Supporting Information for:

Dehydrogenation of Cyclic-Thioethers Bound to a [Rh(diphosphine)]⁺ Fragment.

Romaeo Dallanegra, Ben S. Pilgrim, Adrian B. Chaplin, Timothy J. Donohoe* and Andrew S. Weller*

Department of Chemistry, University of Oxford, Oxford, OX1 3TA, UK.

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Experimental Techniques for ligands I-IV

All non-aqueous reactions were carried out in flame-dried glassware under an atmosphere of argon, unless otherwise specified. Petrol refers to the petroleum ether fraction that boils in the range 40-60 °C. THF and CH₂Cl₂ were dried by purification through two activated alumina purification columns.¹ Reagents were obtained from Acros, Aldrich, Fluka and Strem and were used as supplied.¹ ¹H and ¹³C NMR spectra were recorded on a Bruker Avance AV400 spectrometer (400 MHz and 100 MHz respectively) in CDCl₃ and referenced to residual solvent peaks or to tetramethylsilane as an internal standard. Chemical shifts δ are quoted in parts per million (ppm) to the nearest 0.01 for ¹H and 0.1 for ¹³C, coupling constants J are quoted in Hz to the nearest 0.1 and splittings are recorded as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin) and broad (br.). Assignments were based upon DEPT, COSY and HMQC experiments. Infrared spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer as a thin film between NaCl plates for oils. Absorption maxima are quoted in wavenumbers (cm⁻¹) and labelled as strong (s), medium (m), weak (w) and broad (br.). Mass spectra were recorded on a Fisons Platform II spectrometer under electrospray ionisation (ESI) or field ionisation (FI). Relative intensities of assignable peaks are quoted as percentage values. High resolution mass spectra are given to four decimal places and were recorded on a Bruker MicroTof (resolution = 10000 FWHM). Calibration was via the lock-mass of tetraoctylammonium bromide for positive and sodium dodecyl sulfate for negative ions. Melting points (m.p.) were obtained using a Leica VMTG heated-stage microscope and are uncorrected. Flash column chromatography was carried out on silica gel (60 Å, 0.033-0.070 mm, BDH) using Still’s method,² with head pressure provided by bellows. The solvent system is quoted in parentheses. Reactions and columns were monitored by thin layer chromatography analysis on Merck DC-Keisegel 60 F₂₅₄ 0.2 mm precoated plates. Spots were visualised by UV light (λ_max = 254 nm) and/or staining with basic potassium permanganate solution or acidic vanillin solution as deemed appropriate for the compound.

Synthesis of ligands I-IV

Dicyclopentylthioether (I, SCyp₂)

Cyclopentylthiol (205 mg, 2.00 mmol) was added to a stirred solution of bromocyclopentane (298 mg, 2.00 mmol) and Cs₂CO₃ (1.30 g, 4.00 mmol) in anhydrous DMF (10 mL) and the mixture was stirred for 2 h at room temperature. The reaction was quenched with saturated aqueous NaHCO₃ (20 mL) and...
extracted with Et₂O (3 x 25 mL). The combined organics were dried over MgSO₄, filtered and the solvent removed in vacuo. Flash column chromatography [SiO₂, petrol/Et₂O, 99:1 then 49:1] gave thioether I as an oil (276 mg, 81 %).

\[ ^1H \text{ NMR (400 MHz, CDCl}_3] \delta H: 3.09 (2 H, quin, J 7.1, 2 x CH), 2.04-1.93 (4 H, m, 4 x CHCH₂H), 1.77-1.67 (4 H, m, 4 x CHCH₂CH₂H), 1.60-1.45 (8 H, m, 4 x CHCH₂CH₂H).

\[ ^13C \text{ NMR (100 MHz, CDCl}_3] \delta C: 43.7 (C₂H), 34.2 (CHCH₂CH₂), 24.9 (CHCH₂CH₂).

\[ IR \ \nu_{max} \text{ (thin film)/cm}^{-1}: 2957s, 2867s, 2360w, 2341w, 1731w, 1449s, 1378w, 1316m, 1238s, 1137w, 1050w, 1029w, 936w, 821w.

\[ m/z \text{ (ESI+): 209.1 [100, (M + Na + O)⁺], C}_{10}H_{18}NaOS predicted 209.0971, found 209.0976, (Δ - 2.7 ppm).}

This compound has been previously made by different methods but not fully characterised.³

Hepta-1,6-dien-4-ol (a_II)

\[ \text{A solution of ethyl formate (370 mg, 5.00 mmol) in THF (20 mL) was added dropwise via cannula to a stirred solution of allylmagnesium chloride (2 M in THF, 5.13 mL) at 0 °C and the reaction was warmed to room temperature and then heated at reflux for 16 h. The mixture was cooled to 0 °C and quenched with aqueous 1 M HCl (25 mL) and then extracted with Et₂O (3 x 25 mL). The combined organic layers were washed with H₂O (50 mL), saturated aqueous NaHCO₃ (50 mL), and brine (50 mL), dried over MgSO₄, filtered and the solvent removed (cautiously) in vacuo. The crude product was purified by flash column chromatography [SiO₂, petrol/EtOAc, 19:1 then 9:1] to give alcohol a_II (528 mg, 94 %) as an oil.}

\[ ^1H \text{ NMR (400 MHz, CDCl}_3] \delta H: 5.89-5.79 (2H, m, 2 x CH=CH₂), 5.16-5.12 (4H, m, 2 x CH=CH₂), 3.74-3.68 (1H, m, CHOH), 2.34-2.16 (4H, m, 2 x CH₂), 1.83 (1H, br. s, OH).

\[ ^13C \text{ NMR (100 MHz, CDCl}_3] \delta C: 134.7 (CH₂=CH), 118.1 (CH₂=CH), 69.8 (CHOH), 41.2 (CH₂).

Data were consistent with those previously reported.⁴

Hepta-1,6-dien-4-yl 4-methylbenzenesulfonate (b_II)
para-Toluenesulfonyl chloride (273 mg, 1.43 mmol) was added to a stirred solution of alcohol \( \text{a}_{\text{II}} \) (146 mg, 1.30 mmol), triethylamine (145 mg, 1.43 mmol) and 4-dimethylaminopyridine (175 mg, 1.43 mmol) in \( \text{CH}_2\text{Cl}_2 \) (13 mL) and the mixture heated at 40 °C for 16 h. The reaction was quenched with saturated aqueous \( \text{NH}_4\text{Cl} \) (25 mL) and extracted with \( \text{CH}_2\text{Cl}_2 \) (3 x 25 mL) and the combined organics were washed with \( \text{H}_2\text{O} \) (50 mL) and saturated brine (50 mL), dried over MgSO\(_4\), filtered and the solvent removed \textit{in vacuo}. Flash column chromatography [SiO\(_2\), petrol/EtOAc, 19:1] gave sulfonate \( \text{b}_{\text{II}} \) as an oil (301 mg, 87 %).

\[ ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3) \delta\text{H:} \ 7.79 \ (2\text{H, d, } J 8.2, 2 \times \text{HC(Ar)}),\ 7.33 \ (2\text{H, d, } J 8.2, 2 \times \text{HC(Ar)}),\ 5.66-5.56 \ (2\text{H, m, } 2 \times \text{C} = \text{CH}_2),\ 5.06-5.02 \ (4\text{H, m, } 2 \times \text{CH} = \text{CH}_2),\ 4.59 \ (1\text{H, quin, } J 6.0, \text{CHOR}),\ 2.44 \ (3\text{H, s, } \text{CH}_3),\ 2.40-2.31 \ (4\text{H, m, } 2 \times \text{CH}_2). \]

\[ ^{13}\text{C NMR} \ (100 \text{ MHz, CDCl}_3) \delta\text{C:} \ 144.6,\ 134.3 \ (2 \times \text{C(Ar)}),\ 132.1 \ (\text{CH} = \text{CH}_2),\ 129.7,\ 127.9 \ (2 \times \text{HC(Ar)}),\ 118.9 \ (\text{CH} = \text{CH}_2),\ 81.8 \ (\text{CHOTs}),\ 38.1 \ (\text{CH}_2), 21.7 \ (\text{CH}_3). \]

\[ \text{IR } \nu_{\text{max}} \ (\text{thin film})/\text{cm}^{-1} 3079\text{m, } 2980\text{s, } 2926\text{s, } 1643\text{m, } 1599\text{m, } 1496\text{w, } 1435\text{m, } 1363\text{s, } 1037\text{w, } 1097\text{s, } 995\text{m, } 903\text{s, } 816\text{m}. \]

\[ \text{m/z} \ (\text{ESI}^+) 289.1 \ [90, (\text{M} + \text{Na})^+], 555.2 \ [100, (2\text{M} + \text{Na})^+], \text{C}_{14}\text{H}_{18}\text{NaO}_3\text{S} \ \text{predicted} \ 289.0869, \ \text{found} \ 289.0874, \ (\Delta - 1.9 \text{ ppm}). \]

Cyclopent-3-enyl 4-methylbenzenesulfonate \( \text{c}_{\text{II}} \)

\[ \text{A solution of sulfonate } \text{b}_{\text{II}} \ (184 \text{ mg, } 0.772 \text{ mmol}) \text{ in } \text{CH}_2\text{Cl}_2 \ (8 \text{ mL}) \text{ was degassed with argon for 15 min. Grubbs-Hoveyda 2nd generation catalyst (9.7 mg, } 0.015 \text{ mmol) was added and the mixture stirred for 16 h at room temperature. The solvent was removed } \text{in vacuo} \text{ and the crude product was subjected to flash column chromatography [SiO\(_2\), petrol/EtOAc, 9:1] to give sulfonate } \text{c}_{\text{II}} \text{ as prisms (145 mg, 79 %).} \]

\[ ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3) \delta\text{H:} \ 7.80 \ (2\text{H, d, } J 8.3, 2 \times \text{HC(Ar)}),\ 7.35 \ (2\text{H, d, } J 8.3, 2 \times \text{HC(Ar)}), \ 5.68-5.63 \ (2\text{H, m, } \text{CH} = \text{CH}_2),\ 5.17 \ (1\text{H, tt, } J 6.7, 2.5, \text{CHOTs}),\ 2.63 \ (2\text{H, dd, } J 17.1, 6.7, 2 \times \text{CH}_3\text{H}_2),\ 2.53 \ (2\text{H, dd, } J 17.1, 2.5, 2 \times \text{CH}_3\text{H}_2),\ 2.46 \ (3\text{H, s, } \text{CH}_3). \]

\[ ^{13}\text{C NMR} \ (100 \text{ MHz, CDCl}_3) \delta\text{C:} \ 144.6, 134.3 \ (2 \times \text{C(Ar)}), 129.8 \ (\text{HC(Ar)}), 127.9, 127.7 \ (\text{HC(Ar)} + \text{CH} = \text{CH}_2), 81.9 \ (\text{CHOTs}), 39.8 \ (\text{CH}_2), 21.6 \ (\text{CH}_3). \]

\[ \text{m.p. } 52-53 \ ^\circ \text{C}. \]
Data were consistent with those previously reported.\textsuperscript{5}

**Cyclopent-3-enyl(cyclopentyl)thioether (II, SCypCyp')**

\[
\begin{align*}
\text{Cyclopentylthiol (41.6 mg, 0.408 mmol) was added to a stirred solution of sulfonate c\_II (85.9 mg, 0.408 mmol) and Cs\_2CO_3 (266 mg, 0.816 mmol) in anhydrous DMF (2 mL) and the mixture was stirred for 2 h at room temperature. The reaction was quenched with saturated aqueous NaHCO}_3 (20 mL) and extracted with Et}_2O (3 x 25 mL). The combined organics were dried over MgSO}_4, filtered and the solvent removed in vacuo. Flash column chromatography [SiO}_2, petrol/Et}_2O, 99:1 then 49:1] gave thioether II as an oil (57.5 mg, 0.342 mmol, 84 %).}
\end{align*}
\]

\textbf{1H NMR} (400 MHz, CDCl}_3 \delta_H: 5.72-5.68 (2H, m, C\_H=CH), 3.47 (1H, tt, J 8.4, 5.8, C\_HCH\_2CH=CH), 3.12 (1H, quin, J 7.1, CHCH\_2CH\_2), 2.78 (2H, dd, J 14.7, 8.4, 2 \times CH\_3H\_bCH=CH), 2.36 (2H, dd, J 14.7, 8.4, 2 \times CH\_3H\_bCH=CH), 2.05-1.96 (2H, m, 2 \times CHCH\_2CH\_3H\_b), 1.78-1.67 (2H, m, 2 \times CHCH\_2CH\_3H\_b), 1.62-1.47 (4H, m, 2 \times CHCH\_2CH\_3H\_b + 2 \times CHCH\_2CH\_3H\_b).

\textbf{13C NMR} (100 MHz, CDCl}_3 \delta_C: 129.3 (CH=CH), 43.6 (CHCH\_2CH\_2), 41.1 (CHCH\_2CH=CH), 41.0 (CH\_2CH=CH), 34.1 (CHCH\_2CH\_2), 24.8 (CHCH\_2CH\_2).

\textbf{IR} \nu_{max} (thin film)/cm\textsuperscript{-1}: 3056m, 2956s, 2867m, 2844w, 2360w, 1616m, 1447s, 1343m, 1296m, 1238m, 1052m, 932m, 804w.

\textbf{m/z} (ESI\textsuperscript{+}) 207.1 [100, (M + Na + O\textsuperscript{+})], C\textsubscript{10}H\textsubscript{16}NaOS predicted 207.0820, found 207.0814, (\Delta + 2.9 ppm).

**Cyclopentyl(phenyl)thioether (III, SPhCyp)**

\[
\begin{align*}
\text{Thiophenol (551 mg, 5.00 mmol) was added to a stirred solution of bromocyclopentane (745 mg, 5.00 mmol) and Cs\_2CO}_3 (3.26 g, 10.0 mmol) in anhydrous DMF (25 mL) and the mixture was stirred for 2 h at room temperature. The reaction was quenched with saturated aqueous NaHCO}_3 (20 mL) and extracted with Et}_2O (3 x 25 mL). The combined organics were dried over MgSO}_4, filtered and the solvent removed in vacuo. Flash column chromatography [SiO}_2, petrol/Et}_2O, 99:1 then 49:1] gave thioether III as an oil (847 mg, 95 %).}
\end{align*}
\]
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta H\): 7.38 (2H, d, \(J 7.9, 2 \times HC(Ar)\)), 7.29 (2H, t, \(J 7.7, 2 \times HC(Ar)\)), 7.19 (1H, t, \(J 7.3, HC(Ar)\)), 6.32 (1H, quin, \(J 6.3, CHSPh\)), 2.11-2.03 (2H, m, \(2 \times CHCH_2H_bCH_2\)), 1.85-1.75 (2H, m, \(2 \times CHCH_2H_aCH_2\)), 1.68-1.60 (4H, m, \(2 \times CHCH_2H_aH_bCH_2 + 2 \times CHCH_2H_bH_a\)).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta C\): 137.3 (\(C(Ar)\)), 129.9, 128.8, 125.9 (\(3 \times H(Ar)\)), 45.9 (CHSPh), 33.6 (CHCH\(_2\)).

Data were consistent with those previously reported.\(^6\)

**Cyclopent-3-ethyl(phenyl)thioether (IV, SPhCyp')**

\[
\begin{array}{c}
\text{S} \\
\text{C} \\
\text{H} \\
\end{array}
\]

Thiophenol (45.2 mg, 0.410 mmol) was added to a stirred solution of sulfonate c_II (97.8 mg, 0.410 mmol) and Cs\(_2\)CO\(_3\) (267 mg, 0.820 mmol) in anhydrous DMF (2 mL) and the mixture was stirred for 2 h at room temperature. The reaction was quenched with saturated aqueous NaHCO\(_3\) (10 mL) and extracted with Et\(_2\)O (3 x 15 mL). The combined organics were dried over MgSO\(_4\), filtered and the solvent removed in vacuo. Flash column chromatography [SiO\(_2\), petrol/Et\(_2\)O, 99:1 then 49:1] gave thioether IV as an oil (69.3 mg, 96%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta H\): 7.38 (2H, d, \(J 7.9, 2 \times HC(Ar)\)), 7.31 (2H, t, \(J 7.6, 2 \times HC(Ar)\)), 7.21 (1H, t, \(J 7.4, HC(Ar)\)), 5.78-5.74 (2H, m, \(CH=CH\)), 3.98 (1H, tt, \(J 8.1, 4.5, CHSPh\)), 2.88 (2H, dd, \(J 15.2, 8.1, CHCH_2H_b\)), 2.46 (2H, dd, \(J 15.2, 4.5, CHCH_2H_a\)).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta C\): 136.9 (\(C(Ar)\)), 129.7, 129.2, 128.9, 126.0 (\(3 \times H(Ar) + CH=CH\)), 42.8 (CHSPh), 40.4 (CHCH\(_2\)).

IR \(\nu_{\text{max}}\) (thin film)/cm\(^{-1}\) 3058s, 2937s, 2843s, 1616w, 1584s, 1480s, 1438s, 1345m, 1298m, 1244s, 1153w, 1092s, 1069w, 1025s, 931m.

\(m/z\) (EI/FI\(^+\)) C\(_{11}\)H\(_{12}\)S predicted 176.0660, found 176.0662, (\(\Delta - 1.3\) ppm).

**Experimental Techniques for new complexes 1-4**

All manipulations, unless otherwise stated, were performed under an atmosphere of argon, using standard Schlenk and glove-box techniques. Glassware was oven dried at 130°C overnight and flamed under vacuum prior to use. Hexane and pentane were dried using a Grubbs type solvent purification system (MBraun SPS-800) and degassed by successive freeze-pump-thaw cycles.\(^1\) CD\(_2\)Cl\(_2\) and 1,2-C\(_6\)H\(_4\)F\(_2\) were distilled under vacuum from CaH\(_2\) and stored over 3 Å molecular sieves, 1,2-C\(_6\)H\(_4\)F\(_2\) was stirred over alumina for two hours prior to drying, tert-butylethene was dried over sodium, vacuum
distilled and stored over 3 Å molecular sieves. TBAF was purchased from Aldrich and used as supplied. [Rh(nbd)(Ph₂P(CH₂)₃PPh₂)][BAR₄] was prepared as previously described.⁷ NMR spectra were recorded on Varian Unity Plus 500 MHz spectrometer at room temperature unless otherwise stated. In 1,2-C₆H₄F₂, ¹H NMR spectra were referenced to the centre of the downfield solvent multiplet (δ = 7.07). ³¹P spectra were referenced against 85% H₃PO₄ (external). Chemical shifts are quoted in ppm and coupling constants in Hz. ESI-MS were recorded on a Bruker MicrOTOF instrument. Microanalysis was performed by London Metropolitan University.

**In situ** preparation of [Rh(Ph₂P(CH₂)₃PPh₂)(η⁶-C₆H₄F₂)][BAR₄] (1)

[Rh(Ph₂P(CH₂)₃PPh₂)(nbd)][BAR₄] (9 mg, 0.0061 mmol) was dissolved in 1,2-C₆H₄F₂ (400 µL) in a New Era high pressure NMR tube. The NMR tube was placed under hydrogen (4 atm) and shaken at room temperature for 5 minutes. The tube was then freeze thaw degassed and backfilled with argon, NMR spectroscopy and ESI-MS data were then obtained.

¹H NMR (500 MHz, 1,2-C₆H₄F₂): δ 8.33 (m, 8H, BAR₄), 7.68 (m, 4H, BAR₄), 7.58 – 7.33 (m, 20H, Ar-H), 6.07 (m, 2H, C₆H₄F₂), 5.70 (m, 2H, C₆H₄F₂), 2.44 (m, 4H, CH₂), 1.95 (m, 2H, CH₂).

³¹P {¹H} NMR (202 MHz, 1,2-C₆H₄F₂): δ 25.23 [d, J(RhP) 195].

ESI-MS (1,2-C₆H₄F₂, 60°C, 4.5kV) positive ion: m/z, 629.1168 [M]+ (calc. 629.0840).

Preparation of [Rh(Ph₂P(CH₂)₃PPh₂){S(C₅H₇)(η²-C₅H₇)}][BAR₄] (2)

732 µL of a solution of S(C₅H₇)₂ I in pentane (0.1019 M, 0.0746 mmol, 1.1 equivalents) and tert-butylethene (4 equivalents, 40 µL, 0.310 mmol) was added to an *in situ* generated solution of [Rh(Ph₂P(CH₂)₃PPh₂)(C₆H₄F₂)][BAR₄] (1) (0.0678 mmol) in 1,2-C₆H₄F₂ (5 mL). The solution was heated to 338 K for 18 hours after which the solvent was removed in vacuo and the resulting residue was washed with hexane (2 x 5 mL) and sonicated to yield 2 as a yellow orange solid. Diffusion of pentane into a solution of the isolated solid in 1,2-C₆H₄F₂ (3 mL) at 238 K gave 2 as red crystals. Yield: 77 mg, 73 %.

¹H NMR (500 MHz, CD₂Cl₂): δ 7.75 (m, 8H, BAR₄), 7.58 (br, 4H, BAR₄), 7.55 – 7.33 (m, 20H, Ar-H), 4.59 (v br, 2H, HC=CH), 3.22 (m, 1H, CH), 3.03 (apparent quintet, J(HH) 7, 1H, CH), 2.86 – 0.66 (br m, 18H, CH₂).

³¹P {¹H} NMR (202 MHz, CD₂Cl₂): δ 22.34 [dd, J(RhP) 150, J(PP) 55], 3.42 [dd, J(RhP) 152, J(PP) 55].
Selected $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 200 K): $\delta$ 4.69 (m, 1H, HC=CH), 4.34 (m, 1H, HC=CH).

ESI-MS (1,2-C$_6$H$_4$F$_2$, 60°C, 4.5 kV) positive ion: m/z, 683.1615 [M]$^+$ (calcd. 683.1532).

Anal. Calcd for C$_{60}$H$_{54}$B$_2$F$_{24}$P$_2$Rh$_3$S$_3$ (1546.8578 gmol$^{-1}$): C, 53.58; H, 3.52. Found: C, 53.64; H, 3.30.

**In situ** preparation of [Rh(Ph$_2$P(CH$_2$)$_3$PPh)$_2$(S(η$^5$-C$_5$H$_5$)(C$_5$H$_9$))][BAR$_{f_4}$] (3)

12.5 µL of a solution of S(C$_5$H$_5$)Ph III in pentane (0.4883 M, 0.0061 mmol) was added to an in situ generated solution of [Rh(Ph$_2$P(CH$_2$)$_3$PPh)$_2$(C$_6$H$_4$F$_2$)][BAR$_{f_4}$] (1) (0.0061 mmol) in 1,2-C$_6$H$_4$F$_2$ (400 µL).

$^1$H NMR (500 MHz, 1,2-C$_6$H$_4$F$_2$): $\delta$ 8.33 (br, 8H, BAR$_{f_4}$), 7.68 (br, 4H, BAR$_{f_4}$), 7.55 – 7.33 (m, 20H, Ar-H), 6.47 (t, J(HH) 6, 1H, S-Ph), 5.70 (apparent doublet, J(HH) 6, 2H, S-Ph), 5.47 (t, J(HH) 6, 2H, S-Ph), 3.26 (quin, J(HH) 6, 1H, CH), 2.40 (m, 4H, dppp-CH$_2$), 1.90 (m, 2H, dppp-CH$_2$). The SPhCyp-CH$_2$ signals were not ambiguously assigned as they were obscured by excess free SPhCyp ligand and pentane 2.10 – 0.10.

$^{31}$P (1H) NMR (202 MHz, 1,2-C$_6$H$_4$F$_2$): $\delta$ 25.35 [d, J(RhP) 196].

**In situ** preparation of [Rh(Ph$_2$P(CH$_2$)$_3$PPh)$_2$(S(C$_5$H$_5$)(η$^2$-C$_5$H$_7$))][BAR$_{f_4}$] (4)

147 µL of a solution of S(C$_5$H$_5$)Ph III in pentane (0.4883 M, 0.0718 mmol, 1.1 equivalents) and tert-butylethene (40 µL, 0.310 mmol) was added to an in situ generated solution of [Rh(Ph$_2$P(CH$_2$)$_3$PPh)$_2$(C$_6$H$_4$F$_2$)][BAR$_{f_4}$] (1) (0.0651 mmol) in 1,2-C$_6$H$_4$F$_2$ (5 mL). The solution was heated to 378 K for 18 hours after which the solvent was removed in vacuo and the resulting residue was washed with hexane (3 x 5 mL) and sonicated under vacuum to yield 4 as a yellow/brown oil.

$^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 7.75 (m, 8H, BAR$_{f_4}$), [7.69 – 6.65 (v br m, 20H, dppp Ar-H) {7.65, (br, 4H, BAR$_{f_4}$), 7.35 (m, 3H, S-Ph), 7.23 (t, J (HH) 8, 2H, S-Ph)}], 5.00 (br, 1H, HC=CH), 4.23 (br m, 1H HC=CH), 3.30 (m, 1H, Cyp-CH), [2.75 -1.45 (v br m, 8H, dppp-CH$_2$ and SPhCyp'-CH$_2$) {2.33 (d, J(HH) 16, 2H, SPhCyp'-CH$_2$)}].

$^{31}$P (1H) NMR (202 MHz, CD$_2$Cl$_2$): $\delta$ 23.10 [dd, J(RhP) 153, J(PP) 54], 1.76 [dd, J(RhP) 148, J(PP) 54].

**Selected** $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 200 K): $\delta$ 7.30 (m, 3H, S-Ph), 7.17 (t, J (HH) 8, 2H, S-Ph), 6.91 (m, 3H, dppp Ar-H), 6.81 (m, 2H, dppp Ar-H), 4.94 (m, 1H, HC=CH), 4.05 (m, 1H, HC=CH), 2.85 - 2.44 (m, 4H, dppp-CH$_2$), 2.33 (d, J(HH) 16, SPhCyp'-CH), 2.26 (d, J(HH) 16, SPhCyp'-CH), 2.22 – 2.11 (m,
1H, dppp-CH), 2.06 (d, J(HH) 16, 1H, SPhCyp'-CH), 1.70 (m, 1H, dppp-CH), 1.57 (d, J(HH) 16, 1H, SPhCyp'-CH).

ESI-MS (1,2-C₆H₄F₂, 60°C, 4.5 kV) positive ion: m/z, 691.1204 [M]+ (calcd. 691.1219).

Crystallography

Data were collected on an Enraf Nonius Kappa CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and a low-temperature device [150(2) K]; data were collected using COLLECT, reduction and cell refinement was performed using DENZO/SCALEPACK. The structure was solved by direct methods using SIR2004 and refined full-matrix least squares on F² using SHELXL-97. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions using the riding model. Disorder of the thioether ligand was treated by modelling the non-coordinated substituent over two sites and restraining its geometry. Rotational disorder of the CF₃ groups of the anion was treated by modelling the fluorine atoms or, in two cases, the entire CF₃ group over two sites and restraining their geometry. Problematic solvent disorder was treated using the SQUEEZE algorithm. Restraints to thermal parameters were applied were necessary in order to maintain sensible values. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre under CCDC 818288. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
References

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