Experimental

All operations were performed using canula techniques on Schlenk lines under a dry nitrogen atmosphere or in a Braun Labmaster 130 drybox under dry purified argon. [FeClCp*(tmeda)],[31] [RuCp*Cl]$_4$[33] and compounds **18b**,[29] **16a**,[20] **16b**[29] **21**,[34] **27**,[34] **28**[34] were prepared as described previously. The essentially racemic sample of **26** used in the Friedel Crafts experiments was prepared through hydrolysis[29] of equimolar quantites of **16b** and its diastereomer. All solvents were distilled under dry nitrogen: THF and ether from sodium benzophenoneketyl, pentane from sodium benzophenone ketyl/ tetraglyme, methanol from sodium methoxide and dichloromethane from P_4O_{10}. NMR measurements were made on a Bruker Avance 300 spectrometer and are referenced to internal $(CD_3)_2SO$ and CD_3CN and external H_3PO_4 as appropriate. Mass spectra were obtained from dichloromethane solutions on a Bruker electrospray MicroTOF spectrometer; infrared spectra of pure solids were measured by attenuated total reflection on a Perkin Elmer Paragon 1000 spectroscope. Optical rotations were made upon a Perkin Elmer PE 241 polarimeter operating at 589 nm.

17a *(R)*-configured menthylester **16**a (500 mg, 0.89 mmol) was added to 98%v/v trifluoroacetic acid (3mL) and the mixture was sirred under strictly oxygen free conditions in a Teflon- stoppered Carius tube for for 70 h at room temperature. The trifluoroacetic acid was then removed on a water pump at room temperature. The oily solid product was washed three times with pentane (3x 3mL) to give a rust- orange crude material **17a** which was sufficiently pure for further use (350 mg, 93 %). ^{31}P NMR ($CDCl_3$): δ -35.5ppm. ^{1}H ($CDCl_3$): δ 8.6 (br, 1H, OH), 7.42 (Ψd, JHH = 7.5 Hz, 2H), 7.28 (Ψt, JHH = 7.1 Hz, 2H), 7.19 (Ψt, JHH = 7.2 Hz, 1H), 2.36 (br, 3H, Me), 2.19 (s, 3H, Me), 1.66 (s, 15H, Cp*). ^{13}C ($CDCl_3$): δ 180 (br, *C*=O), 138.9 (d, *JP-C* = 17.9 Hz, *ipso*), 129.7 (d, *JP-C* = 9.2 Hz, *o*-Ph), 127.9 (*m*-Ph), 126.0 (*p*-Ph), 103.7 (d, *JP-C* = 52.6 Hz, P*C*), 96.0 (d, *JP-C* = 4.3 Hz, PC*C*Me), 94.3 (d, *JP-C* = 5.6 Hz, PC*C*Me), 83.8 (Cp*), 13.8 (Me) , 12.9 (br, Me), 9.7 (Cp*). EI-MS (m/z, %): 423 ($[MH]^+$, 100%) ; 377 ([M-COOH], 18 %).

(R,R)-**15:** Solid phosphorus pentachloride (209 mg, 1.0 mmol) was added in three portions to a room temperature solution of **17b** (467 mg, 1.0 mmol) and the mixture was stirred for 30 minutes at rooom temperature. The solvent was removed under reduced pressure and the residue was stirred vigorously with toluene, before the mixture was again taken to dryness under reduced pressure. The crude sample of **18b**[29] was then dissolved in THF (20 mL) and transferred through a canula onto a well- stirred room temperature solution of [K(diglyme)(2-Ph-3,4-diMe-PC_4H)] **21** (720 mg, 2.0 mmol) over a period of 30 seconds. The mixture was stirred for 5 minutes and the solvents were then removed under reduced pressure. The crude product was washed with hexane (3x 3mL) to remove phosphole cyclodimers and then resuspended in THF (20 mL). Finely powdered CuBr (143 mg, 1.0 mmol) was added and the mixture was stirred for 16 hours, and the bright red solution was then treated with [FeClCp*(tmeda)] (400 mg, 1.15 mmol). After stirring for 30 minutes, the mixture was passed rapidly through an alumina plug which was then rinsed with dichloromethane. The combined scarlet extracts were combined, evaporated, taken up in acetone, (20 mL) and stirred with sodium sulfide (100 mg, 1.28 mmol) for 3h. The red product was separated from the black precipitate by flash chromatography in dichloromethane on silica (10x 1cm) and the deep red fraction was crystallised from acetone to furnish *(R,R)*-**15** as a red, air- stable microcrystalline solid (350 mg, 42 %). Calculated for $C_{45}H_{52}FeOP_2Ru$: C: 65.29, H: 6.33; found: C: 63.30, H: 6.54; ^{31}P NMR (CD_2Cl_2): δ –24.7 (d, J_{PP} = 211.4 Hz, P-Ru), –38.8 (d, J_{PP} = 211.4 Hz, P-Fe) ^{1}H NMR (CD_2Cl_2): δ 7.46 (d, br, J_{HH} = 7.72 Hz, 2H, Ph), 7.3–7.1 (m, br, 8H, Ph), 2.34 (s, 3H, Me), 2.18 (br, 6H, 2Me), 1.99 (s, 3H, Me), 1.64 (s, 15 H, Cp*-Ru), 1.62 (s, 15 H, Cp*-Fe). ^{13}C NMR (CD_2Cl_2): δ 202.2 (dd, J_{PC} = 20.3 Hz, J_{PC} = 18.8 Hz, CO), 139.8 (t, J_{PC} = 17.8 Hz, ipso-Ph), 138.8 (t, J_{PC} = 17.5 Hz, ipso-Ph), 129.7 (d, J_{PC} = 7.2 Hz, *o*-Ph), 129.6 (d, J_{PC} = 7.9 Hz, *o*-Ph), 128.0 (s, m-Ph), 127.9 (s, m-Ph), 125.8 (s, p-Ph), 125.5 (s, p-Ph), 103.2 (dd, J_{PC} = 60.3 Hz, J_{PC} = 11.7 Hz, Ru-P$\underline{C}$CO), 100.6 (dd, J_{PC} = 57.5 Hz, J_{PC} = 10.3 Hz, Fe-P$\underline{C}$CO), 98.2 (d, J_{PC} = 4.5, Fe-PC(Ph)$\underline{C}$Me), 96.5 (d, J_{PC} = 63.7 Hz, Ru-P$\underline{C}$Ph), 96.3 (d, J_{PC} = 4.3, Ru-PC(Ph)$\underline{C}$Me), 93.5 (d, J_{PC} = 4.5, Ru-PC(CO)$\underline{C}$Me), 93.1 (d, J_{PC} = 59.6 Hz, Fe-P$\underline{C}$Ph), 92.1 (d, J_{PC} = 4.9, Fe-PC(CO)$\underline{C}$Me), 88.9 (Cp*-Ru), 83.7 (Cp*-Fe), 14.08 (Me), 13.16 (Me), 13.04 (Me), 12.96 (Me), 10.29 (Me of Cp*(Ru)), 9.93 (Me of Cp*(Fe)). CI-MS (NH_3) (m/z, %) : 828 (M, 100%) $[\alpha]^{25}_{D}$ (c = 1.0, DCM) = -37.7°cm²g^{-1} IR (ATR, cm^{-1}) = 1698 (CO)

Traces of the pseudo-*meso*- isomer **15′** are observed by ^{31}P NMR at δ -23.2 (d, J_{PP} = 31.3 Hz, P-Ru), -36.6 (d, J_{PP} = 31.3 Hz, P-Fe) in (CH_2Cl_2).

13 Solid phosphorus pentachloride (261 mg, 1.25 mmol) was added in three portions to a room temperature dichloromethane solution of **17a** (528mg, 1.25 mmol) and the mixture was stirred for 30 minutes at room temperature. The solvent was removed under reduced pressure and the residue was stirred vigorously with toluene, before the mixture was again taken to dryness under reduced pressure. The crude sample of **18a** was then transferred by canula onto a THF (15mL) solution of [K(diglyme)(2-Ph-3,4-diMe-PC_4H)] **21** (900 mg, 2.5 mmol) and the mixture was stirred for 20 mins. The solvents were removed an oil pump and the sticky red product was freed from phosphole cyclodimers through their extraction into pentane (4x 5mL). After resuspension in THF (15mL) and treatment with CuBr (143 mg, 1.0 mmol), the mixture was stirred for 14 hours at room temperature and then further treated with [FeClCp*(tmeda)] (500 mg, 1.44 mmol). After 15 mins, sodium sulfide was added and the the red mixture was allowed to stir for a further 5h at room temperature. Flash chromatography as above and crystallisation from acetone gave the product *(R,R)*-**13** as a deep red air- stable microcrystalline solid (450 mg, 40%). Calculated for $C_{45}H_{52}Fe_2OP_2$.: C: 69.07, H: 6.70; found: 68.22, 6.29%. $[\alpha]^{25}_D$ (c = 1.0, DCM) = -10.4°cm²g^{-1}. ^{31}P NMR (CD_2Cl_2) δ -37.3ppm. ^{1}H NMR (CD_2Cl_2): δ 7.45 (d, br, J_{HH} = 7.24 Hz, 4H, *o*-Ph), 7.24 (t, br, J_{HH} = 7.21 Hz, 4H, *m*-Ph), 7.13m, br, 2H, *p*-Ph), 2.36 (s, 3H, Me), 2.19 (s, 3H, Me), 1.58 (s, 15 H, Cp*). ^{13}C NMR (CD_2Cl_2): δ 205.0 (d, J_{PC} = 18.5 Hz, CO), 139.8 (t, J_{PC} = 8.9 Hz, ipso-Ph), 129.5 (t, J_{PC} = 4.7 Hz, *o*-Ph), 128.0 (s, m-Ph), 125.5 (s, p-Ph), 100.5 (t, J_{PC} = 24.9 Hz, PCPh), 98.3 (s, $\underline{C}$Me), 93.7 (t, J_{PC} = 28.9 Hz, P$\underline{C}$CO), 92.1 (s, $\underline{C}$Me), 83.7 (Cp*), 14.1 (PCC$\underline{Me}$), 13.2 (PCC$\underline{Me}$), 9.9 (Me du Cp*) EI-MS (m/z, %) : 783 (M, 100%), 375 (50%), 359 (20%). Crystals for diffraction were prepared analogously from racemic **17**a and grown from dichloromethane/petrol.

25 A dichloromethane (5mL) solution of enantiopure phospharuthenocenoic acid (530mg, 1.13mmol) was treated at ice- bath temperature with powdered phosphorus pentachloride (230mg, 1.10mmol). After stirring for 15 minutes, the solvent was removed under reduced presure and toluene (6mL) was added. The toluene was then also removed under reduced pressure to complete the removal of the $POCl_3$ coproduct. The crude acid chloride so produced was then dissolved in THF (5mL) and treated at room temperature with a THF (15mL) solution of phospholide [K(diglyme)(2-Ph-3,4-diMe-PC_4H)] **21** (800mg, 2.22mmol). After stirring at room temperature for 15 minutes, the solvent was removed and the crude phospholide reagent was extracted with pentane (3x 5mL). The orange air- sensitive solid so obtained was stirred with [RuCp*Cl] (300mg, 1.10mmol) over a period of fifteen minutes at room temperature and then with [FeClCp*(tmeda)] [FeClCp*(tmeda)] (380mg, 1.11mmol). The deep red solution was stirred for a further ten minutes and then stripped under reduced pressure, diluted with dichloromethane, washed with degassed water, dried over magnesium sulfate and passed through a short plug of neutral alumina (5x 1cm Ø). The deep red fraction so obtained was reduced in volume to ca 1mL and crystallised by slow diffusion of ether (*ca* 3 mL) into this concentrated dichloromethane fraction. Calculated for $C_{57}H_{71}Cl_5FeOP_2Ru_2$ C: 53.93, H: 5.64; found: C: 54.11, H: 5.78%. ^{31}P NMR (THF): δ : 49.7 (d, J_{PP} = 79.1 Hz), 42.2 (d, J_{PP} = 79.1 Hz). ^{1}H NMR (C_6D_6): δ : 7.90 (d, J_{HH} = 7.5 Hz, 2H, Ph), δ 7.5–7.1 (m, 8H, Ph), 2.60 (s, 3H, Me), 2.43 (s, 3H, Me), 2.16 (s, 6H, Me), 1.67 (s, 30 H, 2 Cp* ligand), 1.61 (s, 3H, Me), 1.41 (m, br, 15 H, Cp* RuCl). ^{13}C NMR (C_6D_6): δ : 196.9 (t, J_{PC} = 18.0 Hz, CO), 140.5 (d, J_{PC} = 15.1 Hz, ipso-Ph), 137.0 (d, J_{PC} = 15.7 Hz, ipso-Ph), 134.1 (d, J_{PC} = 4.7 Hz, 4 *o*-Ph), 127.5 (s, 4 m-Ph), 126.7 (s, p-Ph), 125.7 (s, p-Ph), 95.1 (d, J_{PC} = 3.5 Hz, PC$\underline{C}$Me), 94.6 (m, PC), 92.8 (t, J_{PC} = 2.1 Hz, $\underline{C}$Me Cp*RuCl), 92.0 (d, J_{PC} = 3.2 Hz, PC$\underline{C}$Me), 91.5 (d, J_{PC} = 3.8 Hz, PC$\underline{C}$Me), 91.0 (d, J_{PC} = 3.0 Hz, PC$\underline{C}$Me), 89.4 ($\underline{C}$Me Cp* metallocene), 87.2 (m, PC), 86.5 ($\underline{C}$Me Cp* metallocene), 81.6 (m, PC), 71.6 (m, PC), 14.34 (PCC$\underline{Me}$), 14.27 (PCC$\underline{Me}$), 13.7 (PCC$\underline{Me}$), 11.9 (d, J_{PC} = 1.7 Hz, PCC$\underline{Me}$), 10.5 (10Me Cp*), 10.2 (5Me Cp*RuCl).

30 [Pt(1,5-cod)Cl_2] (25 mg, 0.072 mmol) was added as a solid to a dichloromethane (2mL) solution of *(R,R)*-**15** (60 mg, 0.072 mmol). The colour deepened and, after ten minutes of stirring, the solvent was removed under reduced pressure and the red air-stable product was rinsed with pentane. Recrystallisation from dichloromethane at 4°C provided air- stable red crystals which were suitable for an X-ray structural determination and microanalysis. Microanalysis: Calculated for $C_{45}H_{52}Cl_2FeOP_2PtRu$: C : 49.42 % ; H : 4.79 % ; found : C : 48.85 % ; H : 4.87 %. ^{31}P NMR (CD_2Cl_2) : δ 3.7 (d, J_{PP} = 59.6 Hz, $J_{P\text{-}Pt}$ = 3897 Hz), -1.1 (d, J_{PP} = 59.6 Hz, $J_{P\text{-}Pt}$ = 3901 Hz). ^{1}H NMR (CD_2Cl_2) : δ 7.50-7.15 (m, 2Ph), 2.37 (s, 3H, Me), 2.29 (s, 3H, Me), 1.99 (s, 3H, Me), 1.89 (s, 3H, Me), 1.71 (s, 15H, Cp*), 1.69 (s, Cp*). ^{13}C NMR (CD_2Cl_2) : δ 194.4 (t, J_{PC} = 15.9 Hz, CO), 133.2 (d, J_{PC} = 11.6 Hz, ipso-Ph), 132.6 (d, J_{PC} = 6.0 Hz, ipso-Ph), 132.0 (d, J_{PC} = 5.0 Hz, *o*-Ph), 129.6 (d, J_{PC} = 7.9 Hz, *o*-Ph), 127.6 (s, m-Ph), 127.5 (s, m-Ph), 127.4 (s, p-Ph), 127.3 (s, p-Ph), 95.3 (d, J_{PC} = 12.4 Hz, CMe), 93.8 (d, J_{PC} = 13.7 Hz, CMe), 93.0 (d, J_{PC} = 11.6 Hz, $\underline{C}$Me), 92.7 (s, Cp*), 92.3 (d, J_{PC} = 11.0 Hz, $\underline{C}$Me), 87.7 (s, Cp*), 85.4 (d, J_{PC} = 14.9 Hz, $\underline{C}$Ph), 83.7 (d, J_{PC} = 23.5 Hz, $\underline{C}$Ph) , 71.4 (d, J_{PC} = 14.4 Hz, $\underline{C}$CO), 67.2 (d, J_{PC} = 14.0, $\underline{C}$CO), 13.4 (d, J_{PC} = 2.4 Hz, Me), 13.2 (d, J_{PC} = 2.0 Hz, Me), 12.5 (d, J_{PC} = 4.6 Hz, Me), 12.3 (d, J_{PC} = 5.1 Hz, Me), 10.01 (s, Me du Cp*), 9.96 (s, Me du Cp*).

24 *(R,R)*-keto-*bis*[η^5-pentamethylcyclopentadienyl-η^5-(3,4-dimethyl-5-phenyl-phosphol-2-yl)ruthenium(II)] [η^5-pentamethylcyclopentadienyl-chloro-ruthenium(II)]

A dichloromethane (40mL) solution of *(R)*-phospharuthenocen-2-oic acid **17b** (400 mg, 0.85 mmol) was treated at room temperature with a single portion of finely powdered phosphorus pentachloride (179 mg, 0.85 mmol). After stirring the yellow mixture for 30 minutes, the solvents were removed under reduced pressure to leave a pale oil. This was washed with toluene, again taken to dryness under reduced pressure, and maintained at low pressure for an hour to ensure the complete removal of $POCl_3$. The crude product was redissolved in THF (20 mL) and transferred by canula over 2-3 minutes onto a well stirred THF (20 mL) solution of **21** (641 mg, 1.78 mmol). The complete and near-instantaneous conversion into **20b** can be monitored by ^{31}P NMR [δ 115.1; -20.0 ppm (J_{PP} = 63.6 Hz)]. Solid

[RuCp*Cl]$_4$ (508 mg, 0.47 mmol) was then added and the mixture was stirred for 30 minutes at room temperature. After removal of solvents under reduced pressure, the product was purified by flash chromatography on a short column of neutral alumina (10 cm x 1cm Ø). Crystallisation by diffusion of pentanes into its dichloromethane solution gave orange, acceptably air-stable, crystals of the product *(R,R)*-**24**. (510 mg, 53 %). Calculated for $C_{57}H_{71}Cl_5FeOP_2Ru_2$ C: 53.93, H: 5.64; found: C: 53.82, H: 5.61% ^{31}P NMR (THF): δ 55.1 (d, J_{PP} = 79.5 Hz), 39.8 (d, J_{PP} = 79.5 Hz). ^{1}H NMR (CD_2Cl_2) : δ 7.48 (d, J_{HH} = 6.5 Hz, 2H, Ph), δ 7.3–7.1 (m, 8H, Ph), 2.28 (s, 3H, Me), 2.26 (s, 3H, Me), 2.10 (s, 3H, Me), 1.73 (s, 15 H, Cp*), 1.69 (s, 3H, Me), 1.62 (s, 15H, Cp*), 1.23 (m, br, 15 H, Cp*$_{RuCl}$). ^{13}C NMR (CD_2Cl_2) : δ 194.3 (m, CO), 139.3 (d, J_{PC} = 15.6 Hz, ipso-Ph), 136.9 (d, J_{PC} = 15.8 Hz, ipso-Ph), 133.6 (d, J_{PC} = 5.0 Hz, 4 *o*-Ph), 127.3 (s, 4 m-Ph), 126.3 (s, p-Ph), 125.5 (s, p-Ph), 95.2 (m, PC), 95.0 (d, J_{PC} = 3.5 Hz, PC$\underline{\mathrm{C}}$Me), 92.3 (d, J_{PC} = 3.1 Hz, PC$\underline{\mathrm{C}}$Me), 92.1 (t, J_{PC} = 2.4 Hz, $\underline{\mathrm{C}}$Me Cp*RuCl), 92.0 (d, J_{PC} = 2.9 Hz, PC$\underline{\mathrm{C}}$Me), 91.9 (m, PC), 91.8 (d, J_{PC} = 3.9 Hz, PC$\underline{\mathrm{C}}$Me), 91.3 ($\underline{\mathrm{C}}$Me Cp*), 89.5 ($\underline{\mathrm{C}}$Me Cp*), 79.8 (m, PC), 76.7 (m, PC), 13.8 (2Me), 13.5 (Me), 11.7 (d, J_{PC} = 2.0 Hz, Me), 10.4 (Me Cp*), 10.3 (Me Cp*), 10.2 (Me Cp*).