Development of Novel Bissulfoxide and Phosphine-Olefin Ligands for Transition Metal Catalysis

Dissertation

zur

Erlangung der naturwissenschaftlichen Doktorwürde
(Dr. sc. nat.)

vorgelegt der

Mathematisch-naturwissenschaftlichen Fakultät

der

Universität Zürich

von

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Zürich 2011

Parallels can be drawn between the trends observed for the Pt complexes and those observed with the Pd complexes. Above we have seen that Cl appears to exert a stronger *trans*-influence on the bissulfoxide ligand than TFA in the neutral Pt complexes discussed. Similarly,we saw earlier that the in the Pd-bissulfoxide dichloride complex (**4**) the binaso seemed to coordinate weakly, whereas the Pd-bissulfoxide TFA complex (**6**) was a stable, isolable compound.

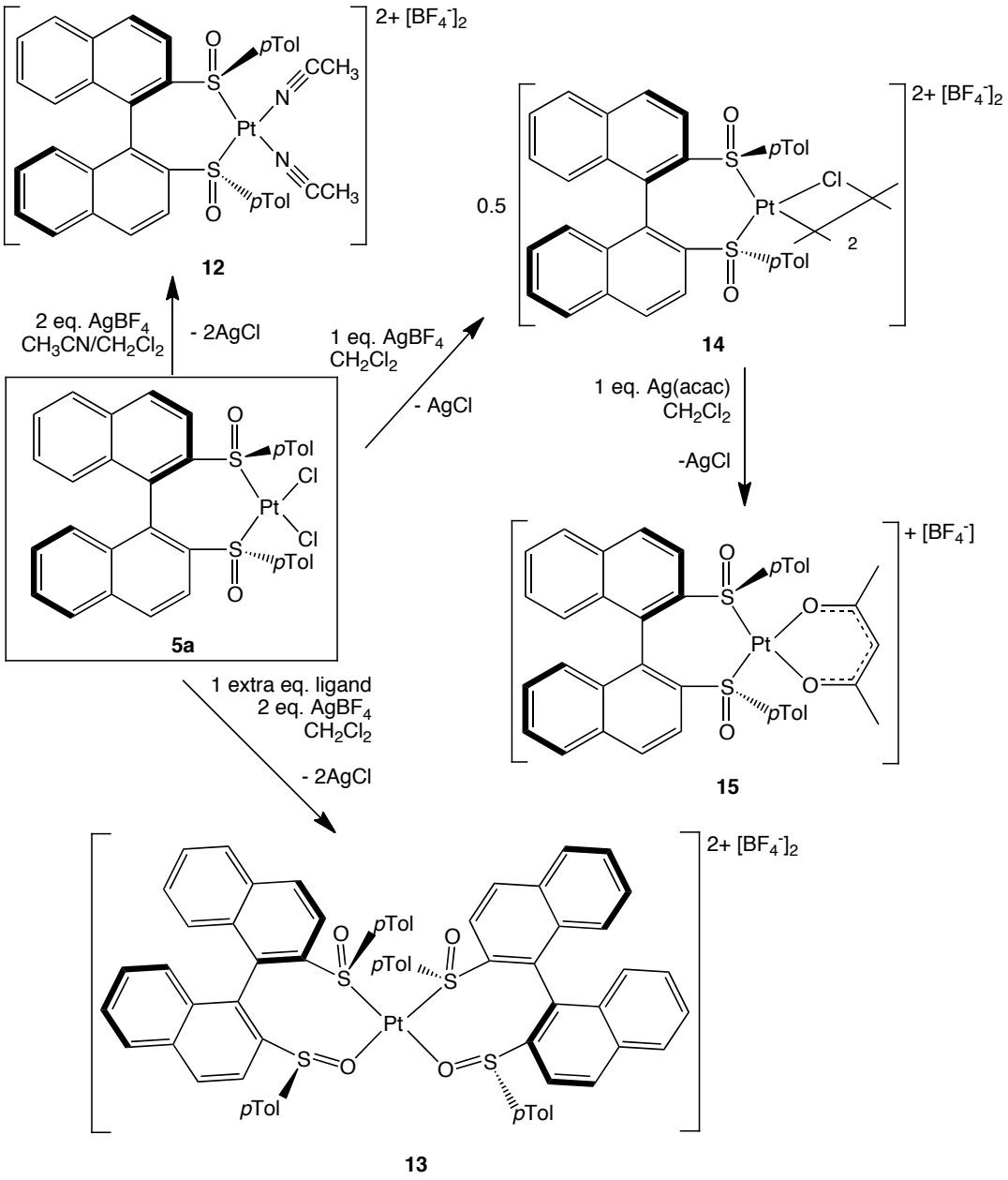

Figure 13 Cationic platinum complexes made from **5a**

Various cationic Pt complexes could also be synthesised employing **5a** as the starting point. When **5a** was treated with 2 equivalents of $AgBF_4$ in a solvent mixture of CH_2Cl_2 and CH_3CN, the chlorides were abstracted and replaced by 2 CH_3CN

molecules to form complex **12**. The bound CH_3CN could clearly be seen in the ^1H and ^{13}C NMR spectra. This complex was quite stable inside the glovebox and could be stored at room temperature. Similarly, complex **13** could be formed by again reacting **5a** with 2 equivalents of $AgBF_4$, but also with 1 equivalent of *p*-tolyl-binaso in a CH_2Cl_2 solution. We were not able to obtain a crystal of this complex to confirm the structure unambiguously, but we believe it is analogous to the Pd complex **7** (figure 13). The ^1H NMR spectrum of **13** shows the binaso ligand to be desymmetrised, which suggests formation of the proposed structure.

When **5a** was treated with only 1 equivalent of $AgBF_4$, unlike in the Pd case, the stable complex **14** was formed. No crystals could be grown to confirm the structure, but the ^1H NMR spectrum of the complex shows the ligand is still symmetric. There is precedence for this type of chloro-bridged Pt dimers in the literature with phosphine ligands.[13] Pregosin *et al.* were able to obtain an X-ray crystal structure of a dimeric Pt complex with the ligand MeO-Biphep.[14] **14** could then react cleanly with 1 equivalent of Ag(acac) (acac = acetylacetonate) to give the monocationic complex **15**. This complex was stable at room temperature under nitrogen and ^1H and ^{13}C NMR spectra revealed both acac and binaso ligands to be bound.

Finally, another group of cationic platinum complexes were made from the precursor $Pt(COD)Cl_2$ (COD = cyclooctadiene). It was found that treating the precursor with one equivalent of ligand and two equivalents of $AgBF_4$, the chlorides were abstracted and the ligand co-ordinated to Pt to produce the dicationic complexes **16a**, **b** and **c** (figure 14). ^1H NMR spectra confirmed that both the bissulfoxide ligand and cyclooctadiene were bound in each case.

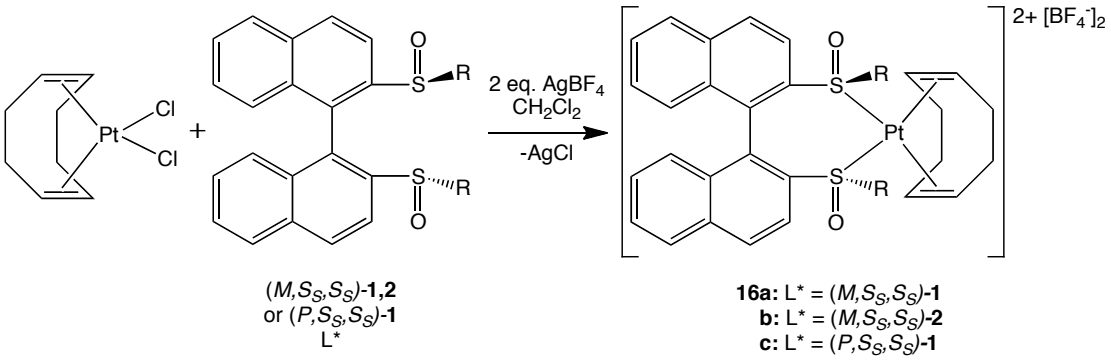

Figure 14 Synthesis of $[Pt(binaso)(COD)][BF_4]_2$ complexes, **16a**, **b** and **c**.

1.96 (s, 6H), 6.48-6.51 (d, *J* = 8.6 Hz, 2H), 6.56-6.58 (d, *J* = 7.8 Hz, 4H), 7.11-7.15 (t, *J* = 7.4 Hz, 2H), 7.47-7.51 (m, 6H), 7.77-7.79 (d, *J* = 7.9 Hz, 2H), 8.16-8.18 (d, *J* = 9.0 Hz, 2H), 8.52-8.54 (d, *J* = 9.0 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, CD_2Cl_2): δ = 21.54, 122.00, 127.68, 127.81, 128.54, 128.81, 129.04, 129.09, 129.56, 129.62, 129.75, 130.27, 132.06, 132.33, 135.70, 139.84, 145.03 ppm. Elemental analysis: Calculated for $PtC_{34}H_{26}Cl_2O_2S_2$: C = 51.26%, H = 3.29%; Found: C = 51.32%, H = 3.43%.

Pt(II)(*M*,*S*$_S$,*S*$_S$)-cyclohexyl-binasoCl_2 (5b): A 100ml Schlenk tube was charged with 92mg (0.194 mmol) $Pt(PhCN)_2Cl_2$ and 100mg (0.194 mmol) (*M*,*S*$_S$,*S*$_S$)-cyclohexyl-binaso. 10ml dry toluene was added, and the yellow suspension was stirred at 100°C overnight. The reaction was then allowed to cool to room temperature; the Schlenk tube was then taken inside the glove box. Pentane was added to the stirred yellow suspension, the solid was allowed to settle, and the supernatant solvent was decanted off *via* Pasteur pipette. The remaining yellow solid was washed twice with toluene (2 x 5ml), and twice with pentane (2 x 5ml). The complex was then dried thoroughly under high vacuum to give 129mg (85% yield) of product. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = -0.81--0.69 (m, 1H), 0.41-0.51 (m, 1H), 0.76-0.88 (m, 3H), 1.02-1.37 (m, 9H), 1.53-1.59 (m, 2H), 1.69-1.81 (m, 2H), 2.53-2.56 (m, 1H), 7.21-7.23 (d, *J* = 8.8 Hz, 1H), 7.43-7.47 (t, *J* = 7.7 Hz, 1H), 7.53-7.57 (t, *J* = 7.8 Hz, 4H), 7.71-7.79 (m, 6H), 8.14-8.16 (d, *J* = 8.4 Hz, 1H), 8.42-8.48 (q, *J* = 3.8 Hz, *J* = 12.9 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 23.85, 24.51, 24.73, 26.05, 28.30, 29.93, 65.00, 109.32, 117.02, 123.50, 127.13, 128.11, 129.11, 129.37, 129.69, 130.01, 132.08, 132.40, 133.99, 135.45, 135.52, 135.96 ppm. Elemental analysis: Calculated for $PtC_{32}H_{34}O_2S_2Cl_2.2CDCl_3$: C = 39.98%, H = 3.55%; Found: C = 40.06%, H = 3.07%.

Pd(II)(*M*,*S*$_S$,*S*$_S$)-*p*-tolyl-binaso$(OC(O)CF_3)_2$ (6): A vial was charged with 49mg (0.188 mmol) $Pd(PhCN)_2Cl_2$,100mg (0.188 mmol) (*M*,*S*$_S$,*S*$_S$)-*p*-tolyl-binaso and 83mg (0.376 mmol) $Ag(OC(O)CF_3)$. 5ml CH_2Cl_2 was added, the vial was covered, and the reaction was left stirring in the dark for three hours. After this time, the precipitated AgCl was filtered off over celite to leave a yellow solution. Solvent was removed to leave a volume of about 1ml, and diethyl ether (20ml) was added dropwise, with stirring, to precipitate a yellow solid. The vial was centrifuged for 5 minutes, so the

Elemental Analysis: Calculated for $PdC_{68}H_{52}B_2F_8O_4S_4.3H_2O$: C = 58.53%, H = 4.18%; Found: C = 58.57%, H = 3.95%.

Pt(II)(*M,S*$_S$,*S*$_S$)-*p*-tolyl-binaso(OC(O)CF$_3$)$_2$ (8): A vial was charged with 100mg (0.126 mmol) of **5** and 56mg (0.252 mmol) Ag(OC(O)CF$_3$). 5ml CH_2Cl_2 was added and the vial was covered. The reaction was left stirring in the dark for four hours, after this time it was filtered over celite to remove the precipitated AgCl. The resulting colourless solution was concentrated to a volume of about 1ml, and diethyl ether (20ml) was added dropwise to the stirred solution to precipitate a white solid. The vial was centrifuged for five minutes, so that the supernatant solvent could be decanted off *via* Pasteur pipette. The solid was washed twice with diethyl ether (2 x 5ml) and then dried thoroughly under high vacuum to give 97mg (81% yield) of the complex. Colourless crystals suitable for x-ray analysis could be grown by diffusion of THF into a concentrated solution of the complex in CH_2Cl_2. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 1.96 (s, 6H), 6.44-6.46 (d, *J* = 8.6 Hz, 2H), 6.59-6.61 (d, *J* = 8.2 Hz, 4H), 7.12-7.16 (t, *J* = 7.7 Hz, 2H), 7.50-7.53 (t, *J* = 7.6, 2H), 7.65 (br s, 4H), 7.79-7.81 (d, *J* = 8.3 Hz, 2H), 8.21-8.23 (d, *J* = 9.0 Hz, 2H), 8.51-8.53 (d, *J* = 9.0 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, CD_2Cl_2): δ = 21.40, 121.52, 127.55, 128.54, 129.06, 129.46, 129.91, 130.15, 131.75, 132.47, 134.70, 135.80, 137.64, 145.33, 145.34 ppm. ^{19}F-NMR (400 MHz, CD_2Cl_2): δ = -74.46 (s) ppm. Elemental Analysis: Calculated for $PtC_{38}H_{26}F_6O_6S_2$: C = 47.95%, H = 2.75%; Found: C = 47.92%, H = 3.01%.

Pt(II)(*M,S*$_S$,*S*$_S$)-*p*-tolyl-binaso(Me)$_2$ (9a): A vial was charged with 100mg (0.174 mmol) $[Pt(Me)_2\mu\text{-}S(Me)_2]_2$ and 185mg (0.348 mmol) (*M,S*$_S$,*S*$_S$)-*p*-tolyl-binaso. 4ml CH_2Cl_2 was added, after 30 minutes a white precipitate began to appear. The mixture was left stirring overnight and then 10ml pentane was added to yield more precipitation of the white solid. The vial was centrifuged for five minutes, so the supernatant solvent could be decanted off *via* Pasteur pipette. The white solid was then redissolved in CH_2Cl_2, and filtered over celite. The complex was precipitated again by adding pentane to the colourless solution, and was centrifuged. The supernatant solvent was removed in the same way as before, and the solid was dried thoroughly under high vacuum to give 202mg (79% yield) of product. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 0.91-1.11 (t, *J* = 41.0 Hz, 6H), 1.89 (s, 6H), 6.27-6.29 (d, *J* = 8.6

Hz, 2H), 6.43-6.45 (d, *J* = 8.2 Hz, 4H), 6.92-6.96 (t, *J* = 7.8 Hz, 2H), 7.29-7.31 (d, *J* = 7.7 Hz, 4H), 7.34-7.38 (t, *J* = 7.5 Hz, 2H), 7.67-7.69 (d, *J* = 8.1 Hz, 2H), 8.06-8.08 (d, *J* = 8.8 Hz, 2H), 8.52-8.55 (d, *J* = 8.9 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, CD_2Cl_2): δ = -0.35, 21.29, 121.31, 126.39, 127.28, 127.51, 127.60, 128.09, 128.59, 129.19, 129.68, 129.73, 130.74, 132.64, 134.89, 139.10, 142.71, 143.99 ppm. Elemental Analysis: Calculated for $PtC_{36}H_{32}S_2O_2.0.8(C_5H_{12})$: C = 59.05%, H = 5.15%; Found: C = 59.06%, H = 4.96%.

Pt(II)(*M,S*$_S$*,S*$_S$)-cyclohexyl-binaso(Me)$_2$ (9b): Made by the same method as described for **9a**, using 179mg (0.348 mmol) (*M,S*$_S$*,S*$_S$)-cyclohexyl-binaso. 165mg of the white solid product were obtained (64% yield). Colourless crystals were grown from a solution of the complex in a 10:1 hexane/CH_2Cl_2 mixture, after being left at -20°C for several weeks. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = -0.57--0.50 (m, 1H), 0.39-0.48 (m, 2H), 0.72-0.95 (m, 1H), 0.82 (t, *J* = 34.9 Hz, 6H), 1.05-1.71 (m, 17H), 2.12-2.14 (m, 1H), 7.06-7.11 (m, 2H), 7.32-7.37 (m, 2H), 7.61-7.66 (m, 2H), 8.06-8.15 (m, 3H), 8.25-8.37 (m, 3H) ppm. ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 0.20, 22.04, 23.39, 24.89, 24.97, 25.25, 25.49, 25.94, 26.12, 26.18, 27.25, 27.94, 59.75, 61.56, 122.19, 123.28, 125.80, 127.12, 127.87, 127.93, 128.09, 128.13, 128.57, 129.11, 129.38, 129.77, 130.24, 130.95, 133.01, 133.14, 134.53, 134.78, 140.13, 140.49 ppm. Elemental Analysis: Calculated for $PtC_{34}H_{40}S_2O_2$: C = 55.19%, H = 5.45%; Found: C = 55.23%, H = 5.34%.

Pt(II)(*M,S*$_S$*,S*$_S$)-*p*-tolyl-binaso(OC(O)CF$_3$)Cl (10): A vial was charged with 50mg (0.063 mmol) **5** and 14mg (0.063 mmol) $AgOC(O)CF_3$. 3 ml CH_2Cl_2 was added and the vial was covered. The reaction was left stirring in the dark for 4 hours and was then filtered over celite. The clear, colourless solution obtained was concentrated to a volume of about 1 ml and 20ml diethyl ether was added dropwise to the stirred solution so that a white precipitate appeared. The vial was centrifuged for 10 minutes, so the supernatant solvent could be removed by Pasteur pipette. The white solid was then dried thoroughly under high vacuum to give 45mg (82% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.91 (s, 3H), 1.94 (s, 3H), 6.38-6.54 (m, 6H), 7.04-7.17 (m, 2H), 7.43-7.79 (m, 8H), 8.06-8.22 (m, 2H), 8.53-8.56 (m, 2H) ppm. ^{13}C-NMR (400 MHz,

$CDCl_3$): δ = 21.33, 21.35, 21.39, 21.41, 66.07, 68.20, 121.50, 121.65, 121.73, 121.82, 127.18, 127.23, 127.28, 127.30, 127.52, 127.74, 127.86, 127.97, 128.00, 128.10, 128.21, 128.62, 128.65, 128.72, 128.77, 129.10, 129.13, 129.40, 129.59, 129.67, 129.77, 129.82, 130.06, 131.44, 131.47, 131.63, 131.70, 131.78, 131.85, 132.01, 132.10, 134.29, 134.63, 135.18, 135.24, 135.31, 135.42, 136.14, 137.81, 138.38, 139.10, 144.31, 144.65 ppm. Elemental Analysis: Calculated for $PtC_{36}H_{26}O_4F_3S_2Cl$: C = 49.46%, H = 3.00%; Found: C = 49.16%, H = 3.14%.

Pt(II)(*M*,S_S,S_S)*p*-tolyl-binasoI$_2$ (11): A vial was charged with100mg (0.126 mmol) **5** and 38mg (0.252 mmol) NaI. Acetone was added to the stirred mixture and the solution instantly became red. The reaction was left for 30 minutes, after which time an orange-red precipitate had appeared. The vial was centrifuged for 5 minutes and the supernatant solvent was decanted off, to leave the solid. The solid was redissolved in CH_2Cl_2 (2ml) and filtered over celite, to give a clear red solution. Diethyl ether (20ml) was added dropwise to the solution to precipitate the complex. The vial was centrifuged and the supernatant solvent was decanted off *via* Pasteur pipette. The deep orange solid was washed twice more with diethyl ether (2 x 5ml) and dried thoroughly under high vacuum to give 91mg (74% yield) of the product. Crystals suitable for x-ray analysis were grown by slow diffusion of diethyl ether into a concentrated solution of the complex in CH_2Cl_2. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 1.95 (s, 6H), 6.46-6.49 (d, *J* = 9.0 Hz, 2H), 6.53-6.55 (d, *J* = 7.3 Hz, 4H), 7.08-7.12 (t, *J* = 7.7 Hz, 2H), 7.38 (br s, 4H), 7.47-7.51 (t, *J* = 7.1 Hz, 2H), 7.75-7.79 (d, *J* = 8.1 Hz, 2H), 8.12-8.16 (d, *J* = 9.1 Hz, 2H), 8.53-8.55 (d, *J* = 9 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, CD_2Cl_2): δ = 120.16, 122.31, 126.24, 126.45, 127.62, 128.32, 129.00, 129.48, 129.77, 131.39, 131.99, 132.08, 135.57, 136.26, 140.44, 144.53 ppm. Elemental Analysis: Calculated for $PtC_{34}H_{26}I_2S_2O_2.H_2O.CH_2Cl_2$: C = 38.83%, H = 2.79%, S = 5.93%; Found: C = 38.35%, H = 2.74%, S = 6.06%.

Pt(II)((*M*,S_S,S_S)-*p*-tolyl-binaso)$(CH_3CN)_2(BF_4)_2$ (12): A vial was charged with 100mg (0.126 mmol) **5** and 49mg (0.252 mmol) $AgBF_4$. 4ml of a 3:1 mixture of CH_2Cl_2/CH_3CN was added and the vial was covered. The reaction was left stirring in the dark for 3 hours. After this time, the precipitated AgCl was filtered off over celite, to leave a clear, yellow solution. The solution was concentrated to a volume of about

1ml, and diethyl ether (20ml) was added slowly to the stirred solution to precipitate a yellow solid. The vial was centrifuged, so the supernatant solvent could be decanted off by Pasteur pipette. The complex was washed twice more with diethyl ether (2 x 5ml), and then dried thoroughly under high vacuum to give 101mg (82% yield) of product. ^{1}H NMR confirmed that both the ligand and two equivalents of CH_3CN were bound. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.99 (s, 6H), 2.63 (s, 6H), 6.56-6.58 (d, *J* = 8.7 Hz, 2H), 6.62-6.83 (m, 4H), 7.22-7.25 (t, *J* = 7.7, Hz, 2H), 7.54-7.58 (t, *J* = 7.5, 6H), 7.80-7.82 (d, *J* = 8.3 Hz, 2H), 8.24-8.26 (d, *J* = 9.0 Hz, 2H), 8.55-8.57 (d, *J* = 9.0 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, CD_2Cl_2): δ = 4.05 (s), 21.51 (t, *J* = 80 Hz), 122.29, 127.21, 128.94, 129.13, 129.54, 130.35, 130.92, 131.41, 132.47, 133.24, 135.05, 135.95, 146.49 ppm. ^{19}F-NMR (400 MHz, CD_2Cl_2): δ = -151.37 (s) ppm. Elemental analysis: Calculated for $PtC_{38}H_{32}B_2F_8N_2O_2S_2.CH_2Cl_2$: C = 43.92, H = 3.21, N = 2.63; Found: C = 43.63, H = 3.25, N = 2.68.

Pt(II)((*M*,*S*$_S$,*S*$_S$)-*p*-tolyl-binaso)$_2$(BF$_4$)$_2$ (13): A vial was charged with 50mg **5** (0.063 mmol), 33mg (0.063 mmol) (*M*,*S*$_S$,*S*$_S$)-*p*-tolyl-binaso) and 25mg (0.126 mmol) $AgBF_4$. 3ml CH_2Cl_2 was added and the vial was covered. The reaction was left stirring in the dark for 2 hours. It was then filtered over celite to remove precipitated AgCl. The clear yellow solution was then concentrated to a volume of around 1ml and diethyl ether was added dropwise. The complex precipitated as a yellow solid. The vial was centrifuged for 10 minutes, so the supernatant solvent could be removed by Pasteur pipette. The solid was washed twice more with diethyl ether and then thoroughly dried under high vacuum to give 77g (85% yield) of product. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.10 (s, 3H), 2.28 (s, 3H), 6.42-6.44 (d, *J* = 8.6 Hz, 1H), 6.74-6.98 (br s, 2H), 7.14-7.17 (m, 6H), 7.43-7.59 (m, 5H), 7.86-7.88 (d, *J* = 8.2 Hz, 2H), 8.34 (s, 2H), 8.37-8.39 (d, *J* = 7.3 Hz, 1H), 8.48-8.50 (d, *J* = 9.0 Hz, 1H) ppm. ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 21.54, 21.75, 121.03, 121.18, 125.86, 126.79, 126.99, 128.91, 129.03, 129.54, 130.24, 130.56, 131.15, 131.38, 131.83, 132.26, 133.99, 135.30, 135.94, 147.55 ppm. ^{19}F-NMR (400 MHz, $CDCl_3$): δ = -152.51 (s) ppm. Elemental Analysis: Calculated for $PtC_{68}H_{52}B_2F_8S_4O_4.3H_2O$: C = 55.70%, H = 3.85%; Found: C = 55.77%, H = 3.80%.

Pt(II)((*M*,S_S,S_S)-*p*-tolyl-binaso)(acac)(BF_4)$_2$ (14): A vial was charged with 100mg (0.126 mmol) **5a** and 24mg (0.126 mmol) $AgBF_4$. 2ml CH_2Cl_2 was added, the vial was covered and the reaction was left stirring in the dark for 2 hours. After this time, the reaction was filtered over celite to remove AgCl. Solvent was then removed to leave a yellow residue in the vial, to this The remaining clear, yellow solution was concentrated to a volume of about 1ml, and diethyl ether was added in a dropwise manner to the stirred solution to precipitate a yellow solid. The vial was centrifuged so the supernatant solvent could be decanted off by Pasteur pipette. The yellow solid was washed twice more with ether and the dried completely under high vacuum to give 91mg (85% yield) of product. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.99 (s, 6H), 2.21 (s, 6H), 5.90 (s, 1H), 6.48 (d, *J* = 8.7 Hz, 2H), 6.63-6.65 (d, *J* = 7.3 Hz, 4H), 7.18-7.22 (t, *J* = 7.1 Hz, 2H), 7.42-7.44 (d, *J* = 7.5 Hz, 4H), 7.52-7.56 (t, *J* = 7.2 Hz, 2H), 7.86-7.88 (d, *J* = 8.2 Hz, 2H), 8.31-8.34 (d, *J* = 9 Hz, 2H), 8.47-8.49 (d, *J* = 8.8 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 21.56, 26.62, 104.20, 120.88, 126.94, 127.20, 128.94, 129.27, 129.53, 130.19, 130.48, 131.62, 133.15, 133.66, 135.71, 137.04, 146.06, 187.75 ppm. ^{19}F-NMR (400 MHz, $CDCl_3$): δ = -152.00 (s, 3F), -151.95 (s, 1F) ppm. Elemental Analysis: Calculated for $PtC_{39}H_{33}BF_4O_2S_2$: C = 51.38%, H = 3.65%; Found: C = 51.19, H = 3.54%.

[Pt{(*M*,S_S,S_S)-*p*-tolyl-binaso}(COD)][BF_4]$_2$ (15a): A vial was charged with 35.2mg (0.094 mmol) $PtCODCl_2$, 50mg (0.094 mmol) (*M*,S_S,S_S)-*p*-tolyl-binaso and 36.6mg (0.188 mmol) $AgBF_4$. 2 ml CH2Cl2 was added, the vial was covered and then the reaction was left stirring for 30 minutes. After this time the mixture was filtered over celite to remove precipitated AgCl. The solution was concentrated to about 1 ml and diethyl ether (20 ml) was added slowly, with stirring, to precipitate the complex as a white solid. The vial was centrifuged for 10 minutes and the supernatant solvent was removed by Pasteur pipette. The solid was washed twice more with diethyl ether (2 x 5 ml) and then thoroughly dried under high vacuum to give 92mg (97% yield) of product. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.95-2.22 (m, 4H), 2.36 (s, 6H), 2.69-2.83 (m, 2H), 2.87-3.02 (m, 2H), 5.54-5.66 (m, 2H), 6.09-6.22 (m, 2H), 7.03-7.05 (d, *J* = 7.9 Hz, 2H), 7.26-7.41 (m, 8H), 7.47-7.50 (t, *J* = 7.5 Hz, 2H), 7.73-7.77 (t, *J* = 7.6 Hz, 2H), 7.81-7.83 (d, *J* = 8.8 Hz, 2H), 8.11-8.13 (d, *J* = 8.3 Hz, 2H), 8.38-8.40 (d, *J* = 8.8 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 22.11, 30.68, 101.41, 122.16,

126.17, 127.36, 129.86, 130.12, 131.11, 131.89, 132.80, 134.79, 136.19, 137.07, 145.79 ppm. ^{19}F-NMR (400 MHz, $CDCl_3$): δ = -151.82 (s, 3F), -151.77 (s, 1F) ppm. Elemental Analysis: Calculated for $PtC_{42}H_{38}B_2F_8O_2S_2.2H_2O$: C = 48.33, H = 4.06; Found: C = 48.48, H = 3.90.

[Pt{(*M*,*S*$_S$,*S*$_S$)-cyclohexyl-binaso}(COD)][BF$_4$]$_2$ (15b): Same procedure followed as in the synthesis of **15a**, except 50mg (0.097 mmol) (*M*,*S*$_S$,*S*$_S$)-cyclohexyl-binaso, 36.3mg (0.097 mmol) $PtCODCl_2$ and 37.8mg (0.194 mmol) $AgBF_4$ were used. 94 mg (98% yield) of a white solid was obtained. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.45-0.53 (m, 2H), 0.98-1.52 (m, 16H), 1.77-1.79 (m, 2H), 1.95-2.16 (m, 6H), 2.82-2.91 (m, 2H), 2.99-3.05 (m, 2H), 3.69-3.81 (m, 2H), 5.48-5.65 (m, 2H), 5.97-6.13 (m, 2H), 7.15-7.18 (d, *J* = 8.6 Hz, 2H), 7.44-7.48 (t, *J* = 7.7 Hz, 2H), 7.72-7.76 (t, *J* = 7.6 Hz, 2H), 8.13-8.15 (d, *J* = 8.3 Hz, 2H), 8.32-8.34 (d, *J* = 8.9 Hz, 2H), 8.48-8.50 (d, *J* = 8.9 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 24.56, 24.72, 24.77, 25.20, 27.06, 30.13, 30.56, 62.10, 101.41, 103.28, 121.93, 127.38, 129.07, 129.85, 130.68, 132.19, 133.68, 134.42, 136.02, 138.78 ppm. ^{19}F-NMR (400 MHz, $CDCl_3$): δ = -151.60 (s, 3F), -151.55 (s, 1F) ppm. Elemental Analysis: Calculated for $PtC_{40}H_{46}B_2F_8O_2S_2.0.5CH_2Cl_2$: C = 47.04, H = 4.58; Found: C = 47.16, H = 4.59.

[Pt{(*P*,*S*$_S$,*S*$_S$)-*p*-tolyl-binaso}(COD)][BF$_4$]$_2$ (15c): Same procedure followed as in the synthesis of **15a**, except 50mg (0.094 mmol) (*P*,*S*$_S$,*S*$_S$)-*p*-tolyl-binaso was used. 94 mg (99% yield) of a white solid was obtained. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.94-2.42 (m, 4H), 2.09 (s, 6H), 3.06-3.29 (m, 4H), 5.73-5.84 (m, 2H), 5.86-6.03 (m, 2H), 6.12-6.14 (d, *J* = 8.2 Hz, 2H), 6.58-6.73 (m, 8H), 6.78-6.82 (t, *J* = 7.4 Hz, 2H), 7.42-7.46 (t, *J* = 7.5 Hz, 2H), 7.90-7.92 (d, *J* = 8.2 Hz, 2H), 8.35-8.37 (d, *J* = 8.7 Hz, 2H), 8.61-8.63 (d, *J* = 7.4 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 21.40, 29.74, 31.49, 102.34, 104.78, 124.66, 126.27, 127.40, 128.05, 128.71, 128.86, 130.08, 132.06, 133.35, 135.39, 143.21 ppm. ^{19}F-NMR (400 MHz, $CDCl_3$): δ = -150.55 (s, 3F), -150.49 (s, 1F) ppm. Elemental analysis: Calculated for $PtC_{42}H_{38}B_2F_8O_2S_2$: C = 50.07, H = 3.80; Found: C = 49.69, H = 3.92.

General Procedure for the Hydroamination of Cyclohexenone with *p*-tolyl sulfonamide: A vial was charged inside the glovebox with Pt precatalyst (0.05 mmol)