A supramolecular approach to chiral ligand modification: coordination chemistry of a multifunctionalised tridentate amine-phosphine ligand†

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Received (in Durham, UK) 16th August 2007, Accepted 10th December 2007
First published as an Advance Article on the web 10th January 2008
DOI: 10.1039/b712612c

A novel chiral amine-phosphine tagged with an amido-napthyridine moiety has been synthesised and found to bind complementary pyridinone additives. These additives were found to have a modest but measurable promotional effect on the catalytic activity and/or enantioselectivity of Ir- and Rh-catalysed reductions. One explanation for the relatively poor results obtained with the Ir and Ru catalysts is the formation of complexes, in which the ligand adopts an anionic tridentate coordination mode. Pt and Rh complexes of this type were isolated and characterised.

Introduction

The important advances made in transition metal catalysis generally rely on the careful and time-consuming optimisation of catalyst structure to obtain maximum selectivity and catalytic activity. Very subtle changes to catalyst structure can often make large and unpredictable differences to catalyst performance, especially to the enantioselectivity of asymmetric catalysis. Given the great advances made in high throughput catalyst screening and analysis techniques, the slow step in the screening of asymmetric catalysts is now catalyst synthesis. There is therefore great interest in new methodologies that allow the synthesis of structurally diverse catalyst libraries, and in the synthesis of distinctive new types of catalysts.[1] In recent years, several new methodologies that facilitate the synthesis of catalyst libraries have been introduced.[2–5] One of the most intriguing approaches has been using the supramolecular synthesis of pseudo bidentate ligands from two smaller libraries of complementary monodentate ligands. The self-assembly of bidentate ligands using either coordination or hydrogen bonding interactions have been reported by the groups of Reek, Breit and Takacs.[4] Our group have been investigating a conceptually different approach, where intact chiral catalysts or ligands are modified by binding a small library of complementary additives. We have recently demonstrated this new approach to supramolecular catalyst libraries in metal-free organocatalysis. The results were dramatic: a range of programmed additives interacted with the organocatalyst to deliver supramolecular catalysts that each gave distinctive catalytic properties. The best chiral additive improved the enantioselectivity from <20% ee without additive present up to 94% ee.[5] Catalysts that lack the desired hydrogen bonding sites to bind additives did not show the same promotional effect. All the mechanistic data obtained thus far points towards the self-assembly of new asymmetric supramolecular catalysts. Due to the great importance of transition metal catalysis, we were particularly interested in expanding this concept to asymmetric transition metal catalysis. In this paper, we report our progress towards this goal, including coordination chemistry experiments that have shed light on the relatively low catalytic activity observed in the hydrogenation experiments using this first prototype ligand system.

Results and discussion

The amido-napthyridine:pyridinone hydrogen bonding network[6] was utilised in our previous catalysts, hence our design focused on incorporating an amido-napthyridine moiety into a chiral ligand structure. In part, due to their straightforward synthesis and our interest in amine-phosphine ligands in catalysis,[7] the simple phosphine-imine ligand was chosen as the template to investigate the self-assembly approach, and we envisaged that the ligand and pyridinones would assemble in the manner shown as **1b** (Fig. 1).

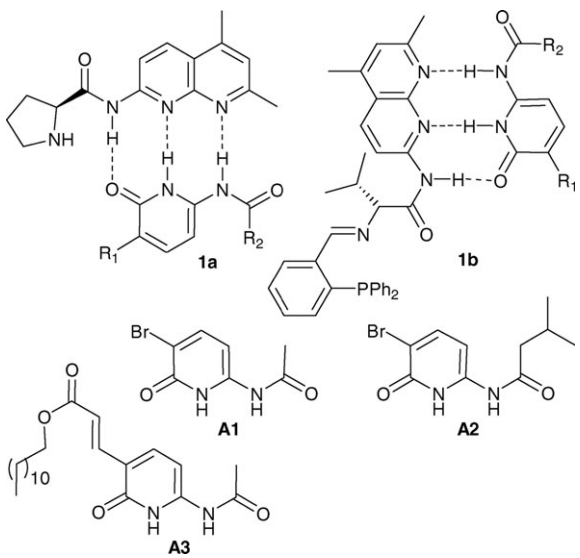

Fig. 1 Pyridinone additives binding to napthyridine-functionalised catalysts and ligands.

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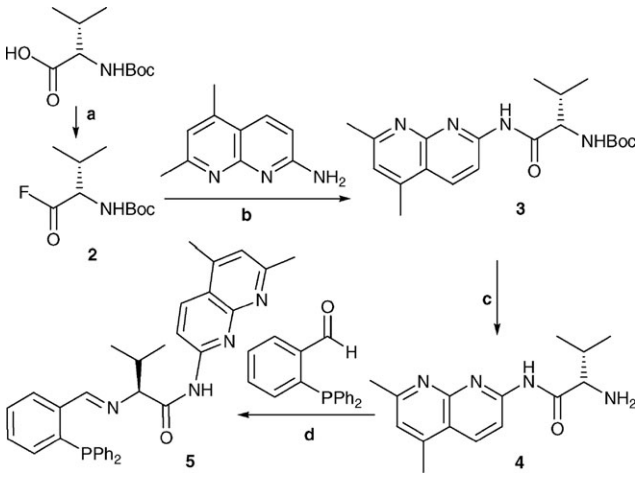
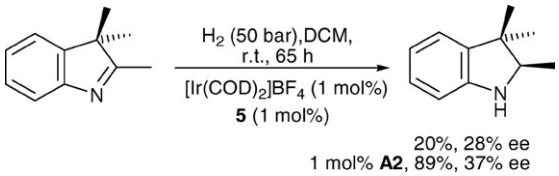
† Electronic supplementary information (ESI) available: Further experimental details, NMR spectra of products, and bond lengths and distances of the X-ray structure determination. See DOI: 10.1039/b712612c



Scheme 1 Conditions: (a) Pyridine, cyanuric fluoride, DCM, −20 °C; (b) pyridine, DMF, 140 °C, 30 min, MW irradiation (66% yield); (c) TFA, DCM, r.t.; then aq. NaOH, r.t. (81% yield); (d) DCM, $MgSO_4$, r.t. (64% yield).

The synthesis of ligand **5** was relatively straightforward using the route shown in Scheme 1. It is worth noting here that many other coupling reagents failed to couple the poorly nucleophilic amino-napthyridine to (*S*)-*N*-Boc-valine. The use of an acid fluoride and rapid heating gave good results, and this is recommended as a useful method for amide bond formation with poorly nucleophilic amines. Due to the forcing conditions employed, individual samples of (*S*)-**4** and (*R*)-**4** were converted to diastereomeric ureas by reaction with enantiomerically pure (*S*)-1-phenylethylisocyanate. ^{1}H NMR spectra of these ureas showed a single diastereomer in each case, confirming that no racemisation took place (see ESI†).

Several pyridinones, **A1**, **A2** and **A3**, were employed to investigate the self-assembly approach. Before the catalytic studies were initiated, the complementary binding of the most soluble additive, **A3**, to host ligand **5** was examined by ^{1}H NMR titration experiments. These revealed that the equilibrium between bound host–additive duplexes and free components was 105: 1, confirming its proposed structure as that shown in Fig. 1. The binding was felt to be sufficiently strong to prove the potential of the approach. Our initial goal was to see if the complementary additives would have any effect on reaction yields or selectivities. Three main classes of reaction were studied: imine hydrogenation, ketone hydrosilylation and alkene hydrogenation. When ligand **5** was tested in the Ir-catalysed hydrogenation of 2,3,3-trimethylindoline (Scheme 2), a rather low activity was observed, although catalysis was clearly observed. More intriguingly, the addition of additive **A2** increased the reaction rate and ee of these reactions (other additives were less effective). Combinations of $[Rh(cod)Cl]_2$ or $[Rh(cod)_2]BF_4$ and ligand **5** were found to give very low activity in the hydrogenation of dimethyl itaconate, with or without additives. When these *in situ*-formed Rh complexes were tested as catalysts for the hydrosilylation of 4′-fluoroacetophenone (Scheme 3), the catalysts also failed to effectively control the enantioselectivity, but the presence of the complementary additives had a clear effect; reactions carried-out without additives gave racemic material, whereas in the

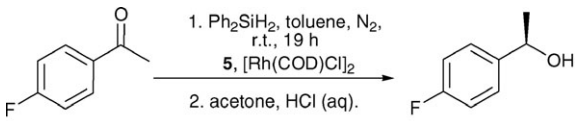


Scheme 2 Asymmetric hydrogenation of 2,3,3-trimethylindoline.

presence of additive **A1**, a reproducible and meaningful enantioselectivity was recorded.

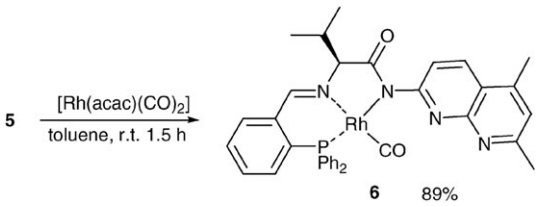
Catalyst screening was halted at this early stage, since despite an indication that the additives had a measurable effect on these catalysts, the overall activity of this type of catalyst was quite low. This highlighted to us the importance of understanding the coordination chemistry of this relatively complex ligand. The reaction of ligand **5** with catalyst precursors $[M(cod)_2]BF_4$ (M = Rh, Ir) gave several inseparable products, suggesting that the ligand was not forming a discrete bidentate catalyst, as was hoped. However, the reaction of **5** with $[Rh(acac)(CO)_2]$ proceeded cleanly to give a single species.

The expected product of a reaction between this precursor and a bidentate ligand is a complex of type [Rh(L)(acac)]. However, spectroscopic investigations revealed that the ligand had been deprotonated by $acac^-$, forming complex **6**, where ligand **5** acts as a tridentate anionic ligand. The complex's $^{31}P\{^1H\}$ NMR spectrum showed the expected doublet with $^1J_{P-Rh}$ = 146 Hz. This is somewhat larger than that observed when phosphines are *trans* to each other (typically ~125 Hz), and reflects the lower *trans* influence of the amide ligand. FAB mass spectroscopy gave the expected mass ion and relative isotopic intensities. A tridentate complex of this nature can either bond through nitrogen or oxygen. We have been unable to grow high quality crystals of this complex for X-ray analysis, but an X-ray crystal structure determination carried-out on very small micro-crystals of **6** gave a low quality structure that was sufficient to confirm the connectivity of the complex, as shown in Scheme 4.[8] This preference for protonation of complexed anionic ligands extended to the strongly bound methyl ligands in $[Pt(cod)Me_2]$. It is well known that strong acids protonate Pt–Me bonds,[9] although examples where the acid is part of a ligand system are more unusual.[10] Ligand **5** reacted cleanly (>95% by NMR) with this precursor at 50 °C to give **7**, in which a tridentate anionic coordination mode for **5** was also observed. This protonation and coordination also takes place at r.t., although more slowly. The protonation reaction also takes place in the presence of the additives. FAB mass spectrometry revealed the expected MH^+ ion and isotope patterns. The proton NMR spectrum showed a methyl resonance with the expected relative integrals and ^{195}Pt coupling ($^1J_{H-Pt}$ = 42 Hz), and did not show a

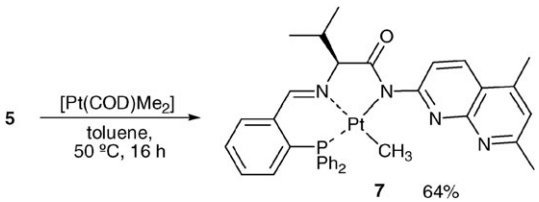


[Rh(COD)Cl]$_2$ (0.5 mol%), **5** (2 mol%), 67%, 0% ee
[Rh(COD)Cl]$_2$ (0.5 mol%), **5** (2 mol%), **A1** (2 mol%), 27%, 13% ee
[Rh(COD)Cl]$_2$ (0.25 mol%), **5** (1 mol%), **A1** (1 mol%), 33%, 10% ee

Scheme 3 Hydrosilylation of 4-fluoroacetophenone.



Scheme 4 Synthesis of a tridentate Rh complex.



Scheme 5 Synthesis of a tridentate Pt complex.

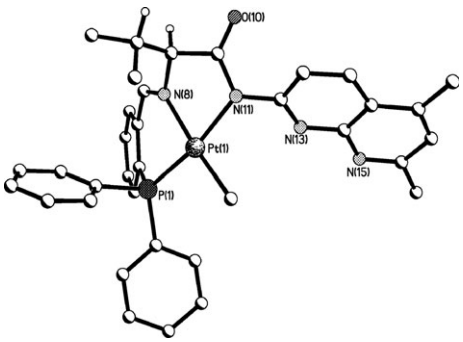


Fig. 2 X-Ray structure of Pt complex **7**. Key bond lengths (Å): Pt(1)–P(1) = 2.1904(15), Pt(1)–N(11) = 2.094(5), Pt(1)–N(8) = 2.061(5) and Pt(1)–CH_3 = 2.083(6).

resonance that could be assigned to an amide proton, consistent with the anionic coordination mode. Coupling to ^{195}Pt is also evident in the carbon NMR of the Pt–Me group.

Crystals of *rac*-**7** were grown by slow evaporation of a sample of *rac*-**7** in $CDCl_3$ over several months. The structure determination unambiguously confirmed the structure in Scheme 5 (Fig. 2). The Pt–P bond lengths are similar to those observed in Pt–phosphine dihalide complexes, in which P is *trans* to a halide.[11] This is consistent with a weak *trans* influence of the amido ligand, as expected from the magnitude of $^{1}J_{P-Pt}$. The most significant deviations from square planar geometry arise in the very narrow bite angle of the N^N part of the ligand (N(8)–Pt(1)–N(11) = 79.60(19)°.

It is not clear if the formation of complexes with a tridentate anionic coordination mode is a general reaction of phosphine-imines derived from amino acid amides. The literature suggests amide coordination does not occur without prior deprotonation of the ligand and reaction with a precursor containing a more labile anion.[10] Since it is such a strongly electron withdrawing substituent, the napthyridine moiety is likely to be a key feature that renders ligand **5** highly acidic.

Conclusions

The isolation of complexes **6** and **7** provides one possible explanation for the low activity of the metal complexes of ligand **5** in catalysis. We have not completely demonstrated the effectiveness of the ligand additive approach using this ligand system, and it is still too early to state with certainty whether the proposed self-assembly mechanism is in operation in transition metal catalysis. However, the study does suggest that ligands that can bind complementary additives are a viable area of investigation if a better ligand design, that does not present the opportunity for tridentate anionic coordination modes, can be employed.

Experimental

All chemicals and solvents were obtained through commercial sources. Solvents were removed by rotary evaporation on a Heidolph Labrota 4000. Flash column chromatography was performed using Davisil silica gel 35–70u 60A (Fluorochem). Melting points were determined with a Gallenkamp melting point apparatus no 889339 and are uncorrected. NMR spectra were recorded on Bruker Avance 300 and 400 instruments. Chemical shifts are reported in ppm from TMS, with the solvent resonance as the internal standard. Proton signal multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad) or some combination of them. All spectra were recorded at r.t., and the solvent for a particular spectrum is given in parentheses. Infrared spectra were recorded on a Perkin-Elmer Spectrum GX FT-IR system. Liquids were analysed as films, solids were analysed as KBr disks. Mass spectra were recorded on Waters Micromass LCT (fitted with lockspray for accurate mass) (ESI) or GCT (CI) instruments. Optical rotations were measured on an Optical Activity Ltd. AA-1000 digital polarimeter using a 5 ml cell with a 1 cm path length at r.t. using the sodium D-line, or in a Perkin-Elmer 341 polarimeter using a 1 ml cell with a 1 cm path length at 20 °C using the sodium D-line. Microwave reactions were carried out in a Biotage® initiator using 5 ml heavy-walled reactor vials equipped with an air tight seal. The temperature was measured by an infrared temperature probe that measured the temperature on the surface of the vial. The pressure was measured by directly reading the deflection of the septa on the vial using a load cell behind the inner part of the cavity lid.

Amide 3

To *N*-Boc-amino acid fluoride **2** (219 mg, 1.0 mmol) and 1,8-aminonapthyridine (173 mg, 1.0 mmol) in a 5 ml microwave process vial were added, under a nitrogen atmosphere, dry DMF (3 ml) and anhydrous pyridine (0.14 ml, 1.73 mmol). The reaction mixture was heated by microwave irradiation at 140 °C for 30 min. After being cooled to ambient temperature, the solvent was evaporated under reduced pressure, and the reaction crude purified by chromatography on a SiO_2 column using EtOAc as the eluent to give *N*-Boc amine **3** (246 mg, 66%) as a yellow solid. mp 82–84 °C; $[\alpha]_D^{20}$ −30.0 (*c* 0.333 in $CHCl_3$); IR ($CDCl_3$): 3242, 2969, 2932, 1689, 1601, 1510, 1407, 1393, 1367, 1312, 1277 and 1170 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90 (3H, d, J = 6.9 Hz, CH_3), 0.97 (3H, d, J = 6.7 Hz, CH_3), 1.40 (9H, s, 3 × CH_3), 2.23–2.49 (1H, m, CH), 2.59 (3H, s, CH_3), 2.64 (3H, s, CH_3), 4.18–4.25 (1H, m, CH), 5.03 (1H, br d, J = 8.7 Hz, NH), 7.07 (1H, s, ArCH), 8.27 (1H, d, J

= 9.0 Hz, ArCH), 8.43 (1H, d, J = 9.0 Hz, ArCH) and 9.03 (1H, br s, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.4 (CH_3), 18.1 (CH_3), 19.3 (CH_3), 25.3 (CH_3), 28.3 (CH_3), 30.7 (CH), 60.8 (CH), 80.6 ($C(CH_3)_3$), 113.7 (ArCH), 118.8 (ArC), 122.4 (ArCH), 135.7 (ArCH), 145.7 (ArC), 152.6 (ArC), 154.2 (C=O), 154.3 (ArC), 162.9 (ArC) and 171.3 (C=O). MS(ES) m/z: 373.2 $[MH]^+$ (100%), 317.2 (18), 273.2 (41) and 174.1 (28). Found (ES) 373.2234 $[MH]^+$; $C_{20}H_{29}N_4O_3$ requires 373.2234.

Amine 4

N-Boc amine **3** (110 mg, 0.29 mmol) was treated with trifluoroacetic acid (0.3 ml, 3.9 mmol) in DCM (5 ml) at r.t. for 24 h. The reaction mixture was then treated with NaOH (0.4 g, 10 mmol) in water (10 ml) and stirred for 1 h. The organic phase was separated and the aqueous solution extracted with DCM (2 × 15 ml) and Et_2O (4 × 15 ml). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to give (*S*)-amine **4** as a white solid (64 mg, 81%). mp 144–146 °C; $[\alpha]_D^{20}$ −15.3 (c 0.333 in $CHCl_3$); IR (KBr): 3355, 3251, 2961, 1698, 1597, 1561, 1508, 1397 and 1308 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (3H, d, J = 6.9 Hz, CH_3), 1.02 (3H, d, J = 7.0 Hz, CH_3), 1.61 (2H, br s, NH_2), 2.31–2.46 (1H, m, CH), 2.59 (3H, s, CH_3), 2.66 (3H, s, CH_3), 3.43 (1H, d, J = 3.6 Hz, CH), 7.05 (1H, s, ArCH), 8.25 (1H, d, J = 9.0 Hz, ArCH), 8.48 (1H, d, J = 9.0 Hz, ArCH) and 10.35 (1H, br s, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.5 (CH_3), 18.4 (CH_3), 20.1 (CH_3), 25.8 (CH_3), 31.4 (CH), 61.1 (CH), 113.7 (ArCH), 118.9 (ArC), 122.5 (ArCH), 135.7 (ArCH), 145.5 (ArC), 153.1 (ArC), 155.2 (ArC), 163.2 (ArC) and 174.7 (C=O). MS(ES) m/z: 273.2 $[MH]^+$ (100%), 256.1 (5), 174 (99) and 72.2 (10). Found (ES) 273.1710 $[MH]^+$; $C_{15}H_{21}N_4O$ requires 273.1710.

Ligand 5

To a solution of (*S*)-amine **4** (0.203 g, 0.75 mmol) in DCM (7 ml), was added 2-(diphenylphosphino)benzaldehyde (0.216 g, mmol) at r.t. The resulting yellow solution was stirred at r.t. for 24 h, and then filtered and evaporated *in vacuo*. The crude mixture was purified by chromatography on a SiO_2 column using EtOAc as the eluent to give compound **5** as a yellow solid (0.257 g, 64%). mp 101–103 °C; $[\alpha]_D^{20}$ −105 (c 0.200 in $CHCl_3$); IR ($CDCl_3$): 3339, 3056, 2964, 2930, 1696, 1637, 1600, 1507, 1435, 1406, 1338, 1312, 1276 and 1182 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.67 (3H, d, J = 6.9 Hz, CH_3), 0.80 (3H, d, J = 6.9 Hz, CH_3), 2.12–2.25 (1H, m, CH), 2.59 (3H, s, CH_3), 2.65 (3H, s, CH_3), 3.57 (1H, d, J = 4.4 Hz, CH), 6.81–6.85 (1H, m, ArCH), 7.05 (1H, s, ArCH), 7.16–7.33 (11H, m, ArCH), 7.39–7.45 (1H, m, ArCH), 8.22–7.17 (1H, m, ArCH), 8.25 (1H, d, J = 9.0 Hz, ArCH), 8.46 (1H, d, J = 9.0 Hz, ArCH), 8.81 (1H, d, J = 5.9 Hz, HC=N) and 9.50 (1H, br s, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.8 (CH_3), 18.5 (CH_3), 19.6 (CH_3), 25.9 (CH_3), 33.9 (CH), 79.9 (CH), 114.2 (ArCH), 119.0 (ArC), 122.6 (ArCH), 128.3 (d, J = 3.9 Hz, ArCH), 128.8 (d, J = 8.0 Hz, ArCH), 129.2 (d, J = 7.1 Hz, ArCH), 129.4 (ArCH), 129.6 (ArCH), 129.7 (ArCH), 131.6 (ArCH), 133.6 (ArCH), 134.4 (d, J = 13.2 Hz, ArCH), 134.7 (d, J = 13.5 Hz, ArCH), 135.8 (ArCH), 136.0 (ArC), 136.2 (d, J = 9.4 Hz ArC), 138.5 (d, J = 3.5 Hz, ArC), 138.7 (ArC), 145.6 (ArC), 153.1 (ArC), 155.2 (ArC), 162.1 (d, J = 25.1 Hz, C=N), 163.2 (ArC) and 172.6 (C=O). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −13.45 (s). MS(TOF-ES) m/z: 567.11 $[MNa]^+$ (87%), 545.13 $[MH]^+$ (100), 295.10 (5), 273.12 (41) and 174.08 (6). Found (TOF ES) 545.2465 $[MH^+]$; $C_{34}H_{34}N_4OP$ requires 545.2470.

Complex 6

Ligand (*S*)-**5** (120 mg, 0.22 mmol) and [Rh(acac)(CO)$_2$] (73.4 mg, 0.22 mmol) were placed in a Schlenk tube and stirred in dry de-gassed toluene (4 ml) at r.t. for 1.5 h under an argon atmosphere. During this time, an orange solid precipitated. Diethyl ether (7 ml) was added and the reaction mixture was filtered *via* cannula. The resulting solid was washed with diethyl ether (3 × 5 ml) and dried under vacuum to obtain complex (*S*)-**6** as a dark orange solid (132 mg, 89%). mp 175–178 °C (decomp.); $[\alpha]_D^{20}$ +145 (c 0.06 in $CHCl_3$); IR ($CDCl_3$): 3054, 2960, 2925, 2001, 1614, 1583, 1506, 1436, 1402, 1332, 1234 and 1097 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.57 (3H, d, J = 6.8 Hz, CH_3), 0.87 (3H, d, J = 6.8 Hz, CH_3), 2.34–2.48 (1H, m, CH), 2.50 (3H, s, CH_3), 2.55 (3H, s, CH_3), 3.97 (1H, d, J = 6.4 Hz, CH), 6.90 (1H, s, ArCH), 6.96–7.02 (1H, m, ArCH), 7.27–7.54 (13H, m, ArCH), 7.81 (1H, d, $^3J_{H-Rh}$ 2.3 Hz, HC=N), 7.84 (1H, d, J = 8.8 Hz, ArCH) and 8.04 (1H, d, J = 8.8 Hz, ArCH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.1 (CH_3), 18.8 (CH_3), 19.6 (CH_3), 25.5 (CH_3), 34.6 (CH), 87.9 (CH), 118.1 (ArC), 119.5 (ArCH), 121.3 (ArCH), 126.9 (d, J = 40.0 Hz, ArC), 128.7 (d, J = 10.8 Hz, ArCH), 130.8 (ArCH), 131.0 (ArCH), 131.1 (ArCH), 132.0 (d, J = 52.9 Hz, ArC), 132.2 (ArCH), 132.4 (d, J = 49.1 Hz, ArC), 133.2 (ArCH), 133.3 (ArCH), 133.5 (d, J = 12.6 Hz, ArCH), 134.1 (d, J = 12.8 Hz, ArCH), 136.2 (d, J = 16.7 Hz, ArC), 136.9 (d, J = 8.0 Hz, ArCH), 144.2 (ArC), 156.1 (ArC), 160.9 (ArC), 161.7 (d, J = 7 Hz, C=N), 164.0 (ArC), 176.4 (C=O) and 191.6 (dd, $^1J_{C-Rh}$ = 75.6 Hz, $^2J_{C-P}$ = 19.0 Hz, CO); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 47.77 (d, $^1J_{P-Rh}$ = 145.7 Hz). MS(ES) m/z: 675.2 $[MH]^+$ (100%), 561.4 (38), 187 (12), 105.0 (46) and 99.1 (58). Found (ES) 675.1391 $[MH]^+$; $C_{35}H_{33}N_4O_2PRh$ requires 675.1391.

Complex 7

A solution of ligand (*S*)-**5** (120 mg, 0.22 mmol) in toluene (2 ml) was added to a solution of [Pt(cod)Me$_2$] (73.4 mg, 0.22 mmol) in toluene (2 ml) in a Schlenk tube under an N_2 atmosphere. The reaction mixture was heated at 50 °C and stirred for 16 h. The reaction was allowed to cool to r.t. and hexane (4 ml) was added. The resulting precipitate was filtered and washed with diethyl ether (3 × 4 ml) to obtain complex (*S*)-**7** as a yellow solid (106 mg, 64%). mp >226 °C (decomp.); $[\alpha]_D^{20}$ −13.0 (c 0.20 in $CHCl_3$); IR ($CDCl_3$): 3058, 2961, 2924, 1726, 1614, 1601, 1550, 1507, 1437, 1403, 1373, 1333, 1236 and 1100 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.04 (3H, d with Pt satellites, $^3J_{H-P}$ = 3.6 Hz, $^2J_{H-Pt}$ = 72.6 Hz, CH_3), 0.81 (3H, d, J = 6.9 Hz, CH_3), 0.97 (3H, d, J = 6.8 Hz, CH_3), 2.42–2.55 (1H, m, CH), 2.51 (3H, s, CH_3), 2.58 (3H, s, CH_3), 4.33 (1H, d, J = 5.0 Hz, CH), 6.95 (1H, s, ArCH), 7.15–7.63 (15H, m, ArCH), 8.13 (1H, d, J = 8.6 Hz, ArCH) and 8.23 (1H, s with

Pt satellites, $^{3}J_{H-Pt}$ = 41.7 Hz, HC=N); ^{13}C NMR (100 MHz, $CDCl_3$): δ −12.2 (d with Pt satellites, $^{2}J_{C-P}$ = 6.9 Hz, $^{1}J_{C-Pt}$ = 671.2 Hz, CH_3), 18.1 (CH_3), 18.6 (CH_3), 19.8 (CH_3), 25.4 (CH_3), 34.8 (CH), 83.3 (CH), 118.4 (ArC), 122.0 (ArCH), 122.1 (ArCH), 124.3 (d, J = 53.7 Hz, ArC), 127.8 (ArC), 128.3 (d, J = 11.2 Hz, ArCH), 128.7 (d, J = 11.0 Hz, ArCH), 130.9 (d, J = 59.4 Hz, ArC), 130.9 (ArCH), 131.1 (ArCH), 131.7 (ArCH), 132.7 (d, J = 7.2 Hz, ArCH), 133.0 (ArCH), 133.8 (ArCH), 133.8 (d, J = 24.5 Hz, ArCH), 134.7 (ArCH), 136.9 (d, J = 8.8 Hz, ArCH), 137.4 (d, J = 13.8 Hz, ArC), 144.5 (ArC), 156.0 (ArC), 156.9 (d, J = 3.4 Hz, C=N), 161.1 (ArC), 162.7 (ArC) and 177.8 (C=O); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 16.20 (s with Pt satellites, $^{1}J_{P-Pt}$ = 3938.8 Hz); MS(FAB) m/z: 755.2 (81%), 754.2 (100), 753.2 (94), 738.2 (48), 482.0 (21), 377.9 (11) and 199.9 (24). Found (FAB) 753.2244 $[M]^+$; $C_{35}H_{35}N_4OP^{195}Pt$ requires 753.2248. Crystals for X-ray structure determination, obtained as the monohydrate, were grown after a long period of slow evaporation of *rac*-**7** in an NMR tube. Found C, 54.60; H, 4.74; N, 7.33. $C_{35}H_{35}N_4OPPt + H_2O$ requires C, 54.47; H, 4.83; N, 7.26%.

X-ray crystallography of *rac*-7. $C_{35}H_{37}N_4O_2PPt$, M = 771.75, yellow prism, 0.08 × 0.03 × 0.03 mm, monoclinic, space group $P2(1)/c$, Z = 4, a = 8.7388(15), b = 14.988(2), c = 25.469(4) Å, β = 94.227(2)°, V = 3326.7(10) Å^3, ρ_{calc} = 1.541 Mg m^{-3}, μ(Mo-K$_\alpha$) = 4.302 mm^{-1} (max./min. transmission = 0.879/0.7125), T = 93 K. Of 28 683 measured data, 5887 were unique (R_{int} = 0.0686) and 5412 observed [$I > 2\sigma(I)$] to give R = 0.0440 and w$R2$ = 0.1095. Data were collected using a Rigaku MM007 high brilliance RA generator (Mo-K$_\alpha$ radiation, confocal optics) and a Saturn70 CCD system. At least a full hemisphere of data was collected using ω scans. Intensities were corrected for Lorentz polarisation and absorption effects. The structures were solved by direct methods. Hydrogen atoms bound to carbon were idealised. Structural refinements were performed with full-matrix least-squares based on F^2 using SHELXTL.[12] There is a disordered water molecule in two locations, with no hydrogen atoms located (water molecules are omitted in Fig. 2 for clarity). CCDC 653579. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b712612c

Acknowledgements

The authors thank the EPSRC for funding this project, and for the use of the National Mass Spectrometry Service. Mrs C. Horsborough and Mrs M. Smith are also thanked for providing technical assistance. Mr Jan Sadownik (Prof. D. Philp's group) is also thanked for his assistance with the K_a determination. The authors also wish to thank Johnson Matthey for the loan of precious metal salts.

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