Chiral Ligands for Transition Metal Complexation

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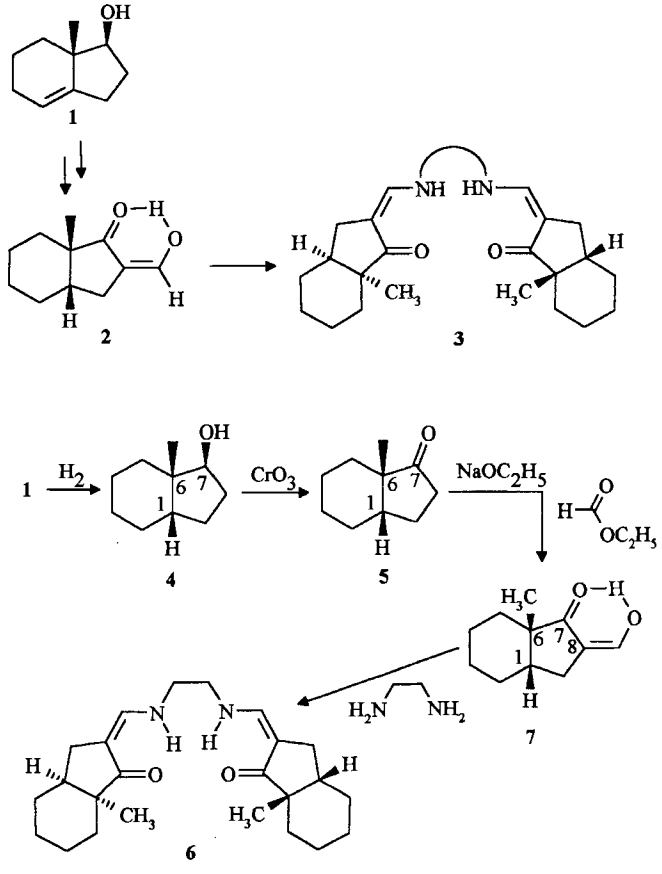
Novel chiral salen- or salphen-type ligands with stereogenic centres in the 1,3-dicarbonyl moiety **2** as well as in the amino bridge in **15**–**18** were synthesized from the enantiomerically pure Hajos-Wiechert ketone.

Chiral transition metal complexes have attracted synthetic chemists considerably already, and such complexes have been successfully employed in enantioselective procedures for the synthesis of enantiomerically pure compounds. A wide range of different types of transition metal complexes has been studied, including compounds based on chiral salen ligands[1–4], bisdihydrooxazoles[5,6], semicorrins[7,8], and vitamin B_{12}[9]. Since the Hajos-Wiechert ketone-derived enantiomerically pure alcohol **1** was easily available in our laboratory[10], we decided to investigate its transformation into the 1,3-dicarbonyl derivative **2**, which on treatment with diamines was expected to undergo a chemoselective attack at the much more easily approached aldehyde group and to generate ligands of type **3**. We were intrigued by the idea that it should be easily possible to introduce in addition a chiral nitrogen bridge thus, hopefully enhancing the directing power of this ligand, and were convinced that cations like Cu^{II}, Co^{III}, Ni^{II}, and Pd^{II} should be efficiently chelated by this ligand and thus trigger reactions like oxidations, reductions, conjugate additions, cyclopropanations, and radical processes[11].

In practice, hydrogenation of the unsaturated alcohol **1** afforded the *cis*-fused alcohol **4** in good yield. No evidence for the formation of the corresponding *trans*-fused compound was obtained. The assignment of the *cis* configuration was based on the melting point (140°C) of the 2,4-dinitrophenylhydrazone of the corresponding ketone **5** obtained by pyridinium chlorochromate oxidation[12]. Standard formylation of **5** provided aldehyde **7**, which turned out to be completely enolized and was expected to react with a wide range of diamines to give a variety of C_2-symmetric ligands.

As the first simple representative, ethylenediamine was chosen which gave rise to ligand **6** in a clean reaction. As an initial study of the behaviour of these novel chiral ligands the aldimine **6** was heated with sodium hydroxide and copper sulfate in aqueous ethanol to afford in a rapid reaction a red-brown crystalline product in excellent yield



which was shown by its analytical and spectroscopic properties to be the expected copper(II) complex **8a**. Reactions of the ligand **6** with cobalt(II) chloride under analogous conditions failed to afford the corresponding Co^{II} complex but, due to the known instability[13] to cobalt(II) in such coordination complexes, this result was not surprising. According to expectations, the corresponding Co^{III} complex was isolated in good yield (73%) as the perchlorate salt by heating cobalt(II) chloride hexahydrate with ligand **6**

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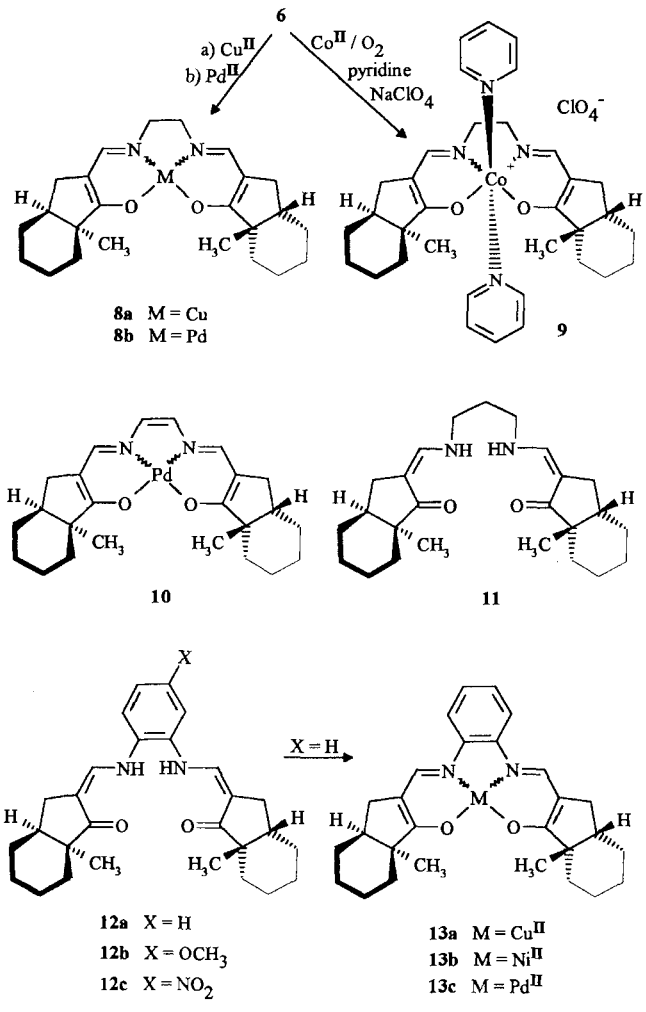
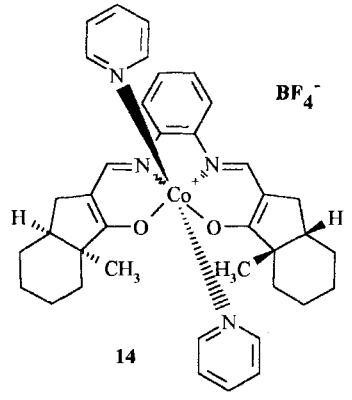
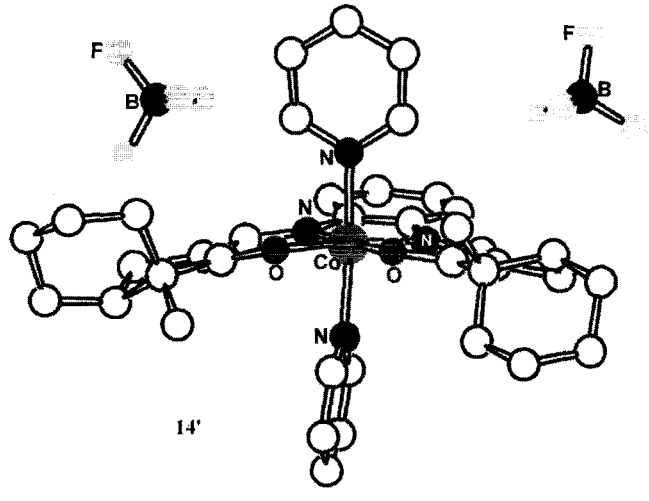


and pyridine in air. The complex **9** was isolated as dark purple needles which displayed spectroscopic and analytical properties in accord with the assigned structure (see Experimental). Subsequently, the complexation was studied with palladium acetate, a process which turned out to be highly temperature-dependant. Heating in aqueous ethanol under the same conditions as used for the preparation of the copper and cobalt complexes provided only a low yield (7%) of the yellow Pd^{II} compound **8b**. Also isolated was the orange Pd^{II} complex **10** in 1% yield, which presumably arose by oxidation of the ethano bridge by palladium acetate. Whether this oxidation occurs in the free ligand or in the already formed complex is not clear. Any attempts to obtain a higher yield of this interesting orange complex by dehydrogenation of complex **8b** (chloranil) failed. Further investigations were terminated when a dramatic improvement in the yield of **8b** to 94% was achieved by performing the complexation at room temperature in an ethanol/dichloromethane mixture. In order to extend the range of complexes available additional diamines were tested for ligand formation. Ligands **11** and **12a** were formed smoothly while a rather low yield (22%) was obtained in the case of the methoxy compound **12b**, and the same was true for the electron-poor nitro compound **12c** (15%). Presumably, in the first case, the high electron density of the aromatic ring gives rise to oxidative degradation, while the electron-withdrawing capacity of the nitro group in **12c** probably lowers the nucleophilicity of the amino groups to quite some extent. For this reason we here restrict ourselves to the non-substituted complexes **13a**, **13b**, and **13c** that were obtained in acceptable yields.

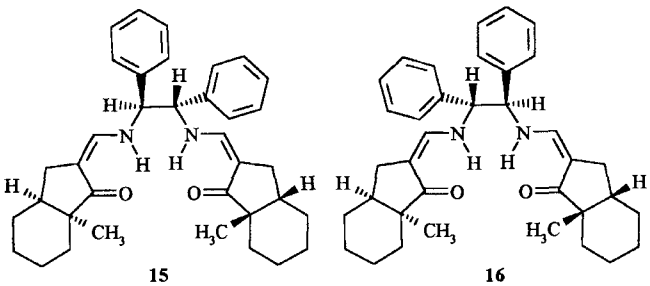




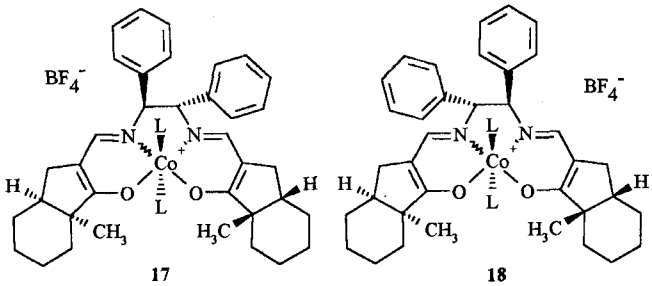
Again, the formation of the corresponding Co^{III} complex was by no means trivial. As in the case mentioned above one had to operate under oxidizing conditions with oxygen and hydrogen peroxide both being used as oxidants. There remained, however, the problem of isolating and purifying the final product. After some experiments the crucial role of the counteranion in this process emerged. When sodium tetrafluoroborate and pyridine were added to the reaction mixture the corresponding salt **14** with the additional pyridine ligands was isolated as dark green needle-like crystals in 91% yield.

At this stage we decided to take advantage of the perfect crystals available in this way to carry out an X-ray structural determination of **14** as a representative of the whole group of complexes. The result of this investigation (see **14'**) confirmed all our expectations with regard to the constitution and configuration of these compounds.

Finally, and with the intention to arrive at complexes with stereogenic centres in the nitrogen bridge as well, we prepared the ligands **15** and **16**.



15 **16**



17 **18**

L = py

The enantiomerically pure diamines needed are easily available according to literature procedures[14], and the corresponding ligands were formed uneventfully and in nearly quantitative yield. The differences in relative configuration are reflected in a much higher solubility of ligand **15** compared to its diastereomer **16**. Both served well in complexation processes. It is interesting to mention that the Co^{III} complexes **17** and **18**, which are more difficult to prepare, were synthesised in the same way as described for **14** and could be isolated in 72% yield. A number of these complexes were easily shown to be active in reductions, conjugate additions, and cyclopropanations and so a systematic investigation of the enantioselectivity in these processes was launched. The results of these efforts will be communicated in due course.

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Experimental

IR: Perkin-Elmer 580 and FT 1710. – ^1H NMR (in $CDCl_3$, unless stated otherwise, TMS as an internal standard): Bruker WP 200 (200 MHz): – MS: Finnigan MAT 312, Finnigan MAT 711, VG-Autospec. – High-resolution MS: Finnigan MAT 312 (peak-matching method). – Elemental analyses: Heraeus CHN-Rapid. – Melting points: Gallenkamp MPD 350, uncorrected values. – Optical rotations: Perkin-Elmer 241 polarimeter, 10-cm cell, 589 nm (Na-D line), in solution. – Thin-layer chromatography: silica gel plates Merck 60 F_{254}. – Column chromatography: Baker silica gel (0.03–0.06 mm).

(1S,6S,7S)-6-Methylbicyclo[4.3.0]nonan-7-ol (**4**): A solution of the alkene **1** (3.0 g, 20 mmol) in ethanol (50 ml) was treated with 10% palladium/charcoal (0.15 g) and the mixture hydrogenated at atmospheric pressure for 18 h. The mixture was filtered and the clear filtrate concentrated to give a colorless oily semisolid (3.1 g, 100%) which was used without further purification. R_f (petroleum ether/Et_2O, 2:1; 10 elutions) = 0.5. – IR ($CHCl_3$): $\tilde{\nu}$ = 3620 (w), 2928 (s), 2860 (m), 1448 (w), 1052 (w) cm^{-1}. – ^1H NMR (200 MHz): δ = 3.84 (dd, J = 3 and 7 Hz, 1H, OH), 2.28–2.06 (m, 1H), 1.88–1.73 (m, 2H), 1.63–1.05 (m, 12H), 0.98 (s, 3H, CH_3). – MS (70 eV), *m/z* (%): 154 (53) [M^+], 110 (75), 95 (100), 81 (86), 67 (62).

(1S,6S)-6-Methylbicyclo[4.3.0]nonan-7-one (**5**): A suspension of pyridinium chlorochromate (3.23 g, 15 mmol) in dichloromethane (20 ml) was stirred and treated in one portion with a solution of the alcohol **4** (1.54 g, 10 mmol) in dichloromethane (10 ml). The brown gummy mixture was stirred at room temp. for 2 h. The mixture was diluted with Et_2O (100 ml) and filtered through a column of silica gel (8 × 4 cm). The residue in the flask was washed with further Et_2O (3 × 100 ml), and the washings were passed through the silica gel column. Evaporation of the solvent from the colorless filtrate at room temp. afforded a liquid which was further purified by chromatography over silica gel (13 × 4 cm, cyclohexane/Et_2O, 10:1) to give the ketone **5** (1.4 g, 92%) as a colorless volatile liquid. – R_f (petroleum ether/Et_2O, 1:1) = 0.48. $[\alpha]_D^{RT}$ = +64 (1, $CHCl_3$). – IR ($CHCl_3$): $\tilde{\nu}$ = 3000 (w), 2932 (s), 2860 (m), 1728 (s), 1468 (w), 1448 (w), 1404 (w), 1376 (w), 1156 (w), 1092 (m) cm^{-1}. – ^1H NMR (200 MHz): δ = 2.48–2.14 (m, 2H), 2.02–1.06 (m, 11H), 1.03 (s, 3H). – MS (70 eV), *m/z* (%): 152 (45) [M^+], 108 (4), 96 (65), 81 (100), 67 (45).

(1S,6S)-6-Methyl-7-oxobicyclo[4.3.0]nonane-8-carboxaldehyde (**7**): A stirred suspension of freshly prepared sodium ethoxide (22 mmol) in anhydrous Et_2O (50 ml) was treated dropwise with a solution of ketone **5** (3.0 g, 20 mmol) and ethyl formate (1.6 g, 22 mmol) in anhydrous Et_2O (50 ml). The mixture, which started to crystallize, was stirred under nitrogen for a further 16 h. Water was added and the resulting aqueous phase separated from the organic layer and washed with Et_2O (50 ml). The aqueous phase was acidified with concentrated hydrochloric acid, and the mixture extracted with Et_2O (3 × 50 ml). The combined extracts were washed with brine (10 ml), dried, and the solvent was evaporated to give the keto aldehyde **7** as a yellow oil which crystallized (3.2 g, 87%). R_f (Et_2O/petroleum ether, 2:1) = 0.4, m.p. 80–81 °C, $[\alpha]_D^{RT}$ = +88 (1, $CHCl_3$). – IR ($CHCl_3$): $\tilde{\nu}$ = 2931 (s), 2852 (s), 1699 (s), 1636 (s), 1569 (s), 1417 (m), 1288 (w), 1246 (w), 1212 (s), 1184 (s) cm^{-1}. – ^1H NMR (200 MHz): δ = 7.11 (t, J = 2 Hz, 1H), 2.51 (ddd, J = 2, 6 and 14 Hz, 1H, HC–C=C), 2.22 (ddd, J = 2, 6 and 14 Hz, 1H, HC–C=C), 2.02–1.85 (m, 1H), 1.83–1.59 (m, 2H), 1.55–1.16 (m, 6H), 1.09 (s, 3H, CH_3). – MS (70 eV), *m/z* (%): 180 (94) [M^+], 165 (35), 152 (32), 133 (40), 95 (100), 81 (84). – $C_{11}H_{16}O_2$ (180.25): calcd. C 73.30, H 8.95; found C 72.92, H 8.88.

Ligand **6**: A stirred solution of the aldehyde **7** (0.9 g, 5 mmol) in Et_2O (50 ml) was treated dropwise with a solution of ethylenediamine (0.15 g, 2.5 mmol) in Et_2O (25 ml). An off-white solid precipitated, and the mixture was stirred at room temp. for 1 h. The solid was filtered off and combined with a second crop obtained by concentration of the filtrate and trituration of the residue with Et_2O to give the ligand **6** as an off-white powdery solid (0.87 g, 91%). M.p. 208–209 °C, $[\alpha]_D^{RT}$ = +67 (0.25, $CHCl_3$). – IR (KBr): $\tilde{\nu}$ = 3290 (m), 1680 (s), 1600 (m), 1560 (m) cm^{-1}. – ^1H NMR [200 MHz, $(CD_3)_2SO$]: δ = 7.12 (d, J = 13 Hz, 2H, CHN), 6.78–6.57 (m, 2H, NH), 3.27–3.18 (m, 4H, CH_2N), 2.4–2.22 (m, 2H), 2.1–1.92 (m, 2H), 1.8–0.95 (m, 18H), 0.87 (s, 6H, CH_3). – MS (70 eV), *m/z* (%): 384 (34) [M^+], 205 (86), 192 (100), 180 (34). –

$C_{24}H_{36}N_2O_2$ (384.6): calcd. C 74.96, H 9.44, N 7.28; found C 74.70, H 9.33, N 7.46.

Complex **8a**: A warm solution (70°C) of the ligand **6** (0.39 g, 1 mmol) in ethanol/water (2:1) (30 ml) and aqueous sodium hydroxide (2.5 M, 0.8 ml) was treated with a solution of copper sulfate pentahydrate (0.25 g, 1 mmol) in water (2 ml). The colour changed from yellow to purple brown, and a solid precipitated. After 1 h the mixture was cooled and extracted with Et_2O (100 ml, then 2 × 25 ml). The combined organic layers were washed with water (10 ml), dried, and the solvent was evaporated to give the copper(II) complex **8a** as fine, purple brown needles (0.43 g, 95%). R_f (Et_2O/petroleum ether, 1:1) = 0.76, m.p. 186–187°C. – IR (KBr): $\tilde{\nu}$ = 1608 (s), 1484 (s) cm^{-1}. – ^1H NMR (200 MHz): not possible, due to the paramagnetic nature of the complex. – MS (70 eV), *m/z* (%): 445 (76) [M^+ (^{63}Cu)], 447 (37) [M^+ (^{65}Cu)], 384 (3), 254 (100). – $C_{24}H_{34}CuN_2O_2$ (446.1): calcd. C 64.62, H 7.68, N 6.28; found C 64.36, H 7.67, N 6.30.

Complex **8b**: Preparation as described for **8a** with additional heating under reflux for 2 h, extraction with dichloromethane and purification by chromatography over silica (13 × 4 cm, cyclohexane/Et_2O, 4:1) to give the palladium(II) complex **8b** (32 mg, 7%) as yellow needles. R_f (Et_2O/petroleum ether, 1:1) = 0.46, m.p. 233–234°C. – IR ($CHCl_3$): $\tilde{\nu}$ = 2928 (m), 2852 (w), 1604 (s), 1476 (m), 1092 (m) cm^{-1}. – ^1H NMR (200 MHz): δ = 6.78 (s, 2H, CH=N), 3.42 (s, 4H, CH_2N), 2.46 (dd, *J* = 7 and 12 Hz, 2H), 2.30 (dd, *J* = 7 and 12 Hz, 2H), 1.93–1.79 (m, 2H), 1.72–1.49 (m, 5H), 1.48–1.28 (m, 11H), 1.13 (s, 6H, CH_3). – MS (70 eV), *m/z* (%): 488 (5) [M^+ (^{106}Pd)], 438 (44), 297 (26), 192 (42), 96 (100). – $C_{24}H_{34}N_2O_2Pd$ (489.0): calcd. C 58.95, H 7.01, N 5.73; found C 58.85, H 7.00, N 5.71.

Complex **10**: Preparation as described for **8b**. Isolated as an orange amorphous solid (4 mg, 1%). R_f (Et_2O/petroleum ether, 1:1) = 0.67. – ^1H NMR (200 MHz): δ = 6.94 (s, 2H, CH=N), 6.21 (s, 2H, C=CH–N), 2.63 (dd, *J* = 7 and 13 Hz, 2H), 2.45 (dd, *J* = 7 and 13 Hz, 2H), 2.03–1.86 (m, 2H), 1.80–1.52 (m), 1.50–1.32 (m), 1.28–1.22 (m), 1.22 (s, 6H, CH_3). – $C_{24}H_{32}N_2O_2Pd$: calcd. 486.1499, found 486.1497 (MS).

Complex **9**: The ligand **6** (0.39 g, 1 mmol) was added to a solution of cobalt(II) chloride hexahydrate (2.4 g, 10 mmol) in water (10 ml) and pyridine (10 ml), and the resulting suspension was stirred and heated at 80°C for 3 h. The red-brown solution was then concentrated under reduced pressure and the residue treated with water (10 ml) and sodium perchlorate (2 g). The mixture was heated on a steam bath and trated dropwise with ethanol until a homogeneous solution was obtained. After cooling of the solution to room temp. and standing for 18 h, long purple needles of the monoethanol solvate of the title compound **9** had deposited, which were collected and combined with a second crop obtained by extraction the filtrate with dichloromethane (100 ml), evaporation of the solvent from the extract and crystallization of the resulting oil from aqueous ethanol (0.57 g, 76%). M.p. 200–201°C. – IR ($CHCl_3$): $\tilde{\nu}$ = 2928 (m), 1608 (s), 1428 (m), 1356 (m) cm^{-1}. – ^1H NMR (200 MHz): δ = 8.02 (dd, *J* = 1 and 7 Hz, $4H_{pyr}$), 7.77 (tt, *J* = 1 and 7.5 Hz, $2H_{pyr}$), 7.31 (dd, *J* = 7 and 7.5 Hz, $4H_{pyr}$), 7.07 (s, 2H, CH=N), 3.87 (s, 4H, CH_2N), 2.50 (dd, *J* = 7 and 13 Hz, 2H, HC–C=C), 2.25 (dd, *J* = 6 and 13 Hz, 2H, HC–C=C), 1.77 (quint, *J* = 6 Hz, 2H), 1.64 (s, 2H), 1.61–1.45 (m, 3H), 1.44–1.31 (m, 8H), 1.22–1.09 (m, 3H), 1.06 (s, 6H, CH_3). – MS (70 eV), *m/z* (%): 442 (21) [M^+ – 2 pyr], 440 (79), 210 (17), 79 (100). – $C_{36}H_{50}ClCoN_4O_6$ (729.2): calcd. C 58.02, H 6.76, N 7.52; found C 57.71, H 6.55, N 7.77.

Ligand **11**: Preparation as described for **6**. Isolated as an off-white powdery solid (0.77 g, 77%). M.p. 176–177°C. – IR (KBr): $\tilde{\nu}$ = 3282 (m), 2924 (s), 2853 (m), 1677 (s), 1572 (s), 1461 (w), 1449 (w) cm^{-1}. – ^1H NMR (200 MHz): δ = 7.32–7.22 (m, 2H, CHN), 6.61 (d, *J* = 12 Hz, 2H, NH), 3.47–3.28 (m, 4H, CH_2N), 2.52–2.29 (m, 2H), 2.26–1.96 (m, 2H), 1.90–1.55 (m, 8H), 1.52–1.11 (m, 12H), 1.05 (s, 6H, CH_3). – MS (70 eV), *m/z* (%): 398 (7) [M^+], 207 (100), 193 (79), 178 (19), 70 (22). – $C_{25}H_{38}N_2O_2$ (398.6): calcd. C 75.33, H 9.61, N 7.03; found C 75.02, H 9.49, N 7.27.

Ligand **12a**: Preparation as described for **6** with 1,2-phenylenediamine (0.27 g, 2.5 mmol) and addition of a catalytic amount of *p*-toluenesulfonic acid and molecular sieves (10 g, 4 Å, globular). Isolated as yellow powdery solid (0.975 g, 90%). M.p. 200–201°C. – IR (KBr): $\tilde{\nu}$ = 3253 (w), 2925 (s), 1700 (m), 1673 (s), 1619 (s), 1583 (s), 1460 (m), 1225 (s) cm^{-1}. – ^1H NMR (200 MHz): δ = 10.65 (dd, *J* = 11 and 26 Hz, 1H), 7.73 (d, *J* = 11 Hz, 1H), 7.2–6.98 (m, 5H), 6.34 (d, *J* = 13 Hz, 1H), 2.58 (dd, *J* = 7 and 13 Hz, 2H, HC–C=C), 2.32 (dd, *J* = 6 and 14 Hz, 2H, HC–C=C), 2.0–1.87 (m, 2H), 1.82–1.6 (m, 4H), 1.54–1.14 (m, 12H), 1.08 (s, 6H, CH_3). – MS (70 eV), *m/z* (%): 432 (24) [M^+], 281 (51), 268 (100), 145 (52), 119 (38). – $C_{28}H_{36}N_2O_2$ (432.6): calcd. C 77.74, H 8.39, N 6.48; found C 77.99, H 8.55, N 6.23.

Ligand **12b**: Preparation as described for **12a** with 4-methoxy-1,2-phenylenediamine (0.35 g, 2.5 mmol) in anhydrous ethyl acetate. The product, a brown solid (0.257 g, 22%), was purified by column chromatography (13 × 4 cm, petroleum ether/Et_2O, 1:1). R_f (ethyl acetate/petroleum ether, 1:1) = 0.47. – IR (KBr): $\tilde{\nu}$ = 3263 (w), 2927 (s), 1673 (m), 1587 (s), 1524 (m), 1463 (m), 1229 (s) cm^{-1}. – ^1H NMR (200 MHz): δ = 10.4–10.2 (m, 1H), 7.81–7.51 (m, 1H), 7.14–6.82 (m, 3H), 6.72–6.49 (m, 2H), 3.18 (s, 3H, OCH_3), 2.65–2.51 (m, 2H, HC–C=C), 2.39–2.25 (m, 2H, HC–C=C), 2.02–1.86 (m, 2H), 1.84–1.62 (m, 3H), 1.53–1.16 (m, 13H), 1.11 (d, *J* = 1 Hz, 3H, CH_3), 1.08 (s, *J* = 1 Hz, 3H, CH_3). – MS (70 eV), *m/z* (%): 462 (40) [M^+], 310 (76), 297 (100), 175 (40). – $C_{29}H_{38}N_2O_3$: calcd. 462.2882; found 462.2897 (MS).

Ligand **12c**: Preparation as described for **12a** with 4-nitro-1,2-phenylenediamine (0.38 g, 2.5 mmol) in anhydrous ethyl acetate. The product, a brown solid (0.18 g, 15%), was purified by column chromatography (13 × 4 cm, petroleum ether: Et_2O, 1:1). R_f (ethyl acetate/petroleum ether, 1:1) = 0.72. – IR (KBr): $\tilde{\nu}$ = 3386 (w), 2928 (s), 1677 (m), 1626 (s), 1583 (s), 1337 (s), 1289 (s) cm^{-1}. – ^1H NMR (200 MHz): δ = 11.0–10.78 (m, 1H), 8.06–7.9 (m, 2H), 7.22–7.03 (m, 4H), 2.64 (dd, *J* = 7 and 14 Hz, 2H, HC–C=C), 2.39 (dd, *J* = 7 and 15 Hz, 2H, HC–C=C), 2.05–1.17 (m, 18H), 1.13 (s, 3H, CH_3), 1.11 (s, 3H, CH_3). – MS (70 eV), *m/z* (%): 477 (10) [M^+], 325 (45), 312 (100), 165 (47). – $C_{28}H_{35}N_3O_4$: calcd. 477.2628; found 477.2647 (MS).

Complex **13a**: A solution of the ligand **12a** (0.22 g, 0.5 mmol) in DMF (10 ml) and aqueous sodium hydroxide (2.0 M, 0.5 ml) was treated with a solution of copper sulfate pentahydrate (0.14 g, 0.56 mmol) in water (2 ml). The colour changed from orange to green, and a solid precipitated. The mixture was stirred for 1 h and diluted with water (70 ml). The solid was filtered off and further purified by chromatography over silica (13 × 4 cm, petroleum ether/Et_2O, 1:1) to give the copper(II) complex **13a** as fine green needles (0.14 g, 55%). R_f (petroleum ether/Et_2O, 1:1) = 0.71, m.p. 161°C. – IR (KBr): $\tilde{\nu}$ = 2924 (s), 1604 (s), 1504 (m), 1472 (s), 1336 (s), 1076 (m) cm^{-1}. – ^1H NMR (200 MHz): not possible, due to the paramagnetic nature of the complex. – MS (70 eV), *m/z* (%): 493 (100) [M^+ (^{63}Cu)], 495 (57) [M^+ (^{65}Cu)], 247 (7). – $C_{28}H_{34}CuN_2O_2$

(494.1): calcd. C 68.06, H 6.94, N 5.67; found C 68.07, H 6.95, N 5.66.

Complex **13b**: Preparation as described for **13a** with nickel dichloride (0.13 g, 1 mmol) to give a red-brown solid (0.164 g, 67%). R_f (petroleum ether/Et_2O, 1:1) = 0.19, m.p. 82°C. – IR (KBr): $\tilde{\nu}$ = 2925 (s), 1604 (s), 1471 (s), 1335 (s) cm^{-1}. – ^1H NMR (200 MHz): δ = 7.43–7.34 (m, 4H), 6.92–6.87 (m, 2H), 2.59 (dd, J = 7 and 13 Hz, 2H, HC–C=C), 2.43 (dd, J = 8 and 14 Hz, 2H, HC–C=C), 1.98–1.86 (m, 2H), 1.71–1.32 (m, 16H), 1.13 (s, 6H, CH_3). – MS (70 eV), *m/z* (%): 488 (100) [M^+ (^{58}Ni)], 490 (43) [M^+ (^{60}Ni)]. – $C_{28}H_{34}N_2NiO_2$ (489.3): calcd. C 68.74, H 7.00, N 5.73; found C 69.15, H 7.27, N 5.45.

Complex **13c**: Preparation as described for **13a** with palladium acetate (0.11 g, 0.5 mmol) to give an orange solid (0.100 g, 37%). R_f (petroleum ether/Et_2O, 1:1) = 0.66, m.p. 254°C. – IR (KBr): $\tilde{\nu}$ = 2925 (s), 1598 (s), 1584 (s), 1460 (s), 1445 (s), 1372 (s) cm^{-1}. – ^1H NMR (200 MHz): δ = 7.64 (s, 2H), 7.55 (dd, J = 3 and 7 Hz, 2H), 6.99 (dd, J = 3 and 6 Hz, 2H), 2.71 (dd, J = 7 and 13 Hz, 2H, HC–C=C), 2.54 (dd, J = 7 and 13 Hz, 2H, HC–C=C), 2.02–1.94 (m, 2H), 1.81–1.35 (m, 16H), 1.24 (s, 6H, CH_3). – MS (70 eV), *m/z* (%): 536 (8) [M^+ (^{105}Pd)], 262 (100), 183 (73), 91 (41). – $C_{28}H_{34}N_2O_2Pd$ (537.0): calcd. C 62.63, H 6.38, N 5.22; found C 63.14, H 6.69, N 5.60.

Complex **14**: Preparation as described for **13a** with cobalt(II) chloride hexahydrate (0.12 g, 0.5 mmol) in pyridine as solvent and with addition of $NaBF_4$ (0.06 g, 0.5 mmol) under oxygen to give after 4 h and without further purification a dark green solid (0.34 g, 91%). Recrystallization from water/MeOH (5:3) gave dark green needles, m.p. >360°C. – IR (KBr): $\tilde{\nu}$ = 2925 (s), 1601 (s), 1446 (s), 1342 (s), 1067 (s) cm^{-1}. – ^1H NMR (200 MHz): δ = 7.86–7.73 (m, 8H), 7.53 (s, 2H), 7.27–7.14 (m, 6H), 2.64 (dd, J = 14 and 7 Hz, 2H, HC–C=C), 2.37 (dd, J = 14 and 7 Hz, 2H, HC–C=C), 1.88 (br. quint, J = 6 Hz, 2H), 1.55–1.72 (m, 6H), 1.51–1.3 (m, 10H), 1.16 (s, 6H, CH_3). – MS (70 eV), *m/z* (%): 490 (50), 489 (100) [M^+ – 2 pyr], 79 (22). – $C_{38}H_{44}BCoF_4N_4O_2$ (734.5): calcd. C 62.14, H 6.04, N 7.63; found C 62.14, H 6.23, N 7.76.

X-Ray Analysis of Complex **14'**: A brown-violet crystal was mounted on a Siemens Stoe AED2 automated four-cycle diffractometer with graphite-monochromated Mo-K_α radiation, λ = 71.07 pm. Crystal data: $C_{28}H_{34}N_2O_2Co(C_5H_5N)_2BF_4$, M = 734.53, monoclinic, space group $P2_1$ (No. 4), a = 1298.9(8), b = 1746.3(10), c = 1624.4(9) pm, β = 101.59(5)°, V_m = 543.5(5) cm^3/mol, Z = 4, D_c = 1.352 g/cm^3 and m(Mo-K_α) = 0.495 mm^{-1}. – The data were collected by using the ω-Q scan technique to a maximum 2Q value of 24.07°. A total of 11290 independent reflections was collected. The data were corrected for Lorentz, background, and polarizations effects. An empirical absorption correction was made with a ψ scan for six reflections. – The heavy atoms were found by the Paterson method and used in a SHELXL-93 refinement. The resulting F map revealed the positions of all non-hydrogen atoms. The refinement of atomic parameters was carried out by a full-matrix least-squares refinement. The parameters of the hydrogen atoms were calculated and not refined. The final refinement with $I > 2\sigma(I)$ and 901 parameters converged R_1 = 0.0763, wR_2 = 0.1870. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.51 and –0.68 e/Å^3, respectively. – All calculations were performed by using the SHELXS-86 and SHELXL-93 crystal structure refinement program[15].

Ligand **15**: A solution of the aldehyde **7** (1.44 g, 8 mmol) and (+)-1,2-diphenylethylenediamine (0.42 g, 2 mmol) in MTB ether (20 ml) was stirred at room temp. for 20 h. An off-white solid precipitated and was filtered off to give **15** as an off-white powdery solid (0.99 g, 93%), m.p. 114°C. – IR ($CHCl_3$): $\tilde{\nu}$ = 2924 (m), 1681 (m), 1596 (s), 1581 (s) cm^{-1}. – ^1H NMR (200 MHz): δ = 7.47–7.09 (m, 12H), 4.76–4.6 (m, 2H, HC–Ph), 2.52–2.36 (m, 2H, HC–C=C), 2.22–2.09 (m, 2H, HC–C=C), 1.89–1.78 (m, 2H), 1.73–1.58 (m, 2H), 1.5–1.23 (m, 8H), 1.06–0.94 (m, 6H). – MS (70 eV), *m/z* (%): 269 (27), 268 (100) [1/2 M^+], 91 (36). – $C_{36}H_{44}N_2O_2$ (536.8): calcd. C 80.56, H 8.62, N 5.22; found C 78.78, H 8.26, N 5.56. – 1/2 ($C_{36}H_{44}N_2O_2$): calcd. 268.1701; found 268.1700 (MS).

Ligand **16**: Preparation as described for **15** with (–)-1,2-diphenylethylenediamine afforded **16** as an off-white powdery solid (0.99 g, 93%), m.p. 114°C. – IR ($CHCl_3$): $\tilde{\nu}$ = 2925 (m), 1678 (m), 1596 (s), 1582 (s) cm^{-1}. – ^1H NMR (200 MHz): δ = 7.44–7.11 (m, 12H), 4.72–4.62 (m, 2H, HC–Ph), 2.52–2.36 (m, 2H, HC–C=C), 2.22–2.04 (m, 2H, HC–C=C), 1.88–1.74 (m, 2H), 1.72–1.56 (m, 3H), 1.5–1.22 (m, 7H), 1.02–0.96 (m, 6H). – MS (70 eV), *m/z* (%): 269 (31), 268 (100) [1/2 M^+], 147 (45). – 1/2 ($C_{36}H_{44}N_2O_2$): calcd. 268.1701; found 268.1710 (MS).

Complex **17**: Preparation as described for **14** with ligand **15** (0.27 g, 0.5 mmol) gave **17** (0.3 g, 72%) as a red-brown solid, m.p. 133°C. – IR (KBr): $\tilde{\nu}$ = 2925 (m), 1681 (m), 1600 (s), 1582 (s), 1230 (m) cm^{-1}. – ^1H NMR (200 MHz): δ = 8.26 (d, J = 5 Hz, 1H), 8.14–8.0 (m, 1H), 7.58 (tr, J = 7 Hz, 2H), 7.46–6.82 (m, 15H), 6.68–6.56 (m, 1H), 5.02 (s, 1H), 4.76–4.6 (m, 1H), 2.53–2.31 (m, 2H), 2.24–2.08 (m, 2H), 1.9–1.75 (m, 2H), 1.73–1.54 (m, 4H), 1.51–1.15 (m, 14H), 1.14–0.94 (m, 6H). – MS (70 eV), *m/z* (%): 593 (10) [M^+ – 2 pyr], 268 (100), 91 (47), 79 (49). – $C_{46}H_{52}BCoF_4N_4O_2$ (838.7): calcd. C 65.88, H 6.25, N 6.68; found C 65.58, H 6.67, N 6.20. – $C_{36}H_{42}CoN_2O_2$ (complex **17** without pyridine and BF_4): calcd. 593.2578; found 593.2579 (MS).

Complex **18**: Preparation as described for **14** with ligand **16** (0.27 g, 0.5 mmol) gave **18** (0.3 g, 72%) as a brown solid, m.p. 138°C. – IR ($CHCl_3$): $\tilde{\nu}$ = 2925 (m), 1682 (m), 1598 (s), 1580 (s), 1231 (m) cm^{-1}. – ^1H NMR (200 MHz): δ = 8.27 (d, J = 6 Hz, 2H), 8.06 (tr, J = 8 Hz, 1H), 7.58 (t, J = 7 Hz, 2H), 7.46–6.8 (m, 14H), 6.68–6.58 (m, 1H), 5.03 (s, 1H), 4.72–4.61 (m, 1H), 2.52–2.33 (m, 2H), 2.2–2.05 (m, 2H), 1.86–1.73 (m, 3H), 1.68–1.56 (m, 3H), 1.5–1.16 (m, 14H), 1.14–0.94 (m, 6H). – MS (70 eV), *m/z* (%): 593 (20) [M^+ – 2 pyr], 268 (79), 91 (100), 77 (62). – $C_{46}H_{52}BCoF_4N_4O_2$ (838.7): calcd. C 65.88, H 6.25, N 6.68; found C 65.8, H 6.73, N 5.44. – $C_{36}H_{42}CoN_2O_2$ (complex **18** without pyridine and BF_4): calcd. 593.2578; found 593.2564 (MS).

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[437/94]