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Synthesis and rhodium complexation of enantiomerically enriched bicyclo[3.3.1]nona-2,6-diene

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ABSTRACT

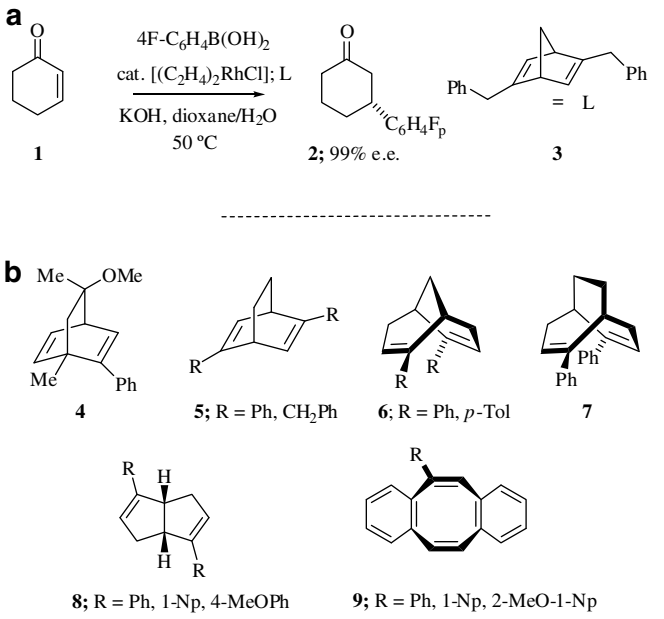
Enantiomerically enriched (*S*,*S*)-bicyclo[3.3.1]nona-2,6-diene has been synthesised from the readily available diketone (*S*,*S*)-bicyclo[3.3.1]nonane-2,6-dione. The stereochemical purity is maintained on complexation to rhodium. There is a very strong preference for the formation of the homochiral over the heterochiral (alkene)$_2$Rh$^+$ OTf$^-$ complex; the self-recognition involved can be rationalised by analysis of DFT calculations.

1. Introduction

Traditionally, asymmetric catalysis by organometallic complexes involves heteroatom ligands that control the stereochemical course of reaction. Phosphorus, nitrogen and mixed P–N chelates feature most prominently. The possibility of using a dialkene chelate for this purpose had not been demonstrated prior to Hayashi's work. In the original paper,[1] rhodium complexes of a chiral bicyclohepta-[2.2.1]diene were used to catalyse the conjugate arylation of αβ-unsaturated ketones (Scheme 1a). Excellent ee's were obtained, and the work was rapidly followed up, extending both the range of viable catalytic asymmetric reactions[2] and the range of chiral dienes (Scheme 1b).[3,4]

The coordination of dialkenes to rhodium, iridium and ruthenium is long established, since the ensuing stable complexes, especially from cycloocta-1,5-diene and bicyclohepta[2.2.1]diene, are the most common precatalysts.[5] The ground state of cycloocta-1,5-diene exists as a pair of rapidly interconverting C_2-symmetric enantiomers.[6] The induced chirality of its cationic rhodium diphosphine complexes has been used occasionally as a tool for predicting the sense of asymmetric hydrogenation.[7]

In contrast to the efforts employed to understand the origins of diphosphine-controlled asymmetric catalysis,[8] comparatively little work has been directed towards the role of enantiomerically pure dienes. Herein, we report the preparation of a simple example, the intent being to understand molecular recognition processes involved in diene-derived selectivity, and also to develop new applications in catalysis.



Scheme 1. (a) The original example of rhodium diene catalysis; (b) further examples of ligands employed.

2. Results and discussion

There are two broad classes of (bi)cyclic chiral diene, and both have been utilised in catalysis. The first is based on a symmetrical and intrinsically achiral framework, most commonly [2.2.*n*]. Compounds **3**–**5** fall into this category. Examples **6**–**8** are distinct in that the bicyclic system is intrinsically chiral, independent of the

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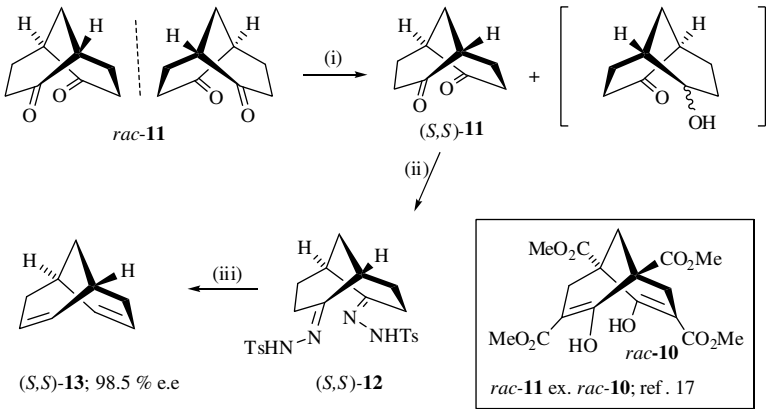
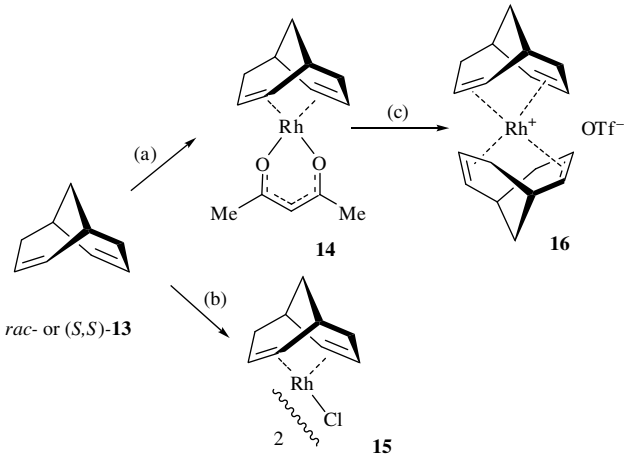


Scheme 2. Reagents and conditions: (i) Yeast, glucose, H_2O, 24 h, 39%; (ii) $TsNHNH_2{\cdot}HCl$, 81%; (iii) $LiN(iPr)_2$, TMEDA, 15 h, 0 °C to rt, 78%.

vinylic substituents. In all cases, they can be regarded as conformationally frozen cycloocta-1,5-dienes. None of the corresponding parent dienes had previously been prepared in enantiomerically pure form. In considering possibilities, ready access to the bicyclo[3.3.1]nonane skeleton afforded by Meerwein's classic route to compound **10** from malonate and formaldehyde weighed strongly.[9] The reports of efficient yeast-promoted kinetic resolution of the derived diketone **11** were a further factor.[10] In addition, a route from racemic diketone via the bis-tosylhydrazone **12** to racemic diene *rac*-**13** had already been developed.[11] In carrying this out, some modifications were made to the yeast reduction in order to ensure a consistently high product ee, since there was evidence of diminution of enantioselectivity if the reaction was allowed to continue for too long (Scheme 2).

The final Shapiro reaction-based step was adapted for small scale synthesis. It proved convenient to store the product diluted with small quantities of pentane. The enantiomeric purity was established by chiral GC (CydexB). Previous DFT calculations predicted that the hitherto unknown (*S*,*S*)-diene would have a specific rotation of −54.8 (zero frequency),[12] compared to the experimental value of −122 at 22 °C in $CDCl_3$. It was first established that diene (*S*,*S*)-**13** formed stable rhodium complexes. Preparation of the neutral pentanedioate complexes *rac*-**14** or (*S*,*S*)-**14** gave single products without any detectable double bond isomerisation. The racemic chloro-bridged dimer *rac*-**15** is known but has not previously been fully characterised by NMR.[13] In repeating the preparation, it was observed that key signals in the ^1H and ^{13}C NMR of the racemate were doubled. In particular, the H alkene protons at 4.74 ppm show further doubling (δ 0.04 ppm) and both alkene ^{13}C signals are likewise doubled by ca. 0.14 ppm, giving a triplet appearance since $J_{C,Rh}$ is comparable to the diastereomeric splitting at 100 MHz. Such complexity was absent from the NMR spectra of the enantiopure form (*S*,*S*)-**15**, indicating that the (R^*,R^*)-homochiral and (R^*,S^*)-heterochiral diastereomers contributed equally to the racemic complex (Scheme 3).

The new bis-alkene complexes *rac*-**16** and (*S*,*S*)-**16** were prepared from complexes *rac*-**14** and (*S*,*S*)-**14**, respectively. Unlike the bridged RhCl dimers **15**, the two diastereoisomeric forms possess simple and indistinguishable NMR spectra, for example, five ^{13}C signals only. Before ascribing this to homochiral recognition in the $(alkene)_2Rh$ cation, coincident signals for the two diastereomeric forms needed to be ruled out. Although X-ray quality crystals of *rac*-**16** were grown, refinement of the data did not distinguish between the two diastereomeric possibilities; the structures are insufficiently distinct.[14] For this reason, DFT calculations were carried out for the cationic part of both forms of **16**, as



Scheme 3. Reagents and conditions: (a) $(C_2H_4)_2Rhacac$, $CHCl_3$, 30 h, then pentane, (b) $[(C_2H_4)_2RhCl]_2$, $CDCl_3$, rt, 24 h, (c) 13, TMSOTf, pentane, 1 h, rt.

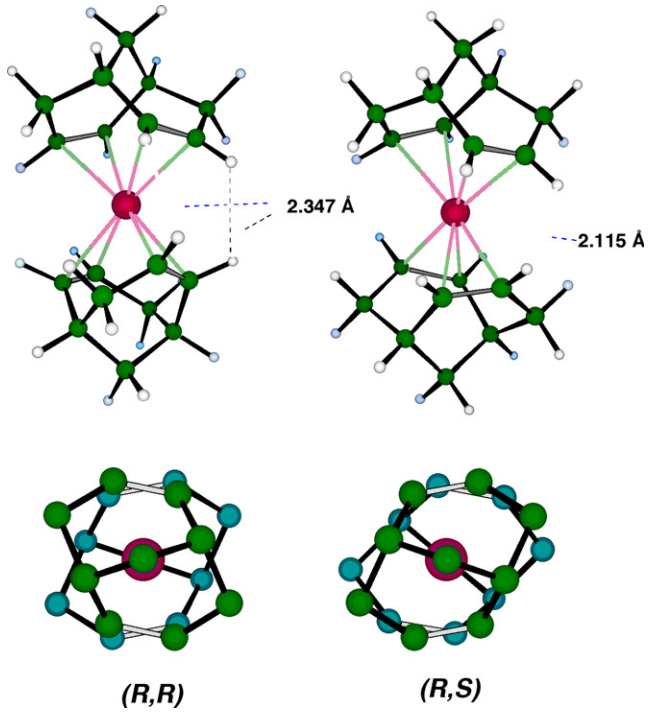


Figure 1. DFT-derived minimum energy structures of homo- and heterochiral **16**, showing closer H–H contacts in the heterochiral form. The lower plan views show only the heavy atom framework.

described in the Experimental. The homochiral diastereoisomer is 16 KJ mol^{-1} more stable than the heterochiral diastereoisomer, corresponding to >99% selectivity towards the homochiral form. Analysis of intercomplex H–H interactions showed that the heterochiral isomer was the more crowded, with one pair of sp^2 CH–CH contacts at 2.115 Å, whilst the closest pair in the homochiral isomer is 2.347 Å apart (Fig. 1). The lower plan views of the two structures show that the homochiral form has a better alignment of double bonds for square-planar coordination; in the heterochiral form, one dialkene is twisted with respect to the other.[15] This view also demonstrates the more compact structure of the heterochiral form indicating greater steric crowding overall.

Figure 2 compares the ring torsional angles for diene **13**, and the homochiral Rh complex **16**, alongside cycloocta-1,5-diene and $(COD)_2Rh^+$, all taken from minimum energy DFT calculations excepting the last where two X-ray structures are available.[16] There is far less distortion of the [3.3.1]-diene on complexation than of cyclooctadiene, where the ground state is twist-boat C_2, but the Rh complex is close to tub-shaped.

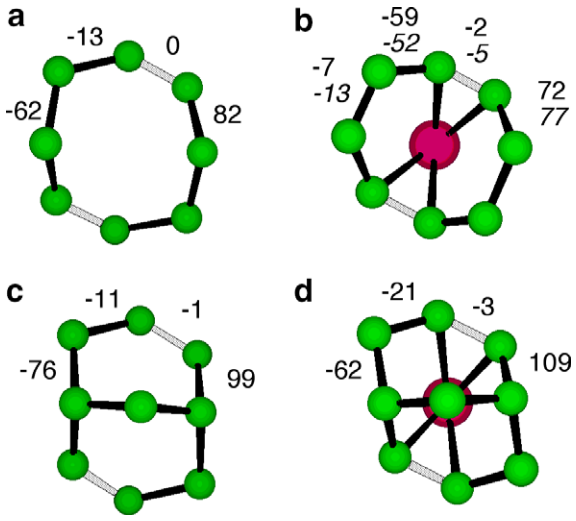


Figure 2. Comparison of the ground-state ring torsion angles of cycloocta-1,5-diene. free (a; DFT) and ligated to Rh^+ (b; X-ray, two independent determinations with different counter-ions). These are shown alongside bicyclo[3.3.1]nona-2,6-diene (c; DFT) and its homochiral $(alkene)_2Rh^+$ complex, (d; DFT).

3. Conclusions

Bicyclo[3.3.1]nona-2,6-diene is the simplest bridged C_2-symmetric chiral diene, and has not been previously prepared enantiomerically pure. The enantiomeric purity is maintained on complexation to rhodium[I]. The chloro-bridged dimer is formed from the racemic diene without any selectivity between (R^*,R^*)- and (R^*,S^*)-forms, but the bis-alkene rhodium cation (as triflate salt) is formed with complete selectivity towards the homochiral (R^*,R^*)-form, with identical ^{13}C NMR, irrespective of whether the racemic or (*S*,*S*)-enantiomer of the diene is employed. The selectivity can be rationalised by DFT-based comparison of the homo- and heterochiral complexes. The selectivity observed encourages application of the diene in catalysis and as a resolving agent for racemic ligands.

4. Experimental

4.1. General

All reactions were conducted in oven- or flame-dried glassware. Reactions involving air- and water-sensitive reagents were performed under a dry Ar atmosphere using a standard vacuum line and Schlenk techniques. Solvents used in chromatography were BDH AnalaR or GPR grade and were used without further purification. Solvents used for reactions were dried via an alumina Grubb's column. Standard chromatographic and TLC procedures were used. NMR spectra were recorded using a Bruker AV400 spectrometer, Bruker DPX400 or Bruker AMX500. FT IR spectra were recorded as thin films on a KBr disc using a Perkin–Elmer Paragon 1000 spectrometer. Mass spectra were recorded by the authors or by Mr. R. Proctor, using either Micromass GCT (CI) or V.G. Autospec spectrometers (EI and CI). Exact masses were measured on a Waters 2790-Micromass LCT spectrometer or a V.G. Autospec spectrometer using EI or CI.

4.2. (*S*,*S*)-Bicyclo[3.3.1]nonane-2,6-dione 11

The reactant was synthesised from Meerwein's ester,[8] following the procedures described by Quast et al.[17] and Mislin et al.[18] Yeast hydrogenase promoted kinetic resolution of *rac*-bicyclo[3.3.1]nonane-2,6-dione has been reported many times with varying ee. On the occasion that a product with 99% ee was reported, experimental details were lacking.[9] A reliable procedure is as follows.

Glucose (81.5 g) was dissolved in water (450 mL) and the solution was heated to 32 °C until completely dissolved. Baker's yeast (35 g; Hovis fast action bread yeast) was then added in one portion and the solution was stirred for 45 min. Racemic bicyclo[3.3.1]nonane-2,6-dione (3.5 g, 23 mmol) was added to the mixture in one portion and then stirred for 24 h. Celite was added to the suspension, which was filtered and washed with H_2O (1.5 L). Next CH_2Cl_2 (500 mL) was added to the aqueous phase and the biphasic mixture stirred for 6 h. The organic phase was separated and the aqueous phase extracted with CH_2Cl_2 (3 × 500 mL), stirring the mixture for 2 h each time. The combined organic phases were dried over Na_2SO_4, filtered and concentrated in vacuo to afford the crude product as a yellow oily solid. Chromatography on silica gel (200 mL, EtOAc/pentane, 35:65) gave the product as a white solid (1.37 g, 9.01 mmol, 39%); $[\alpha]_D^{21} = +176.6$ (*c* 0.50, $CHCl_3$). Chiral GC (β-cyclodextrin column (0.25 mm × 30 m, thickness 0.25 μm), using He as a carrier gas (flow = 0.7 mL/min, injector T = 220 °C; detector: FID, T = 250 °C); 130–160 °C (0.5 °C/min) t_R = 24.4 min, t_S = 25 min): 99.5% ee. NMR, IR spectroscopic data are consistent with those reported in the literature.

4.3. (*S*,*S*)-Bicyclo[3.3.1]nona-2,6-diene 13

(*S*,*S*)-Bicyclo[3.3.1]nonane-2,6-dione (1.42 g, 9.35 mmol) was converted to the corresponding bis-tosylhydrazone **12** as previously described;[10] the reaction mixture was cooled to 0 °C for 2 h to fully precipitate the product; beige solid, 4.5 g, 98% after filtration and drying mp 110–112 °C. (lit. mp 185–189 °C for racemate). Following prior procedures described for the racemic hydrazone, a mixture of Pr^i_2NH (7.4 g, 74 mmol) and TMEDA (37 mL, 320 mmol) was chilled to 0 °C under Ar and then BuLi (1.6 M in hexane, 30 mL, 47 mmol) was added via cannula over 7 min followed by portionwise addition of solid bis-tosylhydrazone (4.5 g, 9.2 mmol) over 3 mins. The cooling bath was removed and the mixture stirred at rt overnight, after which the mixture was chilled to 0 °C. Water was slowly added until all the lithium salts were dissolved. The solution was transferred to a separatory funnel and the organic layer was separated. After standard aqueous workup and $MgSO_4$ drying, the solvent was carefully distilled off to yield a yellow liquid (~5 mL), which was purified further by silica gel chromatography using pentane as eluent. Fractions containing product were combined and pentane was carefully distilled off from the combined product fractions, leaving (*S*,*S*)-bicyclo[3.3.1]nona-2,6-diene (1.54 g; 70% w/w soln. in pentane, 8.9 mmol diene, 78%). Chiral

GC (β-cyclodextrin column): 98.5% ee ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (m, 2H, $H_{2,6}$), 5.66 (ddd, J_1 = 1.26 Hz, J_2 = 4.8 Hz, J_3 = 9.91 Hz, 2H, $H_{3,7}$), 2.47 (m, 2H, $H_{1,5}$), 2.24 (ddd, J_1 = 12.08 Hz, J_2 = 3.7 Hz, J_3 = 18.61 Hz, 2H, $H_{4',8'}$), 1.86 (dd, J_1 = 4.69 Hz, J_2 = 17.6 Hz, 2H, $H_{4,8}$), 1.69 (t, J = 2.97, 2H, H_9); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 131.8 (s, CH_{db}), 125.0 (s, CH_{db}), 30.7 (s, $C_{4,8}$), 28.5 (s, C_9), 28.2 (s, $C_{1,5}$); after further concentration of a sample to 90% w/w soln in pentane: $[\alpha]_D^{21} = -122$ (c 0.89, $CHCl_3$).

4.4. ((*S*,*S*)-Bicyclo[3.3.1]nona-2,6-diene)pentane-2,4-dionato rhodium 14

$(C_2H_4)_2Rh(acac)$ (200 mg, 775 μmol) was dissolved in $CDCl_3$ (4 mL) and treated with a solution of (*S*,*S*)-bicyclo[3.3.1]nona-2,6-diene (346 mg 35 wt % soln in pentane, 1.01 mmol diene) in $CDCl_3$ (4 mL). The reaction mixture was stirred for 30 h at rt, after which $CDCl_3$ was removed in vacuo and the residue was taken up in pentane (10 mL). The mixture was sonicated for 1 min and then the bright yellow solution was filtered off into a new Schlenk tube via cannula. The solvent was removed in vacuo to give the product as a bright yellow solid (200 mg, 80%) (mp = 136–138 °C) ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.33 (s, 1H, CH acac), 4.46 (m, 2H, $H_{3,7}$), 3.83 (m, 2H, $H_{2,6}$), 2.82 (m, 2H, $H_{4,8}$), 2.15 (m, 4H, $H_{4',8'}$, $H_{1,5}$), 1.93 (m, 6H, CH_3 acac), 1.17 (m, 2H, H_9); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 186.3 (C–O acac), 99.9 (CH acac), 78.6 (d, $C_{3,7}$, ^1J (^{13}C, ^{103}Rh) = 12.2 Hz), 71.4 (d, $C_{2,6}$, ^1J (^{13}C, ^{103}Rh) = 14.0 Hz), 39.2 ($C_{4,8}$), 31.4 (C_9), 28.9 ($C_{1,5}$), 27.3 (CH_3 acac); HRMS: m/z 345.0333 (100%) [M+Na$^+$] requires 345.0338; $[\alpha]_D^{21} = -73$ (c 0.51, $CHCl_3$).

4.5. Bis-((*S*,*S*)-bicyclo[3.3.l]nona-2,6-diene)dichloro dirhodium 15

At first $(C_2H_4)_2Rh_2Cl_2$ (200 mg, 514 μmol) was treated with a solution of (*S*,*S*)-bicyclo[3.3.1]nona-2,6-diene (390 mg, 35% w/w soln in pentane, 1.13 mmol diene) in $CDCl_3$ (4 mL). The reaction mixture was stirred for 24 h at rt. The brown/yellow solution was filtered off into a new Schlenk tube via cannula after which $CDCl_3$ was removed in vacuo. The residue was taken up in pentane (10 mL), the mixture was sonicated for 2 min and left for 1 h at −78 °C. The pentane layer was decanted and the remaining brown/yellow solid was dried in vacuo (176 mg, 67%). mp = 202–203 °C, ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.74* (br m, 4H, $H_{3,7}$), 3.94 (m, 4H, $H_{2,6}$), 2.98 (d, ^2J(H,H) = 14.8 Hz, 4H, $H_{4,8}$), 2.17 (d, ^2J(H,H) = 14.4 Hz, 4H, $H_{4',8'}$), 2.07 (m, 4H, $H_{1,5}$), 1.20 (s, 4H, H_9); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 79.3* (d, $C_{2,6}$, ^1J (^{13}C, ^{103}Rh) = 12.5 Hz), 72.2* (d, $C_{3,7}$, ^1J (^{13}C, ^{103}Rh) = 14.4 Hz), 40.6 ($C_{4,8}$), 31.4 (C_9), 28.2 ($C_{1,5}$); $[\alpha]_D^{21} = -260$ (c 0.23, $CHCl_3$). (Starred signals are doubled in the racemic form.)

4.6. (Bis-(*S*,*S*)-Bicyclo[3.3.1]nona-2,6-diene)rhodium trifluoromethanesulfonate 16

((*S*,*S*)-Bicyclo[3.3.1]nona-2,6-diene)pentane-2,4-dionato rhodium (61 mg, 190 μmol) was placed in a Schlenk tube and treated with (*S*,*S*)-bicyclo[3.3.1]nona-2,6-diene (39 mg, 70 w% soln of diene in pentane, 230 μmol diene) in CH_2Cl_2 (4 mL). After stirring for 1 min at rt, TMSOTf (34 μL, 190 μmol) was added and the resulting mixture was stirred at rt for 1 h. Pentane (4 mL) was added to precipitate the product. The precipitate was allowed to settle and then the supernatant solution was decanted and the residue was dried in vacuo to give the product as an orange solid (72 mg, 77%); mp = 190–192 °C; ^{1}H NMR (500 MHz, CD_2Cl_2): δ 5.39 (m, 4H, $H_{2,6}$), 5.09 (m, 4H, $H_{3,7}$), 2.76 (d, ^2J(H,H) = 17.5 Hz, 4H, $H_{4,8}$), 2.63 (m, 4H, $H_{1,5}$), 2.53 (d, ^2J(H,H) = 17.7 Hz, 4H, $H_{4',8'}$), 1.58 (t, ^3J(H,H) = 3.0 Hz, 4H, H_9); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 106.2 (d, C2, 6, J_1 (^{13}C, ^{103}Rh) = 7.7 Hz), 103.1 (d, $C_{3,7}$, ^1J (^{13}C, ^{103}Rh) = 6.9 Hz), 37.8 ($C_{4,8}$), 29.9 (C_9), 28.5 ($C_{1,5}$); HRMS: m/z 343.0913 (100%) [M$^+$] requires 343.0933; $[\alpha]_D^{21} = -217$ (c 0.29, $CHCl_3$). The racemic salt was prepared comparably, with *rac*-**13** employed in both steps.

4.7. Computational details

All the calculations were performed employing density functional theory (DFT) methods. The computations were performed using the hybrid Becke functional (B3)[19] for electron exchange and the correlation functional of Lee, Yang and Parr (LYP),[20] as implemented in the GAUSSIAN 03 software package.[21] For the transition metal atoms, the SDD basis sets with associated effective core potentials have been taken.[22] For the remaining atoms, the 6-31G(d) basis sets have been taken.[23] Geometry optimisations were performed without applying any symmetry constraints. Harmonic vibrational frequencies were calculated to confirm the nature of stationary points, yielding zero imaginary frequencies (minima) for all structures. All complexes were corrected for zero point energy. Wiberg Bond Indices[24] (WBI) were obtained from the Natural Population analysis[25] (NPA) and used for a more detailed understanding of the bonding between metal and ligand.

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