH) and (−)PPh_2(CH−R*−OH). As the formation of these compounds occurs by coordination of the phosphane to one axial coordination site, followed by migration from the axial to the equatorial position, this highly chiral induction could be rationalised in terms of the steric effects in some of the steps of this process. Thus, in Scheme 6 the reaction intermediate is represented with the axial ligand (−)PPh_2(CH−R*−OH) in the two extreme orientations leading to each diastereoisomer. It also shows how the repulsive interaction between the methyl group of the entering phosphane and the monodentate carboxylate group is especially important in the intermediate that leads to the diastereoisomer **P(−)1**, justifying the selective formation of the **M (−)1** isomer. The same applies to the reaction with the phosphane (+)PPh_2(CH−R*−OH), where the only isomer formed is **P(+)1**.



R = isopropenyl
P*= (-)PPh_2(CH-R*-OH)

Scheme 6. Proposed origin of the diastereospecificity

The low activity and selectivity of these catalysts must be a consequence of the relatively strong Rh−O axial ligation. The high temperature needed to reach catalytic activity suggests that, under such thermal conditions, Rh−O bond dissociation can take place supplying free active catalytic sites.

The high temperature needed to liberate the active catalytic site produces the carbene transfer reaction in relatively drastic conditions and precludes the selective diazo transformation. In fact, the selectivities shown by these compounds are similar to those reported for the poorly selective rhodium acetate.[9]

Conclusion

These results confirm the ability of a functionalised chiral phosphane, to induce diastereospecificity in the synthesis of chiral rhodium(II) compounds. The above described catalytic results prove that the relatively strong axial Rh−O coordination lowers the activity of the synthesised species of structural type **V**. In general, this strong axial coordination must be considered as a negative effect in the design of a catalyst. However, we suggest that this property might be used in a beneficial way in the case of complexes of type **II**. In this case the functionalised phosphane could be used to block one axial coordination site, leaving the other metal centre open for interaction with the diazo compound. Thus, the use of this sort of functionalised phosphanes in the synthesis of chiral complexes of type **II**, appears as a useful strategy for obtaining enantiomerically pure species with only one available position for catalytic purposes.

Experimental Section

General Considerations: Commercially available $Rh_2(O_2CCH_3)_4{\cdot}2MeOH$ was purchased from Pressure Chemical Com. $Rh_2(O_2CCF_3)_4$ $2(Me_2CO)$,[12] the phosphanes (+)PPh_2(CH−R*−OH),[8] and (−)PPh_2(CH−R*−OH)[8] and the diazo compounds **3**,[9] **6**,[10] and **9**[11] were prepared according to literature procedures. − Solvents were distilled prior to use. − ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and ^{19}F NMR spectra were recorded with a Varian−300 Unity and with a Bruker AM-250 instrument; spectra were obtained as solutions in $CDCl_3$. − Elemental analyses were performed at Centro de Microanálisis Elemental (Universidad Complutense de Madrid). − Optical rotations were measured with a Perkin−Elmer 241 polarimeter at the Na-D line in 10-cm quartz cuvettes. − The UV/Vis measurements were performed with a Varian Cary 1 spectrophotometer.

X-ray Crystallographic Procedures: Single crystals of compounds **P(+)2** or **M(−)2** were obtained by slow diffusion of hexane into an ethyl ether solution of each compound at room temperature. X-ray diffraction experiments were carried out with a Siemens Smart diffractometer with a CCD detector using Mo-K_α radiation. Unit cell dimensions were determined by a least fit of 50 reflections, ($2.73° < \theta < 23.31°$). All calculations were done using SMART software for data collection.[13] Empirical absorption correction was applied on compound **P(+)2**. The structures were solved by direct methods, and refined on F^2 with the program SHELXTL.[14] The positions of the remaining atoms were located after an alternating series of least-squares cycles and difference Fourier maps. Anisotropic displacement parameters were assigned to all nonhydrogen atoms, except to C51 on **M(−)2**, which was refined isotropically. Hydrogen atoms were placed in geometrically generated positions and refined riding on the carbon atom to which they are attached. Crystal Data: **P(+)2**: $C_{26}H_{26}F_6O_5PRh{\cdot}1/2CHCl_3$, M = 728.05, trigonal, $a = b = 13.0366(8)$, $c = 29.756(2)$ Å, V = 4379.6(5) Å^3, T = 293 K, space group $P3_121$, Z = 6, μ(Mo-K_α) = 0.851 mm^{-1}, 6335 reflections measured, 2615 unique (R_{int} = 0.0426) which were used in all calculations. Data/parameters

2615:351. The final R was 0.0499 ($wR2$ = 0.098). − **M(−)2**: $C_{52}H_{52}F_{12}O_{10}P_2Rh_2{\cdot}2H_2O$, M = 1358.69, trigonal $a = b$ = 12.9751(9), c = 29.685(3) Å, V = 4328.0(6) Å^3, T = 173 K, space group $P3_2$, Z = 3, μ(Mo-K_α) = 0.723 mm^{-1}, 6662 reflections measured, 4751 unique (R_{int} = 0.0547) which were used in all calculations. Data/parameters 4751:715. The final R was 0.0747($wR2$ = 0.1762). − Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-139657 **[P(+)2]** and CCDC-139658 **[M(−)2]**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

General Procedure for Rhodium(II)-Catalysed Reactions of Diazo Compounds: The rhodium(II) compound (1%) was added under argon to a solution containing a diazo compound (0.5 mmol) in dry dichloromethane (4 mL). The mixture was heated at 100 °C in a sealed tube. The extent of reaction was monitored by TLC, using hexane/ethyl acetate as the eluent, until the diazo starting material was consumed. The solution was filtered through a 1-cm plug of silica gel, followed by washing with CH_2Cl_2 (20 mL). The filtrate was concentrated in vacuum and the residue was directly chromatographed with a mixture of hexane/ethyl acetate (10:1).

(*P*)-Rh$_2$(μ-O$_2$CCH$_3$)$_2$(η^1-O$_2$CCH$_3$)$_2${η^2-(+)PPh$_2$(CH−R*−OH)}$_2$ [P(+)1]: $Rh_2(O_2CH_3)_4{\cdot}2$(MeOH) (0.15 g, 0.3 mmol) was refluxed with (+)PPh$_2$(CH−R*−OH) (0.22 g, 0.65 mmol) in toluene/acetic acid (3:1) (30 mL) for 1 h. The resulting green solution was concentrated to dryness to yield a green solid that was crystallised from CH_2Cl_2/hexane giving **P(+)1** (0.30 g, 80%). − $[\alpha]_D$ = −39 (c = 0.125, $CHCl_3$). −^{1}H NMR ($CDCl_3$): δ = 12.0 (s, 2 H, OH), 7.8 (m, 4 H, aromatic protons), 7.0−7.5 (m, 16 H, aromatics), 4.5 (s, 2 H, HC=C), 4.0 (s, 2 H, HC=C), 2.6 (m, 2 H, HC−P), 2.3−1.5 (m, 14 H, cyclohexyl protons), 1.4 (s, 6 H, CH_3), 1.2 (s, 6 H, acetate), 1.1 (s, 6 H, CH_3), 1.0 (s, 6 H, acetate). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 21.6 (CH_3C=C), 23.0 (CH_3, acetate), 23.7 (CH_3COH), 26.2, 29.6, 38.3, 38.6 (cyclohexyl carbons), 55.1 (HC−P), 75.3 (COH), 111.5 (CH_2=C), 127.4, 127.7, 129.5, 129.9, 132.7, 134.5 (aromatic carbons), 143.9 (C=CH_2), 184.6 (OOC acetate), 188.5 (O_2C acetate). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 46 ($^1J_{Rh-P}$ = 163 Hz, $^2J_{Rh-P}$ = −5 Hz, J_{Rh-Rh} = 20 Hz). − UV/Vis ($CHCl_3$): $\lambda_{max}(\varepsilon)$ = 321 nm (41690), 258 nm (32370). − $C_{52}H_{66}O_{10}P_2Rh_2$ (1118.94): calcd. C 55.80, H 5.95; found C 55.49, H 5.58.

(*P*)-Rh$_2$(μ-O$_2$CCF$_3$)$_2$(η^1-O$_2$CCF$_3$)$_2${η^2-(+)PPh$_2$(CH−R*−OH)}$_2$ [P(+)2]: (0.08 g, 0.25 mmol,) of solid (+)PPh$_2$(CH−R*−OH) was added to a solution of $Rh_2(O_2CCF_3)_4{\cdot}2(Me_2CO)$ (0.07 g, 0.1 mmol) in diethyl ether (15 mL). The resulting brown-red solution was stirred overnight. The solvent was removed, the residue was crystallised from CH_2Cl_2/hexane to give **P(+)2** (0.14 g, 86%). − $[\alpha]_D$ = −61 (c = 0.06 in $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 10.1 (s, 2 H, COH), 7.7 (m, 4 H, aromatic protons), 7.2−7.6 (m, 16 H, aromatics), 4.6 (s, 2 H, HC=C), 4.2 (s, 2 H, HC=C), 2.7 (m, 2 H, HC−P), 2.3−1.8 (m, 14 H, cyclohexyl protons), 1.4 (s, 6 H, CH_3), 1.1 (s, 6 H, CH_3). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 21.5 (CH_3C=C), 23.2 (CH_3COH), 26.2, 29.7, 38.4, 38.6 (cyclohexyl carbons), 55.1 (HC−P), 74.5 (COH), 112.4 (CH_2=C), 126.0, 128.1, 128.3, 130.7, 131.5, 134.0, 134.2 (aromatic carbons), 143.2 (C=CH_2), 168.0 (OOC), 168.8 (OOC). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 45.7 ($^1J_{Rh-P}$ = 154.57 Hz, $^2J_{Rh-P}$ = 10.6 Hz). − ^{19}F{^{1}H} NMR ($CDCl_3$): δ = −75.6 (s, 6 F), −75.0 (s, 6 F). − UV/Vis ($CHCl_3$): $\lambda_{max}(\varepsilon)$ = 442 nm (2470), 335 nm (3807), 248 nm (23480). − $C_{52}H_{54}F_{12}O_{10}P_2Rh_2{\cdot}2H_2O$ (1370.86): calcd. C 45.56, H 4.27; found C 45.17, H 3.96.

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