Electronic Supplementary Material (ESI) for Catalysis Science & Technology

SUPPORTING INFORMATION

for

The Effect of Imine-Carbon Substituents in Bis(imino)pyridine-based Ethylene Polymerisation Catalysts Across the Transition Series

Theo M. Smit, Atanas K. Tomov, George J. P. Britovsek*, Vernon C. Gibson*, Andrew J. P. White and David J. Williams

Department of Chemistry, Imperial College London, Exhibition Road, South Kensington, London SW7 2AY, United Kingdom.

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Experimental Section

General

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove box. $FeCl_2 \cdot 1.5thf$,[1] $VCl_3 \cdot 3thf$,[2] $CrCl_3 \cdot 3thf$,[3] $TiCl_3 \cdot 3thf$,[2] $MnCl_2 \cdot 2thf$[4] and $NiBr_2 \cdot DME$[5] were prepared according to literature procedures, all other chemicals were purchased from Aldrich Chemical Co. Solvents were refluxed over an appropriate drying agent and distilled and degassed prior to use. NMR spectra were recorded on a Bruker AC-250 spectrometer. Chemical shifts are referenced to the residual protio impurity in the deuterated solvent. Elemental analysis were performed by the microanalysis services of the London Metropolitan University. Infrared spectra were obtained on a Perkin Elmer 1760X FT-IR spectrometer using KBr plates. Relative intensities of the IR-bands have been described as w (weak), m (medium), s (strong) or vs (very strong). Mass spectra were obtained using chemical ionisation (CI) or fast atom bombardment (FAB). Gel Permeation Chromatography (GPC) analysis of polyethylene samples were performed by BP Chemicals. Magnetic moments were determined by the Evans' NMR method (solvent CD_2Cl_2; reference cyclohexane).[6]

Preparation of Bis(imino)pyridine Ligands

N,N'-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarboxamide.

A solution of 2,6-pyridine dicarbonyl chloride (15.0g, 73.5 mmol) in 50 ml of dry CH_2Cl_2 was added drop-wise to a solution of 2,6-diisopropyl aniline (28.0 ml, 148 mmol) and triethyl amine (20.0 ml, 148 mmol) in 150 ml of dry CH_2Cl_2. The reaction mixture was refluxed for 4 hours and then washed with H_2O and brine. The organic layer was separated and dried over $MgSO_4$. Volatiles were removed under vacuum, the solid was recrystallised from a hexane/toluene (1:1) mixture and dried in a vacuum oven (65 ºC) overnight to give 32.1 g (90%) of product as white crystals. ^{1}H NMR data (δ in ppm, 250 MHz, J in Hz, $CDCl_3$, 298K): 9.07 (s, 2H, N*H*), 8.55 (d, ^{3}J 7.8, 2H, Pyr-H_m), 8.17 (t, ^{3}J 7.8, 1H, Pyr-H_p), 7.29 (m, 6H, Ar-*H*), 3.13 (sept, ^{3}J 6.9, 4H, C*H*$(CH_3)_2$), 1.21 (d, ^{3}J 6.9, 24H, CH(CH_3)$_2$). ^{13}C NMR (δ in ppm, 60 MHz, $CDCl_3$, 298K): 162.5, 148.8, 146.0, 139.6, 130.5, 128.6, 125.8, 123.6, 29.0, 23.5. MS (FAB, *m/z*): 485 $[M]^+$. I.R. (KBr (s), cm^{-1}): 3367 (s), 3285 (s), 2963 (s), 2860 (s), 1694 (s), 1661 (s), 1520 (s), 1457 (s), 1362 (m), 1078 (m), 798 (m), 672 (m). Elemental analysis for $C_{31}H_{39}N_3O_2$ (485.67) found (required): %C = 76.83 (76.67), %H = 8.16 (8.09), %N = 8.59 (8.65).

N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarboxamide

Procedure as descibed for N,N'-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarboxamide using 2,4,6-trimethylaniline (10.2 ml, 72 mmol), 2,6-pyridine dicarbonyl chloride (7.38 g, 36 mmol) and triethylamine (10.0 ml, 72 mmol) yielding 12.0 g (83%) of product as pale yellow crystals. ^{1}H NMR (δ in ppm, 250 MHz, J in Hz, $CDCl_3$): 9.06 (s, 2H, N*H*), 8.49 (d, ^{3}J 7.8, 2H, Pyr-H_m), 8.12 (t, ^{3}J 7.8, 1H, Pyr-H_p), 6.93 (s, 4H, Ar-*H*), 2.28 (s, 6H, Ar-C_pH_3), 2.23 (s, 12H, Ar-C_oH_3). ^{13}C NMR (δ in ppm, 60 MHz, $CDCl_3$, 298K): 161.7, 148.8, 139.1, 136.8, 134.8, 130.6, 128.8, 125.3, 20.8, 18.2. MS (CI, *m/z*): 402 $^{7+}$. I.R. (KBr (s), cm^{-1}): 3307 (s), 3075 (m), 2918 (s), 2866 (m), 1678 (s), 1661 (s), 1525 (s), 1434 (s), 1316 (m), 1232 (m), 1163 (m), 1129 (m), 1074 (m), 1035 (m), 999 (m), 952 (w), 898 (m), 848 (m), 784 (m), 765 (s), 667 (s). Elemental analysis for $C_{25}H_{27}N_3O_2$ (401.5) found (required): %C = 74.60 (74.79), %H = 6.87 (6.78), %N = 10.37 (10.47).

N,N'-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarboximidoyl chloride

N,N'-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarboxamide (20.3 g, 41.9 mmol) was dissolved in a large excess of thionyl chloride (100 ml). A few drops of DMF were added and the reaction mixture was refluxed for 3 hours. The mixture was cooled to room temperature and the volatiles were removed under vacuum. The solid was extracted with a 100 ml heptane/toluene (1:1) mixture at 100 ºC. Upon cooling to -18 ºC, the product crystallised from solution. After filtration the crystals were washed with heptane and dried under vacuum overnight to give 21.5 g (98%) of product. ^{1}H NMR (δ in ppm, 250 MHz, J in Hz, $CDCl_3$, 298K): 8.56 (d, ^{3}J 7.8, 2H, Pyr-H_m), 8.07 (t, ^{3}J 7.8, 1H, Pyr-H_p), 7.26 (m, 6H, Ar-*H*), 2.86 (sept, ^{3}J 6.9, 4H, C*H*$(CH_3)_2$), 1.25 (dd, J 8.4 ^{3}J 6.9, 24H, CH(C$H_3)_2$). ^{13}C NMR (δ in ppm, 60 MHz, $CDCl_3$, 298K): 143.5, 136.7, 135.1, 132.1, 129.4, 128.5, 124.8, 123.1, 28.6, 23.3, 22.9. MS (CI, *m/z*): 522 $^{7+}$, 486 $[M - Cl]^+$. I.R. (KBr (s), cm^{-1}): 2961 (s), 2868 (s), 1655 (s), 1575 (m), 1457 (s), 1445 (s), 1280 (m), 1182 (s), 913 (s), 756 (m), 625 (m). Elemental analysis for $C_{31}H_{37}Cl_2N_3$ (522.56) found (required): %C = 71.18 (71.25), %H = 7.07 (7.14), %N = 7.97 (8.05).

N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarboximidoyl chloride

N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarboxamide (2.60 g, 5.87 mmol) and phosphorous pentachloride (2.44 g, 11.7 mmol) were dissolved in 100 ml of dry toluene. After stirring at 70 °C for 1 hour the volatiles were removed at ambient temperature. The crude dark purple residue was purified by flash chromatography (neutral Al_2O_3, hexane/toluene 1:1) to

afford 1.48 g (52%) of yellow solid. ^{1}H NMR (δ in ppm, 250 MHz, J in Hz, CD_2Cl_2): 8.52 (d, ^{3}J 7.8, 2H, Pyr-H_m), 8.03 (t, ^{3}J 7.8, 1H, Pyr-H_p), 6.97 (s, 4H, Ar-*H*), 2.33 (s, 6H, Ar-C_pH_3), 2.12 (s, 12H, Ar-C_oH_3). ^{13}C NMR (δ in ppm, 60 MHz, CD_2Cl_2, 298K): 151.5, 145.3, 143.8, 138.2, 129.0, 126.2, 20.9, 18.0. MS (CI, *m/z*): 437 $[M]^-$. I.R. (KBr (s), cm^{-1}): 3005 (w), 2968 (m), 1915 (m), 2848 (m), 1717 (m), 1663 (s), 1571 (m), 1475 (s), 1440 (s), 1375 (m), 1278 (m), 1227 (m), 1201 (m), 1143 (m), 898 (s), 848 (m), 811 (m), 731 (m), 618 (s). Elemental analysis for $C_{25}H_{25}Cl_2N_3$ (438.4) found (required): %C = 68.62 (68.49), %H = 5.63 (5.75), %N = 9.56 (9.59).

Dimethyl N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarboximidoate (1)

Methanol (0.18 ml, 4.6 mmol) was added to a suspension of sodium hydride (0.14 g, 5.7 mmol) in 60 ml of dry THF. The resulting sodium methanolate solution was added to a solution of N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarboximidoyl chloride (1.0 g, 2.3 mmol) in 30 ml dry THF. After 24 hours of reflux, the volatiles were removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and water was added. The organic phase was washed with 30 ml H_2O, 30 ml aqueous 2.0 M NaOH and 30 ml brine, dried over Na_2SO_4 and filtered. Removal of the solvent gave the crude product, recrystallisation from hot methanol yielded 0.87 g (89%) of **1** as a white solid. ^{1}H NMR (δ in ppm, 250 MHz, J in Hz, $CDCl_3$): 7.32 (t, ^{3}J 6.5, 1H, Pyr-H_p), 7.69 (d, ^{3}J 6.5, 2H, Pyr-H_m), 6.69 (s, 4H, Ar-*H*), 3.98 (s, 3H, OCH_3), 2.18 (s, 6H, Ar-C_pH_3), 1.90 (s, 12H, Ar-C_oH_3). ^{13}C NMR (δ in ppm, 60 MHz, $CDCl_3$, 298K): 155.6, 149.7, 142.5, 136.2, 131.4, 128.4, 126.9, 123.5, 20.6, 18.2. MS (CI, *m/z*): 430 $^{7+}$, 416 $[M - CH_3]^+$. I.R. (KBr (s), cm^{-1}): 2947 (m), 2911 (m), 1676 (s), 1568 (m), 1479 (w), 1457 (m), 1435 (m), 1375 (w), 1326 (m), 1291 (s), 1234 (m), 1180 (m), 1166 (m), 1137 (m), 1082 (w), 992 (m), 896 (w), 868 (m), 819 (m), 740 (m), 633 (m). Elemental analysis for $C_{27}H_{31}N_3O_2$ (429.6) found (required): %C = 75.38 (75.49), %H = 7.38 (7.27), %N = 9.69 (9.78).

Dimethyl N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarbimidothioate (2)

A mixture of N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarboximidoyl chloride (1.50 g, 3.42 mmol) and sodium methylmercaptide (0.48g, 6.84 mmol) was stirred for 24 h in 50 ml of dry THF. Volatiles were removed *in vacuo* and the residue was dissolved in 40 ml CH_2Cl_2. Washing with H_2O (3x60ml) followed by drying over Na_2SO_4 and removal of the solvent gave the crude product. Recrystallisation from hot methanol yielded 1.20 g (76%) of **2** as a white solid. ^{1}H NMR (δ in ppm, 250 MHz, J in Hz, $CDCl_3$): 7.68 (b, 3H, Pyr-H_p + Pyr-H_m), 6.81 (s, 4H, Ar-*H*), 2.31 (s, 6H, SCH_3), 2.25 (s, 6H, Ar-C_pH_3), 2.06 (s, 12H, Ar-C_oH_3). ^{13}C NMR (δ in ppm,

60 MHz, $CDCl_3$, 298K): 164.1, 153.3, 145.0, 137.5, 132.6, 128.5, 125.8, 122.8, 20.7, 17.9, 14.9. MS (FAB, *m/z*): 462 $[M]^+$, 447$[M - CH_3]^+$, 415 $[M - SCH_3]^+$. I.R. (KBr (s), cm^{-1}): 2968 (m), 2913 (m), 2847 (m) 1601 (s), 1568 (m), 1477 (m), 1446 (m) 1431 (m), 1379 (w), 1319 (w), 1284 (s), 1204 (m), 1143 (m), 1089 (w), 980 (m), 945 (s), 852 (m), 815 (s), 741 (w), 650 (m). Elemental analysis for $C_{27}H_{31}N_3S_2$ (461.7) found (required): %C = 70.17 (70.24), %H = 6.59 (6.77), %N = 8.90 (9.10).

Diphenyl-N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarboximidoate (3)

Procedure as described for **1** employing phenol (0.43 g, 4.6 mmol), sodium hydride (0.12 g, 5.1 mmol) and N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarboximidoyl chloride (1.0 g, 2.3 mmol) yielding 0.48 g (38%) of **3** as a yellow solid. ^{1}H NMR (δ in ppm, 250 MHz, J in Hz, $CDCl_3$): 7.29 (m, 13H, Ar-*H*), 6.74 (s, 4H, Ar-*H*), 2.20 (s, 6H, Ar-C_pH_3), 2.01 (s, 12H, Ar-C_oH_3). ^{13}C NMR (δ in ppm, 60 MHz, $CDCl_3$, 298K): 154.0, 149.6, 141.9, 136.9, 131.8, 129.1, 128.2 126.8, 124.6, 121.1, 20.6, 18.3. MS (CI, *m/z*): 554 $^{7+}$, 478 $[M - C_6H_5]^+$. I.R. (KBr (s), cm^{-1}): 2913 (m), 2848 (w), 1675 (s), 1594 (s), 1567 (m), 1490 (s), 1457 (m), 1374 (w), 1322 (m), 1297 (m), 1220 (s), 1167 (m), 1147 (m), 1099 (m), 1060 (m), 999 (w), 925 (m), 853 (m), 754 (m), 727 (m), 693 (m), 674 (w), 563 (w). Elemental analysis for $C_{37}H_{35}N_3O_2$ (553.7) found (required): %C = 80.30 (80.26), %H = 6.47 (6.37), %N = 7.65 (7.59).

Diphenyl-N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarbimidothioate (4)

Procedure as described for **1** employing thiophenol (0.14 ml, 1.4 mmol), sodium hydride (36 mg, 1.5 mmol) and N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarboximidoyl chloride (0.28 g, 0.64 mmol) yielding 0.35 g (94%) of **4** as a pale yellow solid. ^{1}H NMR (δ in ppm, 250 MHz, J in Hz, $CDCl_3$): 7.80 (d, ^{3}J 6.7, 2H, Pyr-H_m) 7.67 (t, ^{3}J 6.7, 1H, Pyr-H_p), 7.21 (m, 10H, SAr-*H*), 6.87 (s, 4H, Ar-*H*), 2.31 (s, 6H, Ar-C_pH_3), 2.17 (s, 12H, Ar-C_oH_3). ^{13}C NMR (δ in ppm, 60 MHz, $CDCl_3$, 298K): 162.9, 152.9, 144.9, 136.8, 134.0, 133.0, 131.0, 128.5, 128.3, 127.8, 125.6, 123.5, 20.8, 18.0. I.R. (KBr (s), cm^{-1}): 3060 (w), 2912 (m), 2848 (w), 1615 (s), 1572 (m), 1477 (m), 1439 (m), 1266 (m), 1230 (m), 1201 (m), 1144 (m), 1009 (s), 939 (s), 854 (s), 809 (s), 742 (s), 686 (s), 611 (w), 479 (w). MS (CI, *m/z*): 586 $^{7+}$, 478 $[M - SAr]^+$. Elemental analysis for $C_{37}H_{35}N_3S_2$ (585.8) found (required): %C = 75.76 (75.86), %H = 6.05 (6.02), %N = 7.09 (7.17).

Diphenyl N,N'-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarboximidoate (5)

Procedure as described for **1** employing phenol (0.93 ml, 10.6 mmol), sodiumhydride (0.28 g, 11.7 mmol) and N,N'-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarboximidoyl chloride (2.50 g, 4.79 mmol). The reaction time was extended to 48 hours yielding 2.00 g (66 %) of **5** as white crystals. ^{1}H NMR (δ in ppm, 250 MHz, J in Hz, $CDCl_3$, 298K): 7.36 (m, 19H, Ar-*H*), 2.91 (sept, ^{3}J 6.8, 4H, C*H*(CH_3)$_2$), 1.14 (d, ^{3}J 6.8, 24H, CH(C*H*$_3$)$_2$). ^{13}C NMR (δ in ppm, 60 MHz, $CDCl_3$, 298K): 154.6, 151.5, 149.5, 141.7, 137.2, 137.0, 128.9, 125.9, 123.7, 122.8, 120.2, 28.4, 23.3. MS (CI, *m/z*): 638 $^{7+}$. I.R. (KBr (s), cm^{-1}): 3065 (m), 2960 (s), 2868 (m), 1676 (s), 1590 (s), 1489 (m), 1454 (s), 1325 (m), 1214 (s), 1102 (m), 1067 (m), 752 (s), 689 (m). Elemental analysis for $C_{43}H_{47}N_3O_2$ (637.87) found (required): %C = 80.96 (80.97), %H = 7.39 (7.43), %N = 6.56 (6.59).

Diphenyl N,N'-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarboimidothioate (6)

Procedure as described for **5**, using thiophenol (0.91 ml, 8.8 mmol), sodiumhydride (0.23 g, 9.7 mmol) and N,N'-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarboximidoyl chloride (2.30 g, 4.4 mmol). The product **6** was obtained in 75% yield (2.20g) as bright yellow crystals. ^{1}H NMR (δ in ppm, 250 MHz, J in Hz, $CDCl_3$, 298K): 7.29 (m, 19H, Ar-*H*), 2.90 (sept, ^{3}J 6.8, 4H, C*H*(CH_3)$_2$), 1.36 (d, ^{3}J 6.8, 12H, CHC*H*$_3$), 1.19 (d, ^{3}J 6.8, 12H, CHC*H*$_3$). ^{13}C NMR (δ in ppm, 60 MHz, $CDCl_3$, 298K): 162.9, 152.8, 145.2, 136.8, 136.0, 134.3, 131.4, 128.4, 127.8, 124.4, 123.7, 123.1, 28.3, 23.5, 23.2. I.R. (KBr (s), cm^{-1}): 3062 (m), 2959 (s), 2862 (m), 1580 (s), 1439 (s), 1281 (m), 1181 (m), 1001 (m), 940 (s), 750 (s), 704 (m). MS (CI, *m/z*): 670 [MH$^+$], 560 [M – SC_6H_5]$^+$. Elemental analysis for $C_{43}H_{47}N_3S_2$ (669.99) found (required): %C = 77.01 (77.09), %H = 6.97 (7.07), %N = 6.31 (6.27).

Bis(2,6-dimethylphenyl)-N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarboximidoate (7)

Procedure as described for **5** employing 2,6-dimethylphenol (0.56 g, 4.6 mmol), sodium hydride (0.12 g, 5.1 mmol) and N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarboximidoyl chloride (1.0 g, 2.3 mmol). The reaction time was extended to 72 hours yielding 0.45 g (32%) of **7** as a bright yellow solid. ^{1}H NMR (δ in ppm, 250 MHz, J in Hz, $CDCl_3$): 7.57 (t, ^{3}J 7.8, 1H, Pyr-H_p), 7.34 (d, ^{3}J 7.8, 2H, Pyr-H_m) 7.09 (m, 10H, OAr-*H*), 6.64 (s, 4H, Ar-*H*), 2.38 (s, 12H, OAr(C*H*$_3$)$_2$), 2.13 (s, 6H, Ar-C$_p$*H*$_3$), 1.92 (s, 12H, Ar-C$_o$*H*$_3$). ^{13}C NMR (δ in ppm, 60 MHz, $CDCl_3$, 298K): 154.1, 150.1, 142.0, 136.5, 131.7, 130.7, 128.8, 126.8, 125.4, 123.8, 20.6, 18.8, 16.6. MS (CI, *m/z*): 610 $^{7+}$. I.R. (KBr (s), cm^{-1}): 2918 (s), 2857 (m), 1685 (s), 1577 (m), 1479 (s), 1444 (m), 1376 (w), 1313 (m), 1267 (m), 1237 (m), 1174 (s), 1131 (m), 1111 (m), 919 (w), 889 (w), 850

(m), 767 (m), 741 (w). Elemental analysis for $C_{41}H_{43}N_3O_2$ (609.8) found (required): %C = 80.76 (80.75), %H = 6.97 (7.11), %N = 6.80 (6.89).

Bis(2,6-dimethylphenyl)-N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarbimidothioate (8)

Procedure as described for **7** employing 2,6-dimethylthiophenol (0.28 g, 2.1 mmol), sodiumhydride (55 mg, 2.3 mmol) and N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarboximidoyl chloride (0.45 g, 1.0 mmol) yielding 0.56 g (85%) of **8** as a pale yellow solid. ^{1}H NMR (δ in ppm, 250 MHz, J in Hz, $CDCl_3$): 7.66 (m, 13H, Ar-*H*), 2.48 (s, 12H, Ar-C_oH_3), 2.30 (s, 6H, Ar-C_pH_3), 2.22 (s, 12H, SAr-CH_3. ^{13}C NMR (δ in ppm, 60 MHz, $CDCl_3$, 298K): 155.0, 142.7, 136.4, 132.4, 129.5, 129.0, 128.7, 128.1, 127.9, 126.01, 125.3, 122.3, 22.6, 20.8, 17.9. MS (CI, *m/z*): 642 $^{7+}$, 504 $[M - SAr(CH_3)_2]^+$. I.R. (KBr (s), cm^{-1}): 3051 (m), 2915 (s), 2848 (m), 1601 (s), 1563 (s), 1463 (s), 1463 (s), 1434 (s), 1372 (m), 1257 (m), 1228 (m), 1200 (m), 1006 (s), 943 (m), 851 (m), 800 (s), 769 (m), 620 (m), 418 (w). Elemental analysis for $C_{41}H_{43}N_3S_2$ (641.9) found (required): %C = 76.72 (76.71), %H = 6.70 (6.75), %N = 6.51 (6.55).

Bis(2,6-dimethylphenyl)-N,N'-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarbimidothioate (9)

Procedure as described for **7** employing 2,6-dimethylthiophenol (1.0 g, 7.3 mmol), sodiumhydride (0.19 g, 8.0 mmol) and N,N'-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarboximidoyl chloride (1.9 g, 3.6 mmol) yielding 1.62 g (62%) of **9** as a pale yellow solid. ^{1}H NMR (δ in ppm, 250 MHz, J in Hz, $CDCl_3$, 298K): 7.17 (m, 15H, Ar-*H*), 3.01 (br, 4H, $CH(CH_3)_2$), 2.47 (s, 12H, Ar-CH_3), 1.30 (s, 12H, CHCH_3), 1.14 (s, 12H, CHCH_3). ^{13}C NMR (δ in ppm, 60 MHz, $CDCl_3$, 298K): 145.3, 143.1, 136.3, 135.9, 129.7, 129.1, 128.0, 124.1, 123.3, 122.2, 28.1, 23.6, 23.3, 22.5. MS (FAB, *m/z*): 726 $^{7+}$, 588 $[M - S(CH_3)_2C_6H_3]^+$. I.R. (KBr (s), cm^{-1}): 3061 (w), 2961 (s), 2868 (m), 1615 (s), 1589 (m), 1564 (m), 1462 (s), 1443 (s), 1382 (m), 1007 (m), 797 (s), 777 (s), 746 (m). Elemental analysis for $C_{47}H_{55}N_3S_2$ (726.10) found (required): %C = 66.29 (66.19), %H = 6.61 (6.50), %N = 4.86 (4.93).

N^2,N^2,N^5,N^5-tetraphenyl-N'^{2},N'^{5}-bis(2,6-diisopropylphenyl)pyridine carboximidamide (10).

n-BuLi (3.2 ml of 2.5M in hexane, 4.9 mmol) was added dropwise to a solution of diphenylamine (1.36 g, 8.1 mmol) in 70 ml Et_2O at - 78 ºC. The reaction mixture was allowed to warm to 0 ºC, stirred for 4 hours and then cooled to - 78 ºC. A solution of N,N'-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarboximidoyl

chloride (2.00 g, 3.8 mmol) in 100 ml of Et_2O was then added dropwise. After the addition, the yellow reaction mixture was allowed to warm to room temperature and stirred for 40 hours. The solution was washed with water (2 x 50 ml), 0.1 M aqueous NaOH (20 ml) and brine, dried over $MgSO_4$, and filtered. Evaporation of the volatiles and recrystallisation from hexane/CH_2Cl_2 (4:1) afforded **10** as pale yellow crystals. Yield 1.47 g (49 %).

^{1}H NMR (250 MHz, J in Hz, C_7D_8, 357K): δ 7.41 (d, 2H, $^3J_{HH}$ = 7.4 Pyr-*H*$_m$), 6.84 (m, 29H, Ar-*H*), 2.85 (sept, $^3J_{HH}$ = 6.8, 4H, C*H*$(CH_3)_2$), 1.04 (d, $^3J_{HH}$ = 6.8, 12H, CHC*H*$_3$), 1.01 (d, $^3J_{HH}$ = 6.8, 12H CHC*H*$_3$). ^{13}C NMR (62.5 MHz, $CDCl_3$, 298K): δ 144.4, 136.4, 128.5, 126.0, 125.2, 123.9, 121.9, 28.3, 23.5, 21.3. MS (CI, NH_3) *m/z* 788 $^{7+}$, 619 [M - N$(C_6H_5)_2$]$^+$. IR (KBr (s), cm^{-1}): 3059 (m) , 2960 (s), 2867 (m), 1630 (s), 1588 (s), 1491 (s), 1457 (s), 1346 (s), 1286 (s), 1249 (s), 1184 (m), 1112 (m), 1076 (m), 756 (s), 698 (s). Elemental analysis for $C_{55}H_{57}N_5$ (788.10) found (required): % C = 83.77 (83.82), % H = 7.26 (7.29), % N = 8.95 (8.89).

N^2,N^5-dimethyl-N^2,N^5-diphenyl-N'^{2},N'^{5}-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarboximidamide (11).

The procedure used was as described for **10**, using N-methylaniline (0.53 ml, 7.87 mmol), n-BuLi (1.95 ml of a 2.5 M solution in hexane, 4.87 mmol) and N,N'-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarboximidoyl chloride (1.21 g 2.32 mmol) to afford **11** as pale yellow crystals. Yield 0.623g (41%).

^{1}H NMR (250 MHz, J in Hz, $CDCl_3$, 298K): δ 6.80 (m, 19H, Ar-*H*), 3.30(s, 3H, NC*H*$_3$) 3.20 (br, 4H, C*H*$(CH_3)_2$), 1.18 (d, $^3J_{HH}$ = 6.7, 12H, CHC*H*$_3$), 1.15 (d, $^3J_{HH}$ = 6.7, 12H, CHC*H*$_3$). ^{13}C NMR (62.5 MHz, $CDCl_3$, 298K): δ 153.0, 145.3, 137.8, 134.2, 128.6, 125.8, 124.4, 122.3, 38.6, 28.3, 23.6, 21.9, 21.0. MS (CI, NH_3): *m/z* 664 $^{7+}$. IR (KBr (s), cm^{-1}): 2962 (s), 2868 (m), 1627 (s), 1584 (s), 1495 (m), 1365 (m), 1326 (m), 1117 (m), 666 (s). Elemental analysis for $C_{45}H_{53}N_5$ (663.95) found (required): % C = 81.34 (81.41), % H = 8.00 (8.05), % N = 10.55 (10.52).

Preparation of Iron Complexes

Dimethyl N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarboximidoate iron(II) dichloride [Fe(**1**)Cl_2]**.**

$FeCl_2$·1.5THF (0.349 g, 1.49 mmol) and **1** (0.638 g, 1.49 mmol) were stirred for 12 hours in 50 ml of dry THF at room temperature during which time the product partly precipitated out of solution. The reaction volume was concentrated to 20 ml and 40 ml of Et_2O was added. The supernatant solution was removed by filtration and the residue was washed with 2x30ml of Et_2O. After drying *in vacuo* the product was obtained as a green, microcrystalline solid. Yield 0.82 g

(99%). MS (FAB, *m/z*): 555 $[M]^+$, 520 $[M - Cl]^+$. I.R. (KBr (s), cm^{-1}): 3069 (w), 3013 (w), 2956 (m), 2912 (m), 2857 (w), 1668 (m), 1647 (s), 1588 (s), 1479 (m), 1449 (s), 1319 (m), 1274 (vs), 1230 (m), 1180 (w), 1019 (m), 843 (m), 754 (m), 719 (m), 679 (m). Elemental analysis for $C_{27}H_{31}N_3O_2FeCl_2$ (556.32) found (required): %C = 58.17 (58.29), %H = 5.45 (5.62), %N = 7.39 (7.55). μ_{eff}: (Evans NMR method): 6.1 BM.

Dimethyl N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarbimidothioate iron(II) dichloride [Fe(**2**)Cl_2]

The procedure as for [Fe(**1**)Cl_2] using **2** (0.18 g, 0.39 mmol) and $FeCl_2$·1.5THF (91 mg, 0.39 mmol) to give 0.15 g (66%) of [Fe(**2**)Cl_2] as a green microcrystalline solid. ^{1}H NMR (δ in ppm, CD_2Cl_2, broad singlets are observed in each case): 87.8 (2H, Py H_m), 20.4 (6H, Ar_{anil} C_pH_3), 15.5 (4H, Ar_{anil} H_m), 11.0 (1H, Py H_p), 5.9 (12H, $Ar_{anil}C_oH_3$), 0.8 (6H, SCH_3). MS (FAB, *m/z*): 588 $[M]^+$, 553 $[M - Cl]^+$. I.R. (KBr (s), cm^{-1}): 3061 (w), 2989 (m), 2915 (m), 2857 (w), 1607 (w), 1559 (s), 1476 (m), 1453 (m), 1419 (m), 1196 (m), 1145 (m), 1082(m), 854 (m), 821 (m). Elemental analysis for $C_{27}H_{31}N_3S_2FeCl_2$ (588.4) found (required): %C = 54.99 (55.11), %H = 5.21 (5.31), %N = 7.09 (7.14). μ_{eff} (Evans NMR method): 5.5 BM.

Diphenyl-N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarboximidoate iron(II) dichloride [Fe(**3**)Cl_2]

The procedure as for [Fe(**1**)Cl_2] using **3** (0.332 g, 0.60 mmol) and $FeCl_2$·1.5THF (0.141 g, 0.60 mmol) to give 0.32 g (78%) of [Fe(**3**)Cl_2] as a blue microcrystalline solid. ^{1}H NMR (δ in ppm, CD_2Cl_2, broad singlets are observed in each case): 78.7 (2H, Py H_m), 17.9 (6H, Ar_{anil} C_pH_3), 15.5 (4H, Ar_{anil} H_m), 8.8 (4H, Ar_{phenol} H_o or H_m), 8.6 (4H, Ar_{phenol} H_o or H_m), 7.5 (12H, $Ar_{anil}C_oH_3$), 5.6 (2H, Ar_{phenol} H_p), 1.44 (1H, Py H_p). MS (FAB, *m/z*): 679 $[M]^+$, 644 $[M - Cl]^+$. I.R. (KBr (s), cm^{-1}): 3051 (w), 2918 (m), 2857 (m), 1647 (s), 1584 (s), 1488 (s), 1457 (m), 1379 (w), 1319 (m), 1253 (vs), 1221 (s), 1183 (s), 1084 (m), 1023 (m), 913 (w), 853 (m), 754 (s), 689 (m). Elemental analysis for $C_{37}H_{35}N_3O_2FeCl_2$ (680.46) found (required): %C = 65.23 (65.31), %H = 5.19 (5.18), %N = 6.13 (6.18). μ_{eff} (Evans NMR method): 5.7 BM.

Diphenyl-N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarbimidothioate iron(II) dichloride [Fe(**4**)Cl_2]

The procedure as for [Fe(**1**)Cl_2] using **4** (1.97 g, 3.37 mmol) and $FeCl_2$·1.5THF (0.791 g, 3.37 mmol) to give 2.25 g (94%) of [Fe(**4**)Cl_2] as a green microcrystalline solid. ^{1}H NMR (δ in ppm,

CD_2Cl_2, broad singlets are observed in each case): 87.7 (2H, Py H_m), 20.5 (6H, Ar_{anil} C_pH_3), 17.0 (1H, Py H_p), 14.9 (4H, Ar_{anil} H_m), 7.6 (12H, $Ar_{anil}C_oH_3$), 6.6 (4H, Ar_{thioph} H_o or H_m), 4.7 (2H, Ar_{thioph} H_p), 2.3 (4H, Ar_{thioph} H_o or H_m). MS (FAB, *m/z*): 711 $[M]^+$, 676 $[M - Cl]^+$. I.R.(KBr (s), cm^{-1}): 2916 (m), 2857 (m), 1559 (s), 1540 (s), 1474 (s), 1441 (m), 1196 (s), 1142 (m), 1096 (m), 1067 (m), 850 (m), 821 (m), 748 (m), 690 (m), 490 (m). Elemental analysis for $C_{37}H_{35}N_3S_2FeCl_2$ (712.58) found (required): %C = 62.42 (62.37), %H = 5.01 (4.95), %N = 5.86 (5.90). μ_{eff} (Evans NMR method): 5.5 BM.

Diphenyl N,N'-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarboximidoate iron(II) dichloride [Fe(**5**)Cl_2]

The procedure as for [Fe(**1**)Cl_2] using **5** (0.937 g, 1.47 mmol) and $FeCl_2 \cdot 1.5THF$ (0.345 g, 1.47 mmol) to give 0.55 g (49%) of [Fe(**5**)Cl_2] as a blue microcrystalline solid. ^1H NMR (δ in ppm, CD_2Cl_2, broad singlets are observed in each case): 77.3 (2H, Py H_m), 55.2 (1H, Py H_p) 17.4 (4H, Ar_{anil} H_m), 11.7 (4H, Ar_{phenol} H_m or H_o), 10.9 (4H, Ar_{phenol} H_m or H_o), 9.8 (2H, Ar_{phenol} H_p), -7.8 (12H, $CHCH_3$), -9.9 (16H, $CHCH_3$ + Ar_{anil} H_p), -33.1 (4H, $CHCH_3$). MS (FAB, *m/z*): 763 $[M^+]$, 728 $[M - Cl]^+$. I.R. (KBr (s), cm^{-1}): 3064 (m), 2962 (s), 2867 (s), 1631 (m), 1579 (s), 1486 (s), 1459 (s), 1325 (s), 1269 (s), 1205 (s), 1095 (m), 901 (m), 749 (s). Elemental analysis for $C_{43}H_{47}N_3O_2FeCl_2$ (764.62) found (required): %C = 67.58 (67.55), % H = 5.96 (6.20), %N = 5.59 (5.50). μ_{eff} (Evans NMR method): 5.0 BM.

Diphenyl-N,N'-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarbimidothioate iron(II) dichloride [Fe(**6**)Cl_2]

The procedure as for [Fe(**1**)Cl_2] using **6** (0.954 g, 1.42 mmol) and $FeCl_2 \cdot 1.5THF$ (0.334 g, 1.42 mmol) to give 0.81 g (72%) of [Fe(**6**)Cl_2] as a green solid. ^1H NMR (δ in ppm, CD_2Cl_2, broad singlets are observed in each case): 87.7 (2H, Py H_m), 51.6 (1H, Py H_p) 15.6 (4H, Ar_{anil} H_m), 12.3 (4H, Ar_{thioph} H_m or H_o), 10.2 (6H, Ar_{thioph} H_m or H_o + Ar_{thioph} H_p), -4.8 (24H, $CHCH_3$), -11.6 (2H, Ar_{anil} H_p), -22.3 (4H, $CHCH_3$). MS (FAB, *m/z*): 795 $[M]^+$, 760 $[M - Cl]^+$. I.R. (KBr (s), cm^{-1}): 3061 (w), 2964 (s), 2866 (m), 1579 (s), 1504 (s), 1465 (s), 1176 (s), 1107 (s), 808 (m), 748 (s), 698 (m). Elemental analysis for $C_{43}H_{47}N_3S_2FeCl_2$ (796.74) found (required): %C = 64.92 (64.82), %H = 5.65 (5.95), %N = 5.37 (5.27). μ_{eff} (Evans NMR method): 5.4 BM.

Bis(2,6-dimethylphenyl)-N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarboximidoate iron(II) dichloride [Fe(**7**)Cl_2]

The procedure as for [Fe(**1**)Cl_2] using **7** (0.832 g, 1.36 mmol) and $FeCl_2$·1.5THF (0.320 g, 1.36 mmol) to give 0.40 g (40%) of [Fe(**7**)Cl_2] as a green microcrystalline solid. ^{1}H NMR (δ in ppm, CD_2Cl_2, broad singlets are observed in each case): 84.0 (2H, Py H_m), 28.3 (1H, Py H_p), 21.8 (6H, Ar_{anil} C_pH_3), 14.5 (4H, $Ar_{anil}H_m$), 8.5 (4H, $Ar_{phenol}H_m$), 8.4 (2H, $Ar_{phenol}H_p$), 7.7 (12H, $Ar_{anil}C_oH_3$), -4.0 (12H, $Ar_{phenol}CH_3$). MS (FAB, *m/z*): 735 $[M]^+$, 700 $[M - Cl]^+$. I.R. (KBr (s), cm^{-1}): 2920 (s), 2857 (m), 1678 (m), 1637 (m), 1579 (s), 1475 (s), 1378 (m), 1324 (m), 1253 (s), 1219 (s), 1163 (s), 1126 (m), 1093 (m), 1032 (m), 849 (s), 813 (m), 768 (m). Elemental analysis for $C_{41}H_{43}N_3O_2FeCl_2$ (736.57) found (required): %C = 66.74 (66.86), %H = 5.87 (5.88), %N = 5.69 (5.70). μ_{eff} (Evans NMR method): 5.8 BM.

Bis(2,6-dimethylphenyl)-N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarbimidothioate iron(II) dichloride [Fe(**8**)Cl_2]

The procedure as for [Fe(**1**)Cl_2] using **8** (0.343 g, 0.534 mmol) and $FeCl_2$·1.5THF (0.125 g, 0.534 mmol) to give 0.25 g (61%) of [Fe(**8**)Cl_2] as a green solid. ^{1}H NMR (δ in ppm, CD_2Cl_2, broad singlets are observed in each case): 88.5 (2H, Py H_m), 22.2 (6H, Ar_{anil} C_pH_3), 15.1 (4H, Ar_{anil} H_m), 7.4 (4H, Ar_{thioph} H_m), 5.7 (12H, $Ar_{anil}C_oH_3$), 3.7 (2H, Ar_{thioph} H_p), 0.5 (12H, $Ar_{thioph}CH_3$). I.R.(KBr (s), cm^{-1}): MS (FAB, *m/z*): 767 $[M]^+$, 732 $[M - Cl]^+$. I.R. (KBr (s), cm^{-1}): 3050 (w), 2916 (m), 2857 (w), 1581 (m), 1533 (s), 1464 (s), 1379 (m), 1267 (m), 1196 (m), 1170 (m), 1142 (m), 1096 (m), 1034 (m), 1034 (m), 972 (m), 858 (m), 815 (m), 775 (m), 419 (w). Elemental analysis for $C_{41}H_{43}N_3S_2FeCl_2$ (768.69) found (required): %C = 64.23 (64.06), %H = 5.60 (5.64), %N = 5.85 (5.47). μ_{eff} (Evans NMR method): 5.1 BM.

Bis(2,6-dimethylphenyl)-N,N'-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarbimidothioate iron(II) dichloride [Fe(**9**)Cl_2]

The procedure as for [Fe(**1**)Cl_2] using **9** (0.11 g, 0.15 mmol) and $FeCl_2$·1.5THF (36 mg, 0.15 mmol) to give 86 mg (67%) of [Fe(**9**)Cl_2] as a teal green solid. ^{1}H NMR (δ in ppm, CD_2Cl_2, broad singlets are observed in each case): 76.4 (2H, Py H_m), 64.9 (1H, Py H_p) 15.8 (4H, Ar_{anil} H_m), 11.0 (4H, Ar_{thioph} H_m), 9.5 (2H, Ar_{thioph} H_p), -4.5 (24H, $CHCH_3$), -7.0 (12H, $Ar_{thioph}CH_3$), -10.1 (2H, Ar_{anil} H_p), -20.4 (4H, $CHCH_3$). MS (FAB, *m/z*): 851 $[M]^+$, 816 $[M - Cl]^+$. I.R. (KBr (s), cm^{-1}): 3059 (w), 2963 (s), 2867 (m), 1535 (m), 1498 (m), 1464 (s), 1382 (m), 1178 (m), 1108 (m), 8027 (m), 773 (s). Elemental analysis for $C_{47}H_{55}N_3S_2FeCl_2$ (852.85) found (required): %C = 66.29 (66.19), %H = 6.61 (6.50), %N = 4.86 (4.93). μ_{eff} (Evans NMR method): 5.0 BM.

N^2,N^2,N^5,N^5-tetraphenyl-N'^{2},N'^{5}-bis(2,6-diisopropylphenyl)pyridine 2,6-carboximidamide iron(II) dichloride [Fe(**10**)Cl_2].

The procedure used was as described for [Fe(**1**)Cl_2]., using **10** (0.745 g, 0.945 mmol) and $FeCl_2$·1.5thf (0.222 g, 0.945 mmol) to afford the complex as a green solid. Yield 0.48 g (56%). ^{1}H NMR (250 MHz, CD_2Cl_2, 298K, all peaks appear as broad singlets): δ 99.3 (2H, Py H_m), 11.2 (4H, Ar_{anil} H_m), 7.0 (17H, Py H_p + $Ar_{diphenylamid}$ H_p + CHCH_3), 5.0 (4H, $Ar_{diphenylamid}$ H_m or H_o), -2.2 (2H, Ar_{anil} H_p), -5.4 (12H, CHCH_3), -11.9 (4H, $Ar_{diphenylamid}$ H_m or H_o), -24.5 (4H, C*H*CH_3). IR (KBr (s), cm^{-1}): 3059 (m), 2960 (s), 2867 (m), 1630 (s), 1588 (s), 1491 (s), 1457 (s), 1346 (s), 1286 (s), 1248 (s), 1184 (m), 1112 (m), 820 (m), 756 (s), 698 (s). Elemental analysis for $C_{55}H_{57}N_5FeCl_2$ (914.85) found (required): % C = 72.35 (72.21), % H = 6.37 (6.28), % N = 7.61 (7.66). μ_{eff} (Evans' NMR method): 5.1 BM..

N^2,N^5-dimethyl-N^2,N^5-diphenyl-N'^{2},N'^{5}-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarboximidamide iron(II) dichloride [Fe(**11**)Cl_2]..

The procedure used was as described for [Fe(**1**)Cl_2]., using **11** (0.18 g, 0.27 mmol) and $FeCl_2$·1.5thf (64 mg, 0.27 mmol) to afford the complex as a dark blue solid. Yield 140 mg (66%). ^{1}H NMR (250 MHz, CD_2Cl_2, 298K, all peaks appear as broad singlets): δ 99.9 (2H, Py H_m), 13.6 (4H, Ar_{anil} H_m), 4.8 (16H, $Ar_{phenylamid}$ H_o, H_m and H_p, NCH_3), -2.7 (2H, Ar_{anil} H_p), -4.5 (12H, CHCH_3), -11.2 (CHCH_3), -25.0 (4H, C*H*CH_3). IR (KBr (s), cm^{-1}): 3059 (w), 2965 (s), 2927 (m), 2867 (m), 1613 (m), 1581 (m), 1556 (s), 1494 (s), 1359 (s), 1275 (m), 1115 (m), 762 (s), 744 (m), 698 (m), 554 (w). Elemental analysis for $C_{45}H_{53}N_5FeCl_2$ (790.7) found (required): % C = 68.48 (68.36), % H = 6.74 (6.76), % N = 8.95 (8.86). μ_{eff} (Evans' NMR method): 5.3 BM.

Preparation of Vanadium Complexes

Dimethyl N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarboximidoate vanadium(III) trichloride [V(**1**)Cl_3]

VCl_3·3THF (0.877g, 2.35 mmol) and **1** (1.00g, 2.35 mmol) were stirred for 12 hours in 50 ml of dry THF at room temperature during which time the product partly precipitated out of solution. The reaction volume was concentrated to 20 ml and 40 ml of Et_2O was added. The supernatant solution was removed by filtration and the residue was washed with 2x30ml of Et_2O. After drying *in vacuo* the product [V(**1**)Cl_3] was obtained as a red brown, microcrystalline solid. Yield 1.18 g (86%). ^{1}H NMR (δ in ppm, CD_2Cl_2, broad singlets are observed in each case): 78.9 (2H,

Py H_m), 16.6 (6H, OCH_3), 13.8 (4H, Ar$_{anil}$ H_m), 12.7 (12H, Ar$_{anil}$C$_o$$H_3$), 8.5 (6H, Ar$_{anil}$ C$_p$$H_3$), -1.0 (1H, Py H_p). MS (FAB, *m/z*): 552 [M – Cl]$^+$. I.R. (KBr (s), cm^{-1}): 3076 (w), 3010 (w), 2953 (m), 2918 (m), 2855, 1621 (s), 1579 (s), 1442 (m), 1338 (s), 1287 (s), 1227 (m), 1182 (w), 1116 (w) 1088 (w), 1038 (m), 1014 (m), 870 (m), 848 (m), 757 (m), 719 (w), 683 (m), 568 (w). Elemental analysis for $C_{27}H_{31}N_3O_2VCl_3$ (586.86) found (required): %C = 55.12 (55.26), % H = 5.36 (5.32), %N = 6.99 (7.16). μ_{eff} (Evans NMR method): 2.6 BM.

Diphenyl N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarboximidoate vanadium(III) trichloride [V(**3**)Cl$_3$]

The procedure as described for [V(**1**)Cl$_3$] using VCl$_3$·3THF (1.18 g, 3.16 mmol) and **3** (1.75g, 3.16 mmol) to give [V(**3**)Cl$_3$] as a brown microcrystalline solid. Yield 2.00 g (89%). ^{1}H NMR (δ in ppm, CD_2Cl_2, broad singlets are observed in each case): 8.0 (4H, Ar$_{phenol}$ H_o or H_m), 7.9 (4H, Ar$_{anil}$ H_m), 6.9 (2H, Ar$_{phenol}$ H_p), 6.5 (4H, Ar$_{phenol}$ H_o or H_m), 5.5 (12H, Ar$_{anil}$C$_o$$H_3$), 4.1 (6H, Ar$_{anil}$ C$_p$$H_3$), 1.5 (1H, Py H_p), - 1.9 (2H, Py H_m). MS (FAB, *m/z*): 676 [M – Cl]$^+$. I.R. (KBr (s), cm^{-1}): 3081 (w), 2921 (m), 2856 (w), 1617 (w), 1566 (s), 1486 (s), 1457 (m), 1340 (m), 1272 (s), 1221 (m), 1188 (m), 1161 (m), 1154 (m), 1097 (w), 1083 (w), 1034 (m), 1022 (m), 907 (w), 848 (m), 805 (m), 752 (s), 682 (m). Elemental analysis for $C_{37}H_{35}N_3O_2VCl_3$ (711.01) found (required): %C = 62.69 (62.50), % H = 4.71 (4.96), %N = 5.80 (5.91). μ_{eff} (Evans NMR method): 2.7 BM.

Diphenyl-N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarbimidothioate vanadium(III) trichloride [V(**4**)Cl$_3$]

The procedure as described for [V(**1**)Cl$_3$] using VCl$_3$·3THF (1.81 g, 4.86 mmol) and **4** (2.84g, 4.86 mmol) to give [V(**4**)Cl$_3$] as a brown microcrystalline solid. Yield 3.34 g (92%). ^{1}H NMR (δ in ppm, CD_2Cl_2, broad singlets are observed in each case): 8.2 (4H, Ar$_{thioph}$ H_o or H_m), 7.1 (4H, Ar$_{anil}$ H_m), 6.7 (2H, Ar$_{thioph}$ H_p), 6.3 (4H, Ar$_{thioph}$ H_o or H_m), 5.7 (12H, Ar$_{anil}$C$_o$$H_3$), 4.9 (6H, Ar$_{anil}$ C$_p$$H_3$), - 2.7 (1H, Py H_p), - 6.1 (2H, Py H_m). MS (FAB, *m/z*): 708 [M – Cl]$^+$. I.R. (KBr (s), cm^{-1}): 3055 (w), 2959 (m), 2921 (m), 2861 (m), 1608 (w), 1588 (m), 1510 (s), 1473 (s), 1441 (s), 1377 (m), 1304 (w), 1277 (w), 1221 (w), 1194 (s), 1170 (s), 1140 (s), 1095 (m), 1064 (m), 1036 (m), 1022 (m), 998 (m), 973 (m), 910 (w), 849 (m), 821 (s), 753 (m), 742 (s), 703 (m), 686 (m), 653 (w), 644 (w), 542 (w), 517 (w), 506 (w), 488 (w), 481 (w). Elemental analysis for $C_{35}H_{37}N_3S_2VCl_3$ (743.13) found (required): %C = 59.83 (59.80), % H = 4.82 (4.75), %N = 5.71 (5.65). μ_{eff} (Evans NMR method): 2.5 BM.

Diphenyl-N,N'-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarbimidothioate vanadium(III) trichloride [V(**6**)Cl_3]

The procedure as described for [V(**1**)Cl_3] using VCl_3·3THF (0.694 g, 1.86 mmol) and **6** (1.25g, 1.86 mmol) to give [V(**6**)Cl_3] as a brown green microcrystalline solid. Yield 0.942 g (61%). ^{1}H NMR (δ in ppm, $CDCl_3$, broad singlets are observed in each case): 8.5 (4H, Ar_{anil} H_m), 8.3 (4H, Ar_{thioph} H_o or H_m), 6.8 (2H, ArH_p), 5.6 (2H, ArH_p), 5.5 (4H, Ar_{thioph} H_o or H_m), 5.1 (4H, C*H*CH_3), 2.6 (12H, CHCH_3), 0.9 (12H, CHCH_3), - 8.6 (2H, Py H_m), - 32.5 (1H, Py H_p). MS (FAB, *m/z*): 792 $[M - Cl]^+$. I.R. (KBr (s), cm^{-1}): 3060 (w), 2969 (s), 2866 (m), 1583 (m), 1512 (s), 1466 (s), 1442 (m), 1363 (w), 1328 (w), 1215 (m), 1172 (s), 1111 (s), 1056 (w), 1040 (w), 1024 (w), 980 (m), 937 (w), 843 (m), 802 (m), 765 (w), 743 (s), 689 (m), 648 (w), 569 (w), 494 (w). Elemental analysis for $C_{43}H_{47}N_3S_2VCl_3$ (827.29) found (required): %C = 62.53 (62.43), % H = 5.78 (5.73), %N = 5.01 (5.08). μ_{eff} (Evans NMR method): 2.3 BM.

2,6-Diacetylpyridinebis(2,4,6-trimethylanil) vanadium(III) trichloride [V(**12**)Cl_3]

The procedure as described for [V(**1**)Cl_3] using VCl_3·3THF (0.316 g, 0.846 mmol) and **12** (0.336 g, 0.846 mmol) to give [V(**12**)Cl_3] as a green microcrystalline solid. Yield 0.453 g (97%). ^{1}H NMR (δ in ppm, CD_2Cl_2, broad singlets are observed in each case): 60.1 (6H, N=CCH_3), 6.7 (6H, Ar_{anil} C_pH_3), 4.5 (12H, $Ar_{anil}C_oH_3$), 2.9 (4H, Ar_{anil} H_m), - 4.5 (2H, Py H_m), -12.9 (1H, Py H_p). MS (FAB, *m/z*): 520 $[M - Cl]^+$, I.R. (KBr (s), cm^{-1}): 3077 (m), 2917 (m), 2856 (m), 1611 (m), 1576 (s), 1473 (m), 1373 (s), 1269 (s), 1222 (s), 1156 (w), 1114 (w), 1030 (m), 958 (w), 857 (m), 811 (m), 743 (w), 651 (w), 613 (w), 569 (w). Elemental analysis for $C_{27}H_{31}N_3VCl_3$ (554.87) found (required): %C = 58.49 (58.45), % H = 5.68 (5.63), %N = 7.29 (7.57). μ_{eff} (Evans NMR method): 2.6 BM.

Preparation of Chromium Complexes

Dimethyl N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarboximidoate chromium(III) trichloride [Cr(**1**)Cl_3]

A solution of $CrCl_3$·3THF (0.515g, 1.38 mmol) and **1** (0.591g, 1.38 mmol) in 50 ml of dry THF was refluxed for 12 hours. Upon cooling to room temperature, the product precipitated out of solution. The reaction volume was concentrated to 20 ml and 40 ml of Et_2O was added. The supernatant solution was removed by filtration and the residue was washed with 2 x 30 ml of Et_2O. After drying *in vacuo* the product [Cr(**1**)Cl_3] was obtained as a green, microcrystalline solid. Yield 0.703 g (87%). MS (FAB, *m/z*): 588 $[M^+]$, 553 $[M - Cl]^+$, 517 $[M - 2Cl]^+$. I.R. (KBr

(s), cm^{-1}): 3070 (w), 3011 (w), 2954 (m), 2915 (m), 2856 (w), 1621 (m), 1573 (s), 1471 (m), 1437 (m), 1345 (s), 1293 (s), 1228 (m), 1186 (w), 1117 (w), 1085 (m), 1042 (m), 1015 (m), 871 (m), 849 (m), 830 (m), 759 (m), 722 (w), 687 (m), 676 (m), 567 (w). Elemental analysis for $C_{27}H_{31}N_3O_2CrCl_3$ (587.92) found (required): %C = 54.95 (55.16), % H = 5.14 (5.32), %N = 7.04 (7.15). μ_{eff} (Evans NMR method): 3.5 BM.

Diphenyl N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarboximidoate chromium(III) trichloride [Cr(**3**)Cl_3]

The procedure as described for [Cr(**1**)Cl_3] using $CrCl_3$·3THF (0.554 g, 1.47 mmol) and **3** (0.818 g, 0.147 mmol) to give [Cr(**3**)Cl_3] as a green microcrystalline solid. Yield 0.928 g (89%). MS (FAB, *m/z*): 712 $[M]^+$, 677 $[M - Cl]^+$, 641 $[M - 2Cl]^+$. I.R. (KBr (s), cm^{-1}): 3083 (w), 3011 (w), 2920 (m), 2856 (w), 1616 (w), 1560 (s), 1458 (s), 1458 (m), 1352 (s), 1279 (s), 1223 (m), 1188 (m), 1176 (m), 1161 (m), 1154 (m), 1100 (m), 1085 (m), 1039 (m), 1022 (m), 908 (m), 867 (m), 848 (m), 805 (m), 757 (s), 752 (s), 683 (m). Elemental analysis for $C_{37}H_{35}N_3O_2CrCl_3$ (712.06) found (required): %C = 62.31 (62.41), % H = 4.80 (4.95), %N = 5.73 (5.90). μ_{eff} (Evans NMR method): 3.8 BM.

Diphenyl-N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarbimidothioate chromium(III) trichloride [Cr(**4**)Cl_3]

The procedure as described for [Cr(**4**)Cl_3] using $CrCl_3$·3THF (1.90 g, 5.06 mmol) and **4** (2.96 g, 0.506 mmol) to give [Cr(**4**)Cl_3] as a green microcrystalline solid. Yield 3.70 g (98%). MS (FAB, *m/z*): 744 $[M]^+$, 709 $[M - Cl]^+$, 673 $[M - 2Cl]^+$. I.R. (KBr (s), cm^{-1}): 3070 (w), 2959 (m), 2920 (m), 2861 (m), 1607 (w), 1591 (m), 1575 (m), 1508 (s), 1471 (s), 1441 (s), 1377 (m), 1224 (w), 1195 (s), 1170 (s), 1142 (s), 1097 (m), 1064 (m), 1042 (m), 1022 (m), 999 (m), 977 (m), 910 (w), 849 (m), 828 (m), 820 (m), 754 (m), 743 (s), 703 (m), 688 (m), 543 (w). Elemental analysis for $C_{35}H_{37}N_3S_2CrCl_3$ (744.18) found (required): %C = 59.86 (59.72), % H = 4.86 (4.74), %N = 5.49 (5.65). μ_{eff} (Evans NMR method): 3.8 BM.

Diphenyl-N,N'-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarbimidothioate chromium(III) trichloride [Cr(**6**)Cl_3]

The procedure as described for [Cr(**1**)Cl_3] using $CrCl_3$·3THF (0.754 g, 2.01 mmol) and **6** (1.348 g, 2.01 mmol) to give [Cr(**6**)Cl_3] as a green microcrystalline solid. Yield 1.33 g (80%). MS (FAB, *m/z*): 793 $[M - Cl]^+$, 757 $[M - 2Cl]^+$. I.R. (KBr (s), cm^{-1}): 3061 (m), 2965 (s), 2949 (m),

2926 (m), 2904 (w), 2866 (s), 1581 (m), 1512 (s), 1465 (s), 1442 (m), 1382 (s), 1363 (m), 1328 (w), 1219 (m), 1174 (s), 1116 (s), 1045 (m), 985 (m), 932 (w), 845 (m), 802 (m), 768 (m), 744 (s), 701 (m), 690 (m). Elemental analysis for $C_{43}H_{47}N_3S_2CrCl_3$ (828.34) found (required): %C = 62.22 (62.35), % H = 5.61 (5.72), %N = 5.06 (5.07). μ_{eff} (Evans NMR method): 3.6 BM.

Preparation of Cobalt Complexes

Dimethyl N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarboximidoate cobalt(II) dichloride [Co(**1**)Cl_2]

$CoCl_2$ (0.860 g, 6.62 mmol) and **1** (2.85 g, 6.62 mmol) were stirred for 12 hours in 50 ml of dry THF at room temperature during which time the product partly precipitated out of solution. The reaction volume was concentrated to 20 ml and 40 ml of Et_2O was added. The supernatant solution was removed by filtration and the residue was washed with 2 x 30 ml of Et_2O. After drying *in vacuo* the product [Co(**1**)Cl_2] was obtained as a turquoise, microcrystalline solid. Yield 3.43 g (93%). MS (FAB, *m/z*): 559 [M^+], 524 [M – Cl]$^+$, 488 [M – 2Cl]$^+$. I.R. (KBr (s), cm^{-1}): 3071 (w), 3004 (m), 2955 (m), 2914 (m), 2857 (m), 1673 (m), 1642 (s), 1589 (s), 1480 (s), 1448 (s), 1379 (w), 1325 (m), 1319 (m), 1274 (s), 1230 (m), 1183 (m), 1142 (m), 1117 (m), 1091 (w), 1062 (w), 1026 (m), 1013 (m), 868 (m), 842 (s), 813 (m), 760 (m), 719 (s), 680 (m), 673 (m), 567 (w). Elemental analysis for $C_{27}H_{31}N_3O_2CoCl_2$ (559.40) found (required): %C = 57.87 (57.97), % H = 5.49 (5.59), %N = 7.59 (7.51). μ_{eff} (Evans NMR method): 4.9 BM.

Diphenyl N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarboximidoate cobalt(II) dichloride [Co(**3**)Cl_2]

The procedure as described for [Co(**1**)Cl_2] using $CoCl_2$ (0.328 g, 2.53 mmol) and **3** (1.40 g, 2.53 mmol) to give [Co(**3**)Cl_2] as a green microcrystalline solid. Yield 1.37 g (79%). ^{1}H NMR (δ in ppm, CD_2Cl_2, broad singlets are observed in each case): 102.2 (2H, Py H_m), 26.0 (1H, Py H_p), 10.6 (6H, Ar_{anil} C_pH_3), 0.7 (2H, Ar_{phenol} H_p), - 0.5 (8H, Ar_{anil} H_m + Ar_{phenol} H_o or H_m), - 6.8 (4H, Ar_{phenol} H_o or H_m), - 30.5 (12H, $Ar_{anil}C_oH_3$). MS (FAB, *m/z*): 683 [M^+], 648 [M – Cl]$^+$, 612 [M – 2Cl]$^+$. I.R. (KBr (s), cm^{-1}): 3055 (w), 2952 (m), 2919 (m), 2856 (m), 1646 (s), 1584 (s), 1488 (s), 1457 (m), 1319 (m), 1222 (s), 1183 (s), 1167 (m), 1084 (w), 1062 (w), 1027 (w), 914 (w), 853 (m), 807 (m), 754 (s) 689 (s), 503 (w). Elemental analysis for $C_{37}H_{35}N_3O_2CoCl_2$ (683.54) found (required): %C = 65.13 (65.02), % H = 5.00 (5.16), %N = 6.32 (6.15). μ_{eff} (Evans NMR method): 4.4 BM.

Diphenyl-N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarbimidothioate cobalt(II) dichloride [Co(**4**)Cl_2]

The procedure as described for [Co(**1**)Cl_2] using $CoCl_2$ (95.5 mg, 0.736 mmol) and **4** (0.431 g, 0.736 mmol) to give [Co(**4**)Cl_2] as a green microcrystalline solid. Yield 0.42 g (80%). ^{1}H NMR (δ in ppm, CD_2Cl_2, broad singlets are observed in each case): 111.6 (2H, Py H_m), 32.7 (1H, Py H_p), 15.6 (6H, Ar_{anil} C_pH_3), 7.4 (4H, Ar_{anil} H_m), 6.7 (2H, Ar_{thioph} H_p), 5.3 (4H, Ar_{thioph} H_o or H_m), 2.0 (4H, Ar_{thioph} H_o or H_m), - 30.5 (12H, $Ar_{anil}C_oH_3$). MS (FAB, *m/z*): 716 $[M]^+$, 681 $[M - Cl]^+$, 645 $[M - 2Cl]^+$. I.R. (KBr (s), cm^{-1}): 3063 (w), 2967 (m), 2915 (m), 2856 (m), 1593 (w), 1552 (s), 1562 (s), 1473 (s), 1457 (m), 1442 (s), 1372 (w), 1281 (w), 1196 (s), 1166 (m), 1141 (m), 1095 (m), 1064 (m), 1018 (w), 973 (m), 851 (m), 825 (s), 749 (s), 706 (m), 689 (m), 631(w). Elemental analysis for $C_{35}H_{37}N_3S_2CoCl_2$ (715.67) found (required): %C = 62.17 (62.10), % H = 5.03 (4.93), %N = 5.97 (5.87). μ_{eff} (Evans NMR method): 4.9 BM.

Diphenyl-N,N'-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarboximidoate cobalt(II) dichloride [Co(**5**)Cl_2]

The procedure as for [Co(**1**)Cl_2] using **5** (0.529 g, 0.829 mmol) and $CoCl_2$ (0.108 g, 0.829 mmol) gave the product [Co(**5**)Cl_2] in 68% (0.43 g) as an orange microcrystalline solid. ^{1}H NMR (δ in ppm, CD_2Cl_2, broad singlets are observed in each case): 102.4 (2H, Py H_m), 44.1 (1H, Py H_p) 17.8 (4H, Ar_{anil} H_m), 12.3 (4H, Ar_{phenol} H_m or H_o), 10.5 (2H, Ar_{phenol} H_p), 6.2 (4H, Ar_{phenol} H_m or H_o), -9.3 (2H, Ar_{anil} H_p), -18.9 (24H, $CHCH_3$), -86.9 (4H, $CHCH_3$). MS (FAB, *m/z*): 731 $[M - Cl]^+$. I.R. (KBr (s), cm^{-1}): 3069 (w), 2964 (s), 2868 (m), 1639 (m), 1582 (s), 1487 (s), 1464 (m), 1330 (m), 1266 (s), 1206 (s), 1090 (m), 1066 (m), 1024 (m), 938 (w), 803 (w), 770 (m), 753 (m), 690 (m). Elemental analysis for $C_{43}H_{47}N_3S_2CoCl_2$ (799.83) found (required): %C = 64.47 (64.57), % H = 5.84 (5.92), %N = 5.27 (5.25). μ_{eff} (Evans NMR method): 4.8 BM.

Diphenyl-N,N'-bis(2,6-diisopropylphenyl)pyridine-2,6-dicarbimidothioate cobalt(II) dichloride [Co(**6**)Cl_2]

The procedure as for [Co(**1**)Cl_2] using **6** (0.534 g, 0.797 mmol) and $CoCl_2$ (0.104 g, 0.797 mmol) to give gave the product [Co(**6**)Cl_2] in 76% (0.48 g) as a red microcrystalline solid. ^{1}H NMR (δ in ppm, CD_2Cl_2, broad singlets are observed in each case): 109.4 (2H, Py H_m), 43.5 (1H, Py H_p) 14.3 (4H, Ar_{anil} H_m), 13.2 (4H, Ar_{thioph} H_m or H_o), 12.3 (2H, Ar_{thioph} H_p), 8.4 (4H, Ar_{thioph} H_m or H_o), -8.9 (2H, Ar_{anil} H_p) -17.3 (12H, $CHCH_3$), -17.6 (12H, $CHCH_3$), -83.6 (4H, $CHCH_3$). MS (FAB, *m/z*): 763 $[M - Cl]^+$. I.R. (KBr (s), cm^{-1}): 3060 (m), 2964 (s), 2867 (s), 1577 (m), 1535 (s), 1464

(s), 1380 (m), 1359 (m), 1326 (m), 1258 (w), 1217 (w), 1175 (s), 1107 (s), 1066 (m), 979 (m), 937 (w), 911 (w), 850 (m), 807 (m), 748 (s), 701 (s), 562 (w), 495 (w), 437 (w). Elemental analysis for $C_{43}H_{47}N_3O_2CoCl_2$ (767.71) found (required): %C = 67.15 (67.28), % H = 6.04 (6.17), %N = 5.36 (5.47). μ_{eff} (Evans NMR method): 4.5 BM.

Preparation of Titanium, Manganese and Nickel Complexes

Diphenyl-N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarbimidothioate titanium(III) trichloride [Ti(**4**)Cl_3]

A solution of $TiCl_3$·3THF (0.862g, 2.33 mmol) and **4** (1.36g, 2.33 mmol) in 50 ml of dry THF was refluxed for 12 hours. The solution was allowed to cool to room temperature and filtered. The solvent was removed *in vacuo* and the residue was washed with 2 x 30ml of Et_2O. After drying *in vacuo* the product [Ti(**4**)Cl_3] was obtained as a brown, microcrystalline solid. Yield 1.21 g (70%). ^{1}H NMR (δ in ppm, $CDCl_3$, broad singlets are observed in each case): 9.4 (4H, Ar_{anil} H_m), 5.6 (2H, Ar_{thioph} H_p), 4.9 (4H, Ar_{thioph} H_o or H_m), 4.0 (4H, Ar_{thioph} H_o or H_m), 3.3 (12H, $Ar_{anil}C_oH_3$), 1.0 (6H, Ar_{anil} C_pH_3), -3.3 (1H, Py H_p), -37.3 (2H, Py H_m). MS (CI, *m/z*): 705 [M – Cl]$^+$. I.R. (KBr (s), cm^{-1}): 3055 (w), 2989 (w), 2917 (m), 2854 (w), 1607 (m), 1585 (s), 1507 (m), 1 474 (s), 1441 (s), 1378 (w), 1273 (w), 1222 (w), 1194 (s), 1174 (m), 1141 (s), 1098 (m), 1023 (m), 998 (w), 852 (m), 814 (m), 741 (s), 705 (m), 688 (m), 639 (m). μ_{eff} (Evans NMR method): 1.2 BM.

Diphenyl-N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarbimidothioate manganese(II) dichloride [Mn(**4**)Cl_2]

A solution of $MnCl_2$·2THF (0.497 g, 1.84 mmol) and **4** (1.078 g, 1.84 mmol) in 70 ml of toluene was refluxed overnight during which time an orange solid precipitated out of solution. The toluene was removed *in vacuo* and the residue was dissolved in 40 ml of CH_2Cl_2. The orange solution was filtered and layered with heptane yielding 1.01 g (69%) of orange crystals after diffusion. MS (FAB, *m/z*): 712 [M – CH_2Cl_2]$^+$, 677 [M – Cl]$^+$. I.R. (KBr (s), cm^{-1}): 3043 (w), 2968 (m), 2945 (m), 2917 (m), 2857 (w), 1606 (w), 1594 (m), 1563 (s), 1473 (s), 1452 (m), 1442 (m), 1378 (w), 1307 (w), 1271 (m), 1195 (s), 1164 (s), 1141 (s), 1094 (s), 1078 (m), 1024 (m), 1000 (w), 973 (m), 917 (w), 851 (m), 826 (s), 756 (m), 748 (s), 706 (m), 689 (m), 632 (w). Elemental analysis for $C_{35}H_{37}N_3S_2MnCl_2.CH_2Cl_2$ (796.60) found (required): %C = 57.89 (57.30), % H = 4.20 (4.68), %N = 5.29 (5.28). μ_{eff} (Evans NMR method): 6.3 BM.

Diphenyl-N,N'-bis(2,4,6-trimethylphenyl)pyridine-2,6-dicarbimidothioate nickel(II) dibromide [Ni(**4**)Br_2]

$NiBr_2$·DME (0.847g, 2.74 mmol) and **4** (1.61 g, 2.74 mmol) were stirred for 12 hours in 50 ml of dry THF at room temperature during which time the product precipitated from solution. The reaction volume was concentrated to 20 ml and the supernatant solution was removed by filtration. The residue was washed with 2 x 30 ml of Et_2O and dried *in vacuo* to obtain [Ni(**4**)Br_2] as a red brown, microcrystalline solid. Yield 1.93 g (88%). ^{1}H NMR (δ in ppm, CD_2Cl_2, broad singlets are observed in each case): 78.7 (2H, Py H_m), 16.2 (6H, $Ar_{anil}C_pH_3$), 13.6 (4H, Ar_{anil} H_m), 13.1 (12H, $Ar_{anil}C_oH_3$), 8.3 (4H, Ar_{thioph} H_o or H_m), 8.1 (4H, Ar_{thioph} H_o or H_m), 7.0 (2H, Ar_{thioph} H_p), 3.8 (1H, Py H_p). MS (FAB, *m/z*): 724 $[M - Br]^+$. I.R. (KBr (s), cm^{-1}): 3055 (w), 2945 (m), 2915 (m), 2856 (m), 1595 (w), 1576 (w), 1540 (s), 1473 (s), 1442 (s), 1375 (w), 1307 (w), 1281 (w), 1198 (s), 1167 (s), 1143 (s), 1101 (m), 1068 (m), 1025 (m), 1000 (w), 980 (m), 916 (w), 852 (m), 821 (m), 757 (m), 747 (s), 706 (m), 689 (m), 635 (w). Elemental analysis for $C_{35}H_{37}N_3S_2NiBr_2$ (804.35) found (required): %C = 55.29 (55.25), % H = 4.58 (4.39), %N = 5.09 (5.22). μ_{eff} (Evans NMR method): 2.8 BM.

Hydrolysis Reactions of complexes formed from [Fe(**1**)Cl_2]**,** [Fe(**4**)Cl_2]**,** [V(**4**)Cl_3]**,** [Cr(**4**)Cl_3] **and** [Co(**3**)Cl_2] **with MAO**

*Complex [Fe(**1**)Cl_2] with 50 Equivalents of MAO*

Complex [Fe(**1**)Cl_2] (0.23g, 0.42 mmol) was dissolved in 70 ml of toluene. The solution was treated at room temperature with 13.1 ml of 1.6 M MAO in toluene and stirred for 15 minutes. The reaction mixture was subsequently cooled to 0 ˚C, quenched with 10 ml H_2O followed by 10 ml 2.0 M HCl, stirred for 1 min (extending the reaction time or increasing the HCl loading leads to hydrolysis of the ligand) and filtered over celite. The layers were separated and the organic layer was washed with 10 ml 2.0 M HCl and 10 ml H_2O and dried over Na_2SO_4. Removal of the volatiles under reduced pressure yielded 0.16 g (88%) of **1** (^{1}H NMR in $CDCl_3$ and FAB Mass).

*Complex [Fe(**4**)Cl_2] with 50 Equivalents of MAO*

Procedure as described for complex [Fe(**1**)Cl_2] using [Fe(**4**)Cl_2] (0.30 g, 0.42 mmol) yielding 0.22 g (89%) of **4** (^{1}H NMR in $CDCl_3$ and FAB Mass).

*Complex [V(**4**)Cl_3] with 50 Equivalents of MAO*

Procedure as described for [Fe(**1**)Cl_2] using [V(**4**)Cl_3] (0.31 g, 0.42 mmol) at 50 ˚C instead of RT, yielding **4** (0.18 g, 73 %, ^{1}H NMR in $CDCl_3$ and FAB Mass).

*Complex [Cr(**4**)Cl_3] with 50 Equivalents of MAO*

Procedure as described for [Fe(**1**)Cl_2] using [Cr(**4**)Cl_3] (0.31 g, 0.42 mmol) at 70 ˚C instead of RT, yielding **4** (0.18 g, 73%, ^{1}H NMR in $CDCl_3$ and FAB Mass).

*Complex [Co(**3**)Cl_2] with 50 Equivalents of MAO*

Procedure as described for [Fe(**1**)Cl_2] using [Co(**3**)Cl_2] (0.29 g, 0.42 mmol), yielding **3** (0.20 g, 86% ^{1}H NMR in $CDCl_3$ and FAB Mass).

General Polymerisation Procedures

High-Pressure Reactions

A 1 L stainless steel autoclave was baked out overnight at 85 ˚C under vacuum and subsequently cooled under a nitrogen flow to the temperature of the polymerisation. Toluene (0.5 L) and MAO were introduced into the reactor 30 min prior to injection of catalyst. Hydrogen can be introduced into the reactor at this point. The reactor was pressurized with ethylene. The catalyst solution was injected under a nitrogen pressure. The reactor pressure was maintained constant throughout the polymerisation run by computer-controlled addition of ethylene with a maximum flow rate of 3.0 L/min. The polymerisation time was 60 minutes. Runs were terminated by venting off the volatiles and adding MeOH (5 ml) and 2.0 M HCl (5 ml) to the polymerisation mixture. Polymer was precipitated from the toluene slurry by addition of 500 ml of MeOH. The polymer was filtered and dried overnight in a vacuum oven at 65 ˚C.

Fisher Porter Reactions

A Fisher Porter reactor, equipped with injector and mechanical stirrer, was purged with nitrogen for 30 minutes. Toluene (200 ml), scavenger and ethylene were introduced and the solution was stirred for 10 minutes. Catalyst was injected through the injector. The pressure was maintained during the polymerisation run. Runs were terminated by venting off the over-pressure and adding 200 ml of MeOH and 5 ml of 2.0 M HCl to the toluene slurry. The polymer was filtered and dried overnight in a vacuum oven at 65 ˚C.

Schlenk Reactions

Precatalyst was weighed out in the Schlenk flask in a nitrogen filled glove-box. Toluene was added (100 ml) and 1 bar of ethylene was applied. MAO activator was injected and the mixture was magnetic stirred and maintained under 1 bar of ethylene for the duration of the

polymerisation. The polymerisation was terminated by the addition of 2.0 M HCl (aqueous) and MeOH. The solid polyethylene was recovered by filtration, washed with MeOH and dried overnight under vacuum at 65 ˚C.

Supporting Information — X-Ray Crystallography

The diffraction data used for the structure determinations of [Co(**1**)Cl_2], [Fe(**2**)Cl_2], [Fe(**3**)Cl_2], [Fe(**4**)Cl_2], [V(**4**)Cl_3], [Cr(**4**)Cl_3], [Mn(**4**)Cl_2], [Ni(**4**)Br_2], [Fe(**5**)Cl_2], [Co(**5**)Cl_2], [Fe(**6**)Cl_2], [Co(**6**)Cl_2] were collected using Siemens/Bruker 4-circle diffractometers fitted with single point scintillation counter detectors. Thus, the number of data points collected had a direct effect on the total data collection time. Experience with these instruments suggested that data beyond a resolution of *ca*. 0.89 Å was typically so weak that it was not worth the time to collect it, unless the data collection was run at reduced temperature (something that was not always possible). Consequently, many of these data sets are relatively short of data when compared with current standards.

The X-ray crystal structure of [Co(1)Cl_2]

The primary reason for the poor quality of the structure of [Co(**1**)Cl_2] is the weakness of the diffraction data, with the data set having a mean I/σ of just 1.96 even when collected to maximum 2θ of only 120° with Cu-Kα radiation. (This same reason is behind the low observed / unique reflections ratio and the low precision in the bond lengths and angles.) Despite these issues, however, there is little doubt as to the identity of the complex.

The included dichloromethane solvent was found to be highly disordered with the one molecule per complex being found to be distributed over six orientations at two sites (two orientations at one site of *ca*. 20 and 18% occupancy, and four at the other of *ca*. 21, 20, 11 and 10% occupancy). The geometries of all six orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and all of the atoms were refined isotropically.

The X-ray crystal structure of [Fe(4)Cl_2]

The included dichloromethane solvent in the structure of [Fe(**4**)Cl_2] was found to be disordered. Three orientations were identified of *ca*. 45, 32 and 23% occupancy, their geometries optimised, the thermal parameters of adjacent atoms restrained to be similar, and all of the atoms were refined isotropically.

The X-ray crystal structure of [V(4)Cl_3]

Both of the included dichloromethane solvent molecules in the structure of [V(**4**)Cl_3] were found to be disordered. For the C(50)-based molecule, two orientations were identified of *ca*. 81 and 19% occupancy. The C(60)-based molecule is adjacent to a centre of symmetry, and two unique orientations were identified of *ca*. 28 and 22% occupancy (the centre of symmetry generating two more overlapping orientations). The geometries of all four orientations were optimised, the thermal parameters of adjacent

atoms were restrained to be similar, and only the major occupancy non-hydrogen atoms of the C(50)-based molecule were refined anisotropically (the remainder were refined isotropically).

The X-ray crystal structure of [Cr(4)Cl_3]

Both of the included dichloromethane solvent molecules in the structure of [Cr(**4**)Cl_3] were found to be disordered. For the C(50)-based molecule, two orientations were identified of *ca*. 82 and 18% occupancy. The C(60)-based molecule is adjacent to a centre of symmetry, and two unique orientations were identified of *ca*. 28 and 22% occupancy (the centre of symmetry generating two more overlapping orientations). The geometries of all four orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the major occupancy non-hydrogen atoms of the C(50)-based molecule were refined anisotropically (the remainder were refined isotropically).

The X-ray crystal structure of [Mn(4)Cl_2]

The included dichloromethane solvent in the structure of [Mn(**4**)Cl_2] was found to be disordered. Three orientations were identified of 60, 30 and 10% occupancy, their geometries optimised, and only the major occupancy non-hydrogen atoms were refined anisotropically (the remainder were refined isotropically).

The X-ray crystal structure of [Fe(5)Cl_2]

The C(60)-based included dichloromethane solvent molecule in the structure of [Fe(**5**)Cl_2] was found to be adjacent to a centre of symmetry. One orientation was identified of 50% occupancy, its geometry was optimised, and the non-hydrogen atoms were refined anisotropically.

The X-ray crystal structure of [Co(5)Cl_2]

Both of the included dichloromethane solvent molecules in the structure of [Co(**5**)Cl_2] were found to be disordered. For the C(50)-based molecule, three orientations were identified of *ca*. 51, 36 and 13% occupancy. The C(60)-based molecule is adjacent to a centre of symmetry, and one unique orientation was identified of 25% occupancy (the centre of symmetry generating a second overlapping orientation); this occupancy was chosen based on a comparison of the isotropic thermal parameters with those of the three orientations of the C(50)-based molecule. The geometries of all four orientations were optimised, the thermal parameters of adjacent atoms for the three orientations of the C(50)-based molecule were restrained to be similar, and only the major occupancy non-hydrogen atoms of the C(50)-based molecule were refined anisotropically (the remainder were refined isotropically).

The X-ray crystal structure of [Fe(6)Cl_2]

The C(60)-based molecule is adjacent to a C_2 axis, and one unique 50% occupancy orientation was identified (the C_2 axis generating a second overlapping orientation); the non-hydrogen atoms were refined anisotropically.

The X-ray crystal structure of [Co(6)Cl_2]

The crystal used for the X-ray diffraction study of [Co(**6**)Cl_2] decomposed during the data collection, and hence the data set is very truncated. However, as the data that had been collected were sufficient to prove that the structure is isomorphous with that of the iron analogue [Fe(**6**)Cl_2] it was deemed unnecessary to make any further attempts.

The pyridyl ring and the four aryl rings were all refined as idealised hexagons with a side length of 1.39 Å. All of the non-hydrogen atoms were refined anisotropically, though the thermal parameters of all of the atoms were loosely restrained to be isotropic. The C(60)-based dichloromethane molecule is adjacent to a C_2 axis, and one unique 50% occupancy orientation was identified (the C_2 axis generating a second overlapping orientation); the geometry of this orientation was optimised, and the non-hydrogen atoms were refined anisotropically.

Figures

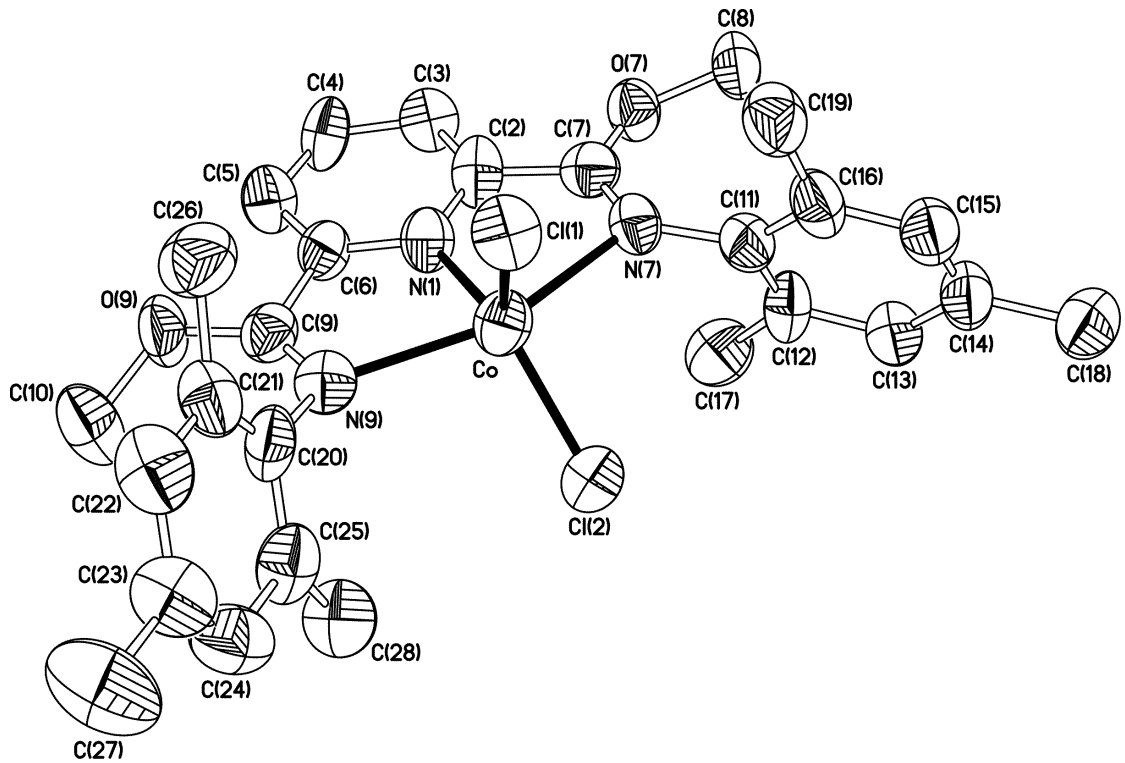

Fig. S1 The molecular structure of [Co(**1**)Cl_2] (30% probability ellipsoids).

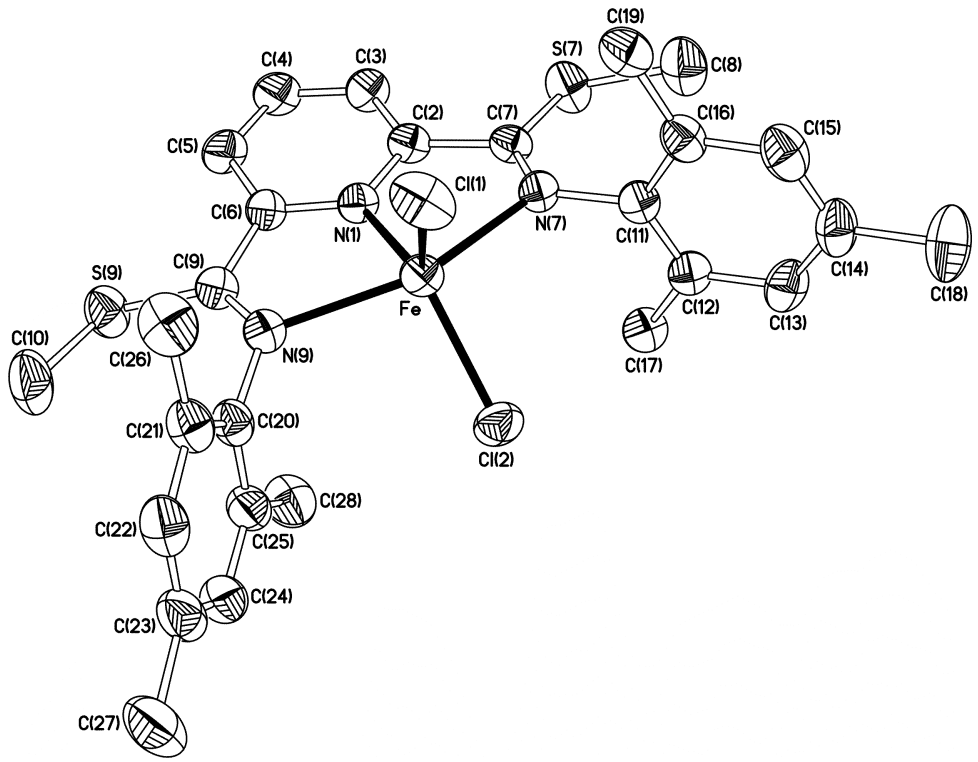

Fig. S2 The molecular structure of [Fe(**2**)Cl_2] (30% probability ellipsoids).

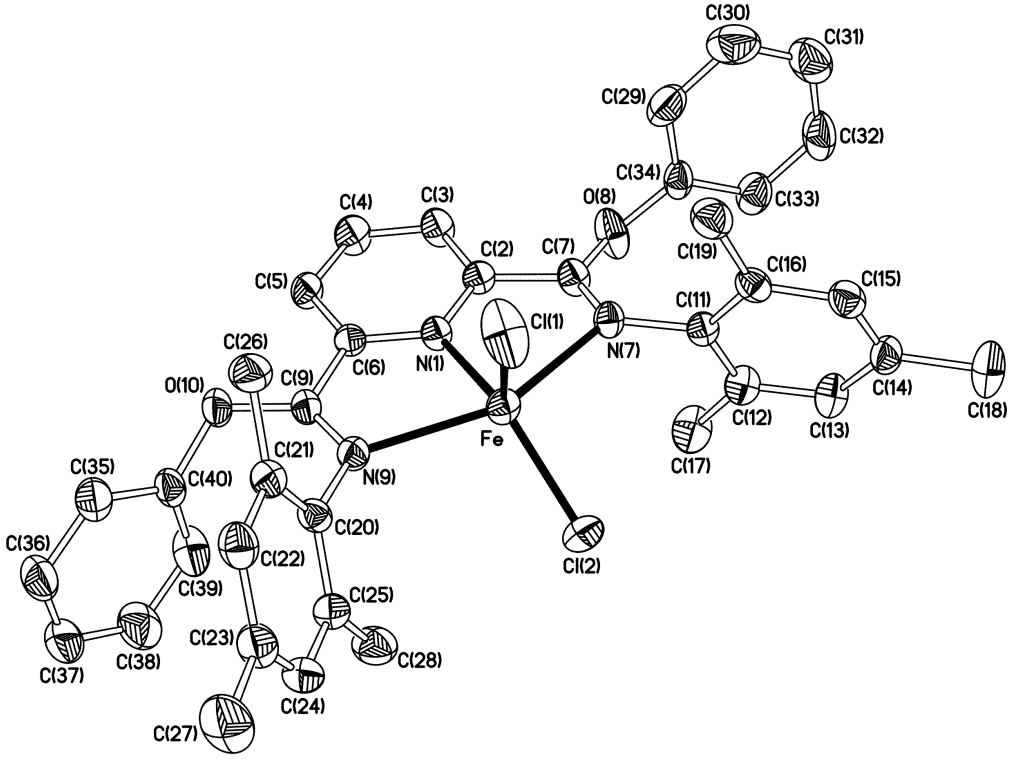

Fig. S3 The molecular structure of [Fe(**3**)Cl_2] (30% probability ellipsoids).

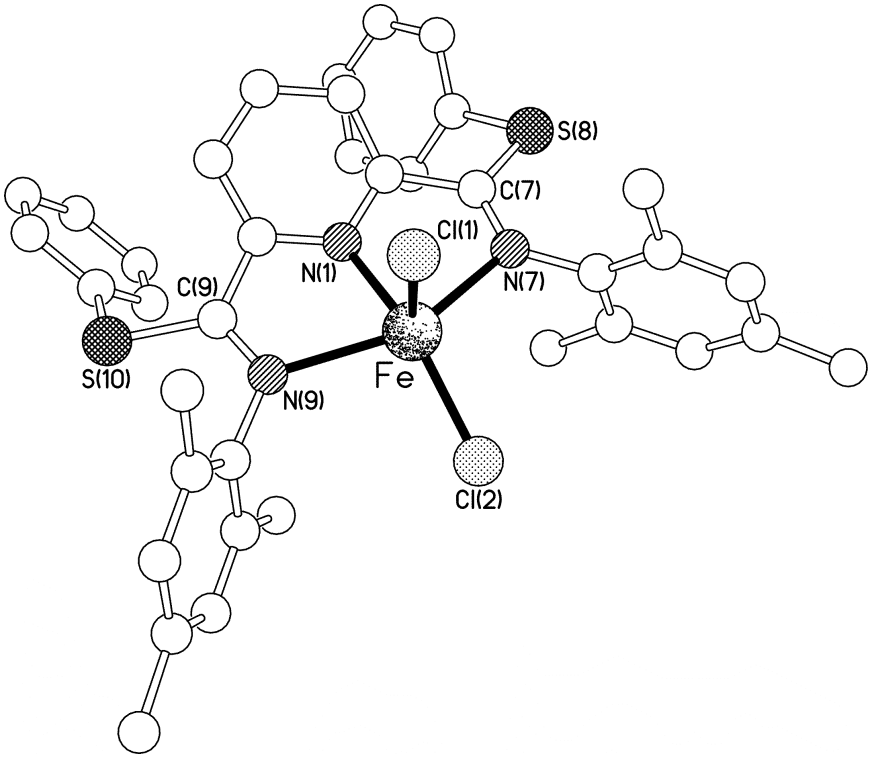

Fig. S4 The molecular structure of [Fe(**4**)Cl_2].

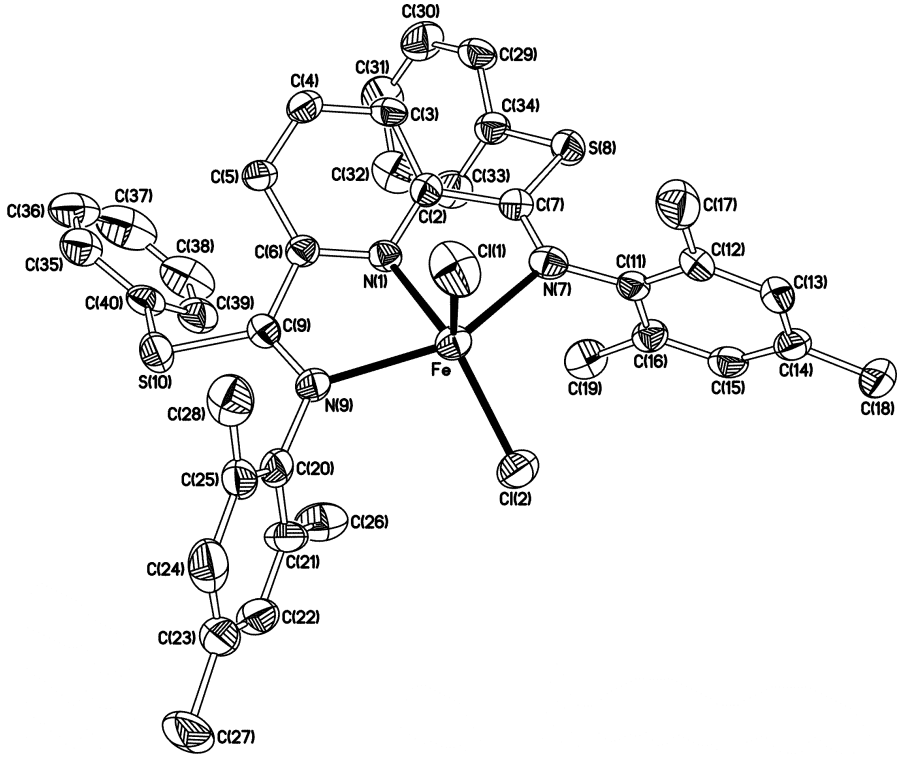

Fig. S5 The molecular structure of [Fe(**4**)Cl_2] (30% probability ellipsoids).

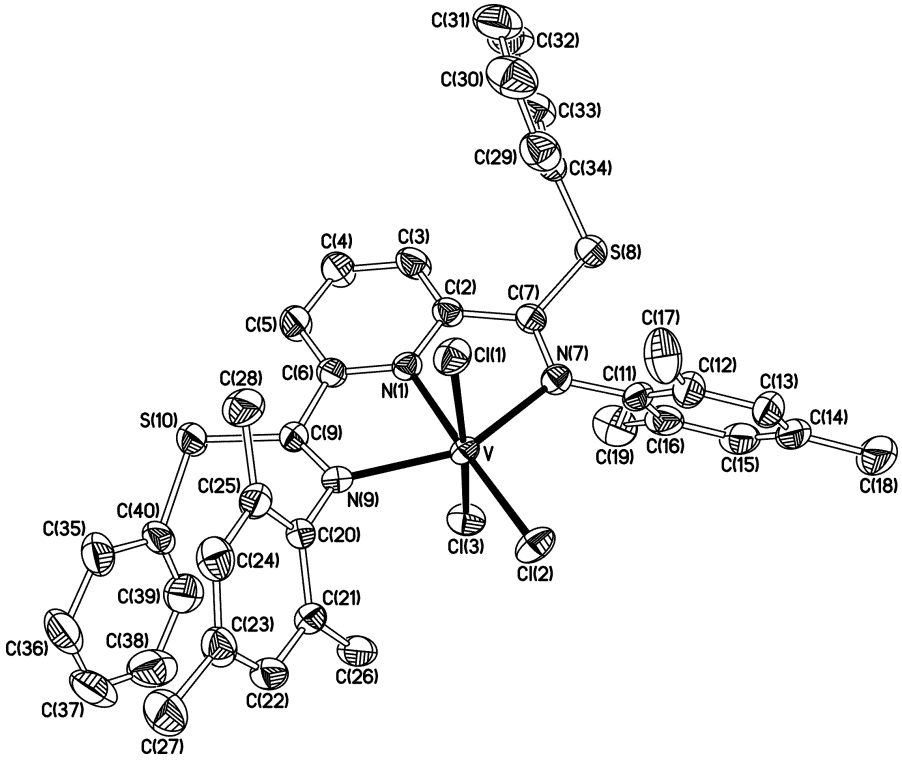

Fig. S6 The molecular structure of [V(**4**)Cl_3] (50% probability ellipsoids).

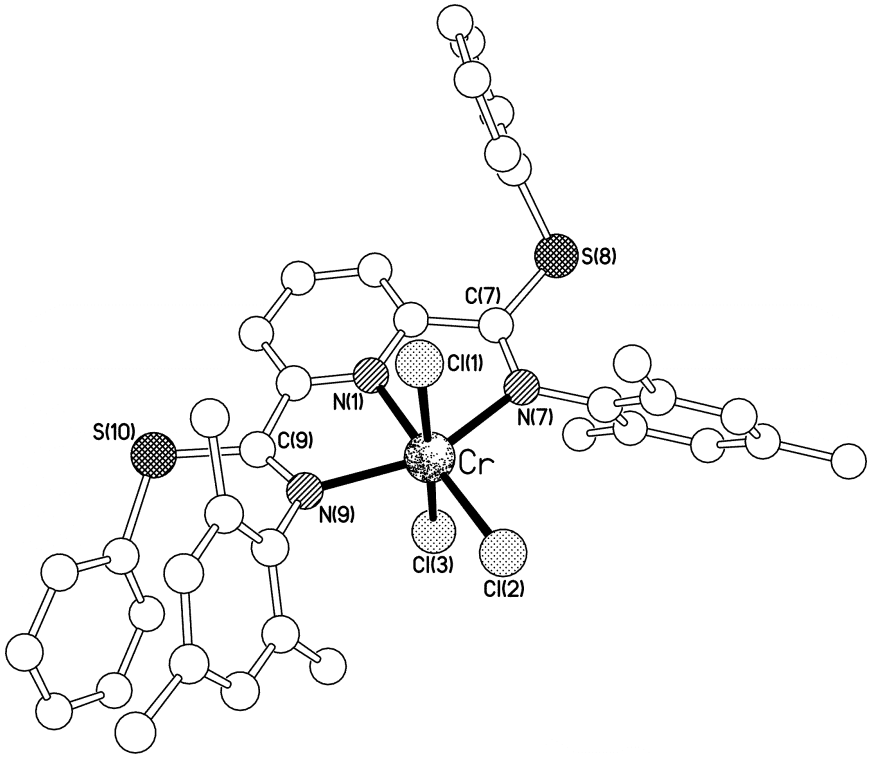

Fig. S7 The molecular structure of [Cr(**4**)Cl_3].

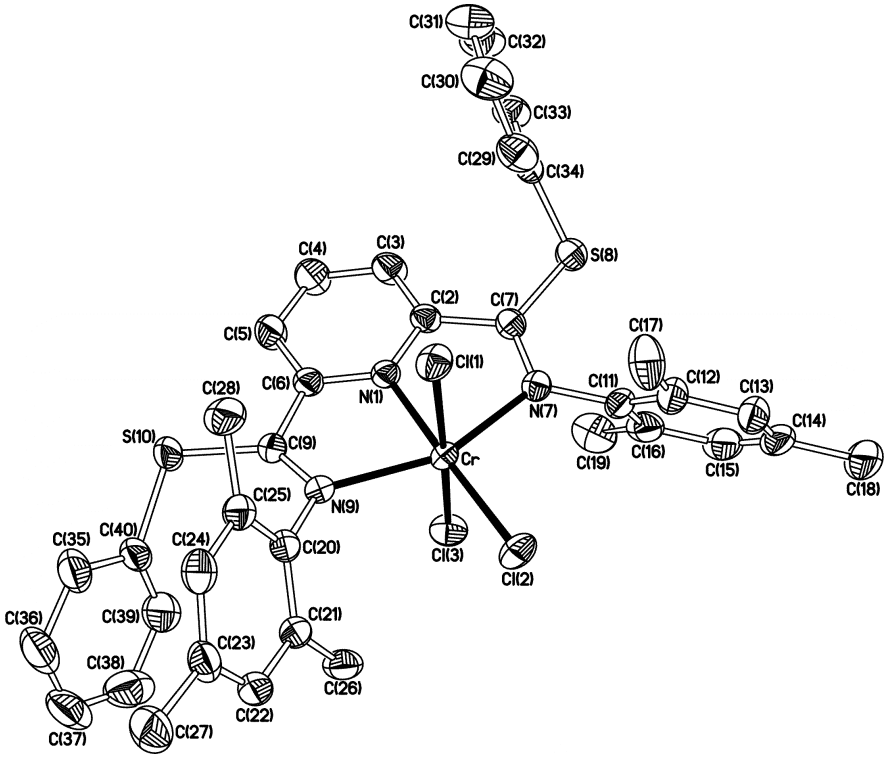

Fig. S8 The molecular structure of [Cr(**4**)Cl_3] (50% probability ellipsoids).

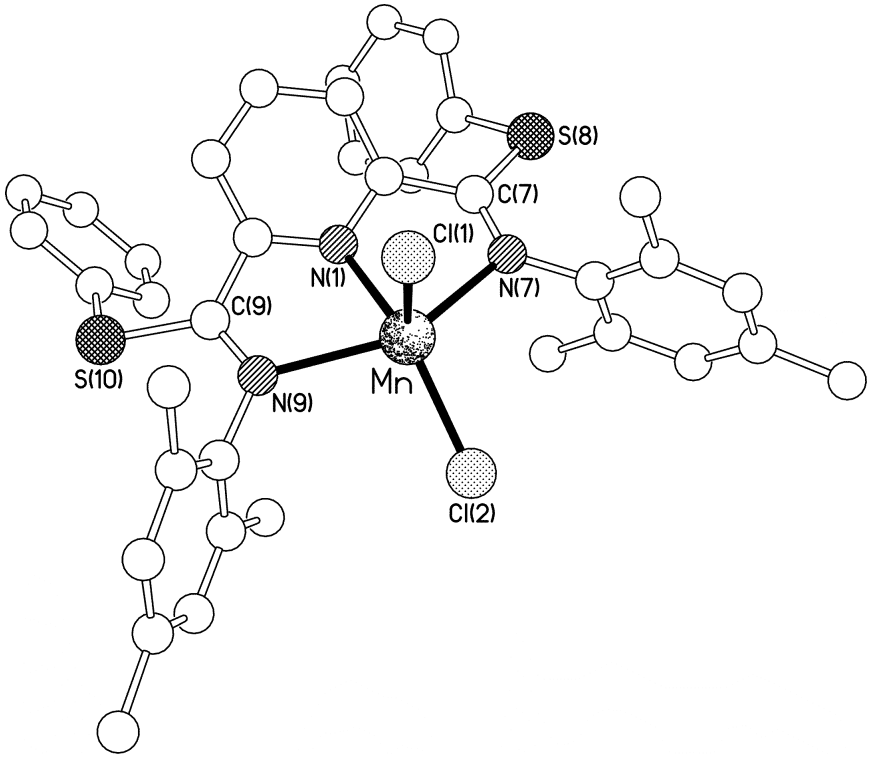

Fig. S9 The molecular structure of [Mn(**4**)Cl_2].

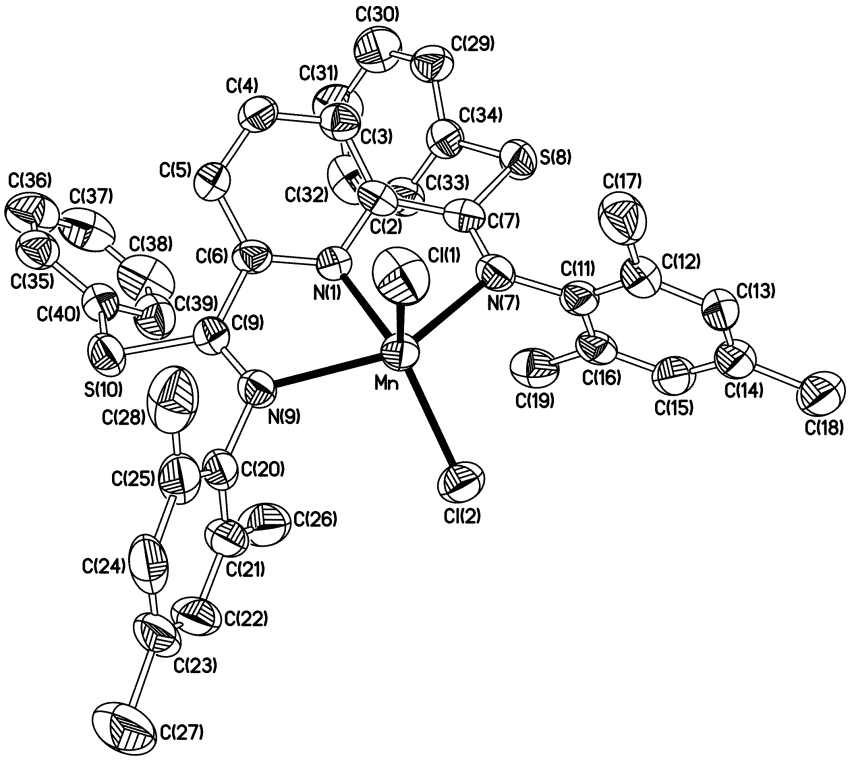

Fig. S10 The molecular structure of [Mn(**4**)Cl_2] (50% probability ellipsoids).

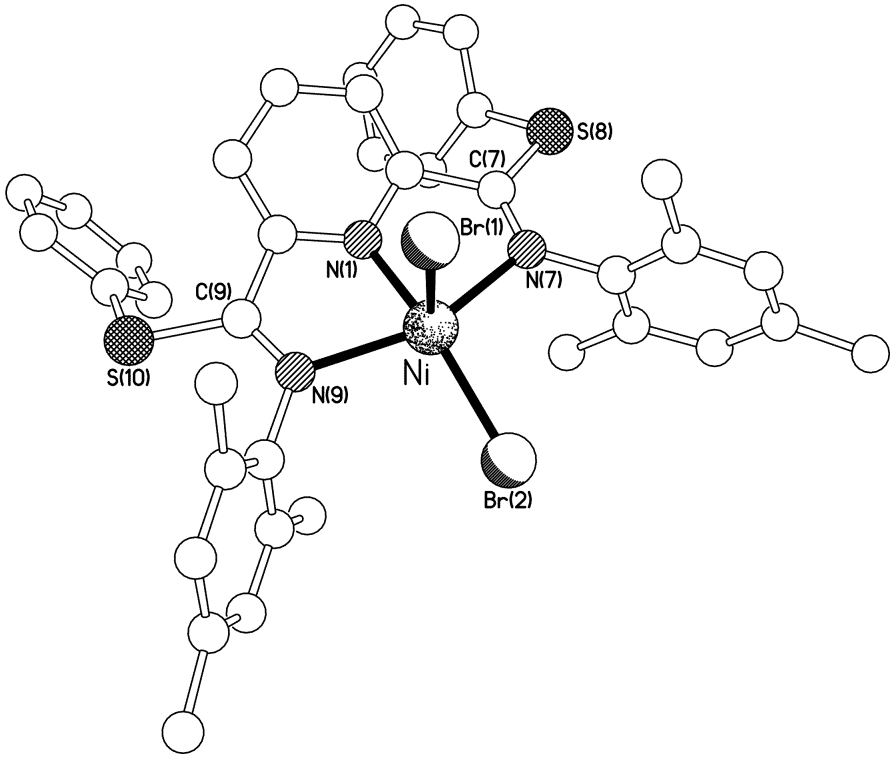

Fig. S11 The molecular structure of [Ni(**4**)Br_2].

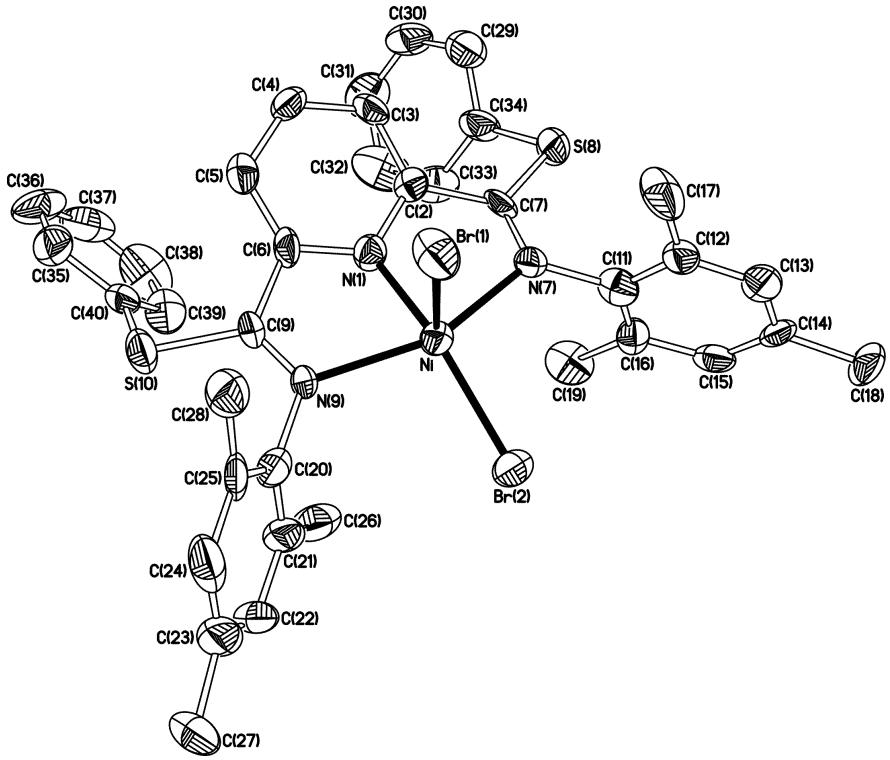

Fig. S12 The molecular structure of [Ni(**4**)Br_2] (50% probability ellipsoids).

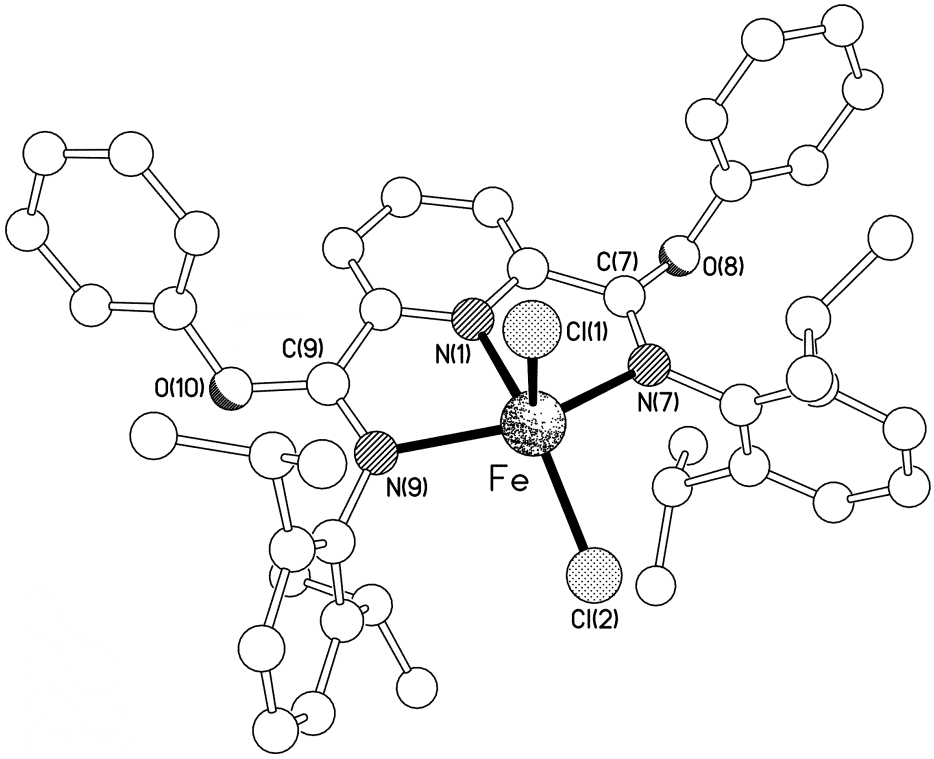

Fig. S13 The molecular structure of [Fe(**5**)Cl_2].

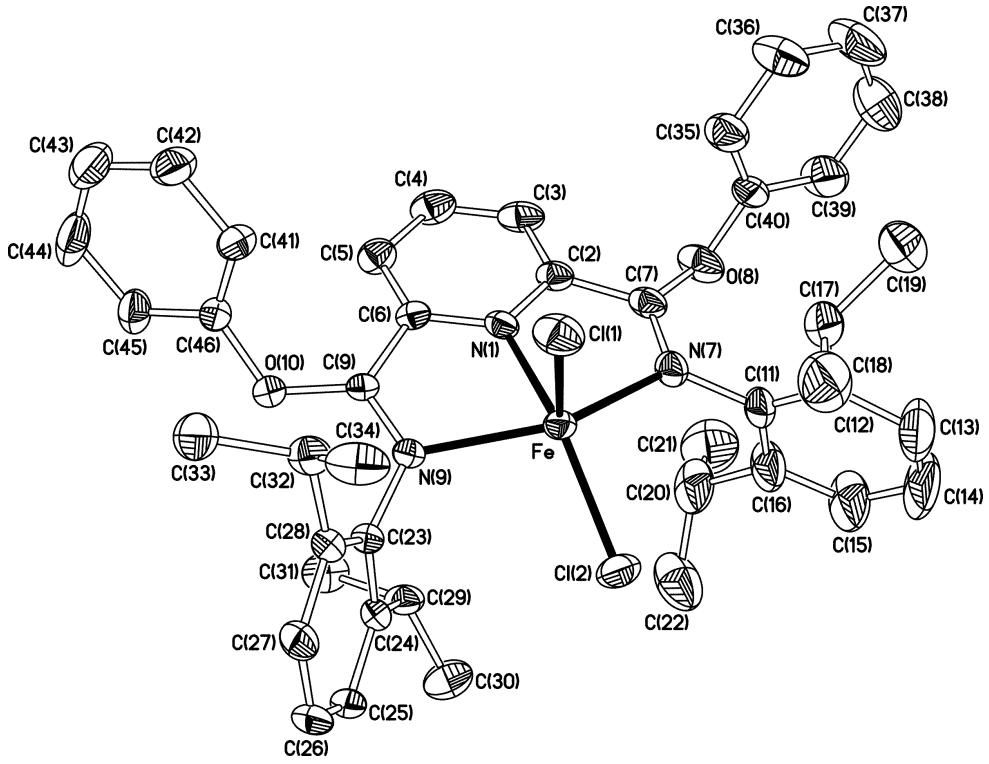

Fig. S14 The molecular structure of [Fe(**5**)Cl_2] (50% probability ellipsoids).

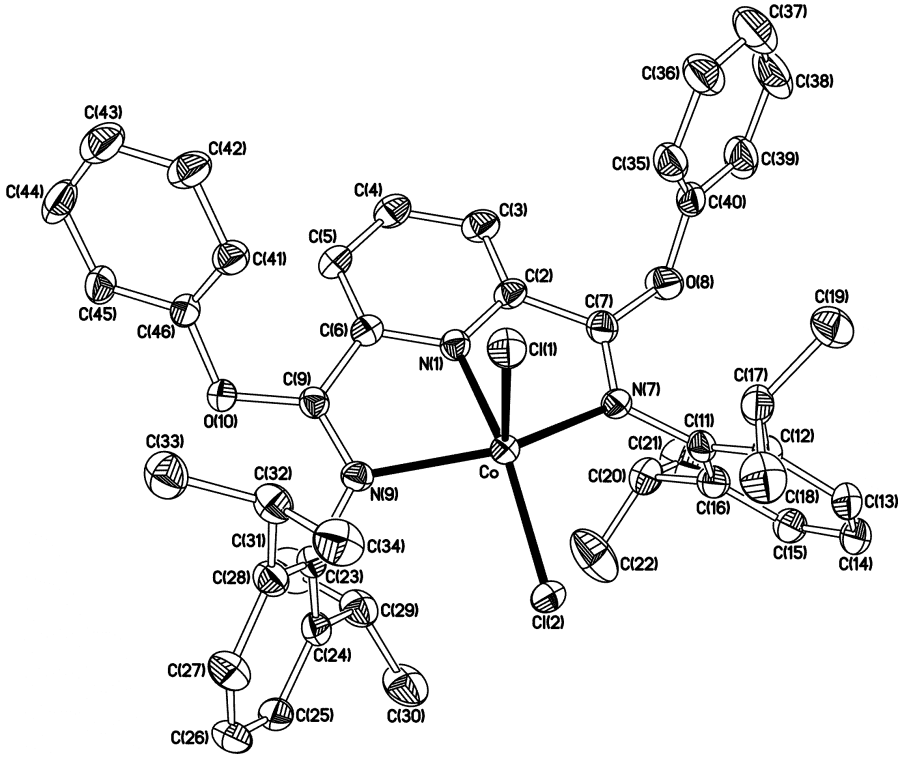

Fig. S15 The molecular structure of [Co(**5**)Cl_2] (30% probability ellipsoids).

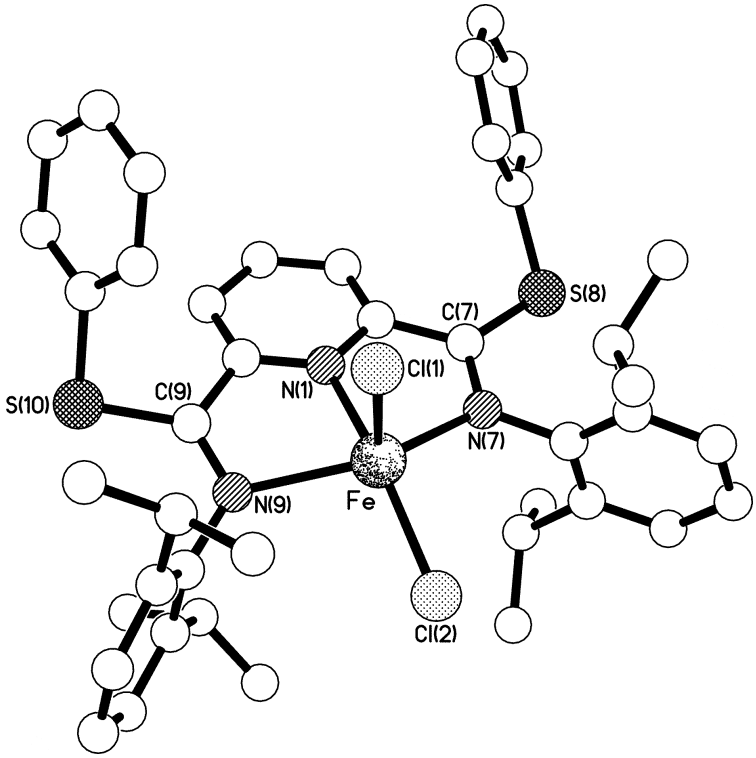

Fig. S16 The molecular structure of [Fe(**6**)Cl_2].

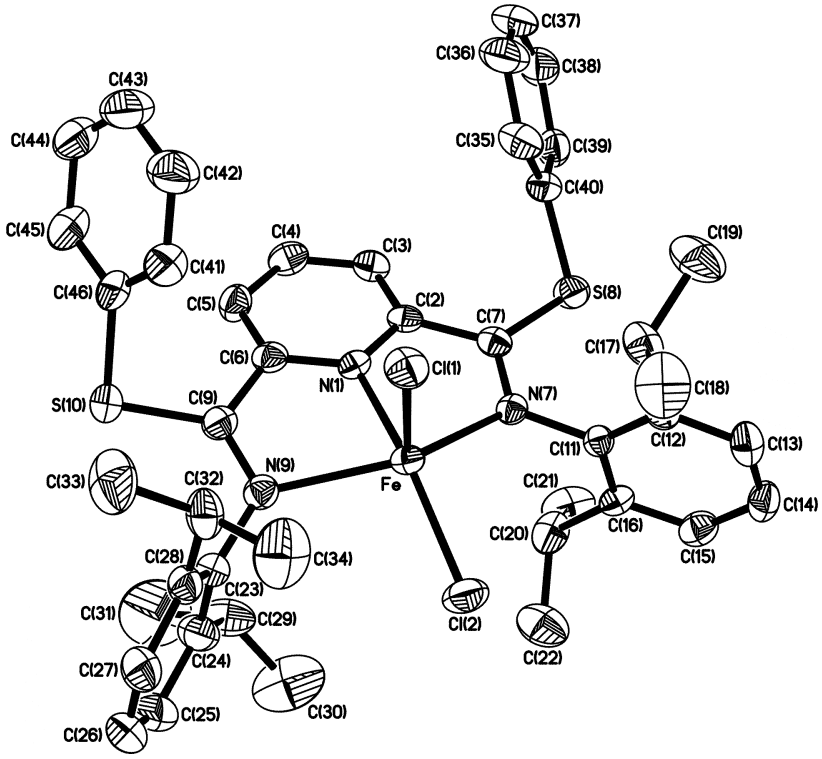

Fig. S17 The molecular structure of [Fe(**6**)Cl_2] (50% probability ellipsoids).

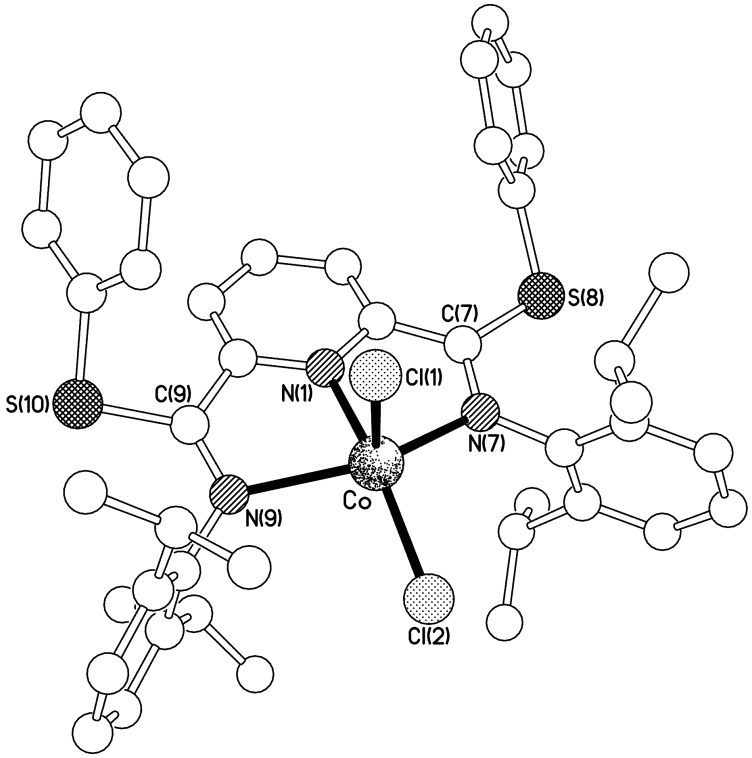

Fig. S18 The molecular structure of [Co(**6**)Cl_2].

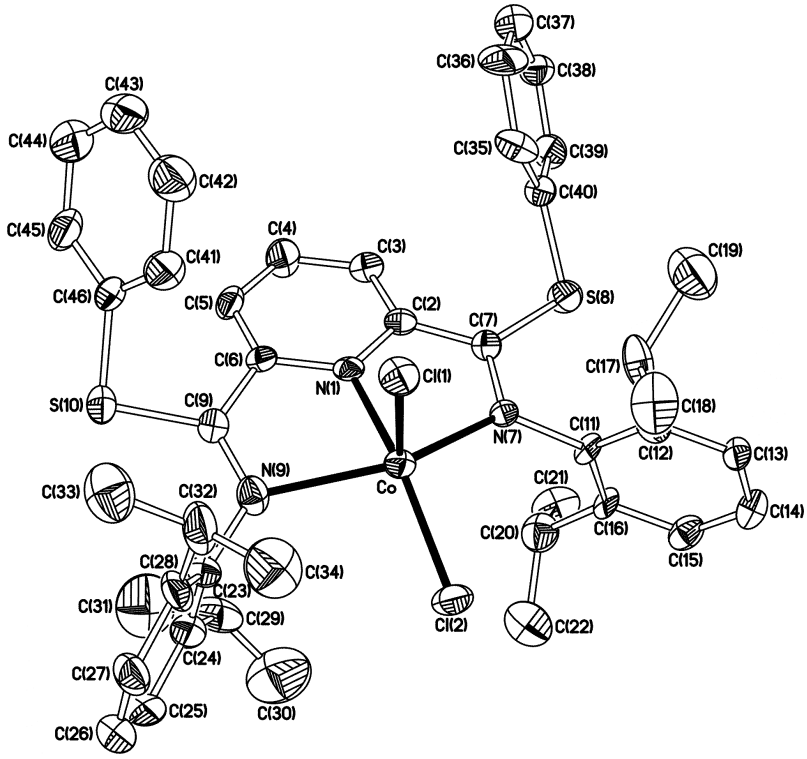

Fig. S19 The molecular structure of [Co(**6**)Cl_2] (30% probability ellipsoids).

Table S1. Crystal Data, Data Collection and Refinement Parameters for the structures of [Co(**1**)Cl_2], [Fe(**2**)Cl_2], [Fe(**3**)Cl_2], [Fe(**4**)Cl_2], [V(**4**)Cl_3], [Cr(**4**)Cl_3], [Mn(**4**)Cl_2], [Ni(**4**)Br_2], [Fe(**5**)Cl_2], [Co(**5**)Cl_2], [Fe(**6**)Cl_2] and [Co(**6**)Cl_2].

data	[Co(**1**)Cl_2]	[Fe(**2**)Cl_2]	[Fe(**3**)Cl_2]	[Fe(**4**)Cl_2]
formula	$C_{27}H_{31}Cl_2CoN_3O_2$	$C_{27}H_{31}Cl_2FeN_3S_2$	$C_{37}H_{35}Cl_2FeN_3O_2$	$C_{37}H_{35}Cl_2FeN_3S_2$
solvent	CH_2Cl_2	CH_2Cl_2	C_4H_8O	CH_2Cl_2
formula weight	644.30	673.34	752.53	797.48
temperature / K	293	293	293	293
space group	*Pbca* (no. 61)	*C*2/*c* (no. 15)	$P2_1/n$ (no. 14)	*Pbca* (no. 61)
***a* / Å**	15.492(8)	23.2849(8)	16.114(2)	17.148(4)
***b* / Å**	17.191(10)	16.2809(4)	8.9394(7)	20.564(4)
***c* / Å**	25.784(10)	17.6654(5)	27.383(4)	22.319(4)
β / deg	—	106.957(3)	99.828(14)	—
***V* / Å^3**	6867(6)	6405.8(3)	3886.7(7)	7870(3)
Z	8	8	4	8
***D*$_c$ / g cm^{-3}**	1.246	1.396	1.286	1.346
radiation used	Cu-Kα	Cu-Kα	Cu-Kα	Mo-Kα
μ / mm^{-1}	6.993	8.237	4.696	0.791
2θ max / deg	120	120	120	47
no. of unique reflns				
measured (Rint)	5039 (n/a)	4743 (0.0506)	5661 (0.0297)	5750 (n/a)
obs, $\|F_o\| > 4\sigma(\|F_o\|)$	1273	3194	3381	2556
no. of variables	400	368	428	451
***R*$_1$(obs), *wR*$_2$(all)** [a]	0.0972, 0.2764	0.0539, 0.1494	0.0586, 0.1604	0.0750, 0.1874

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

Table S1. Continued…

data	[V(**4**)Cl_3]	[Cr(**4**)Cl_3]	[Mn(**4**)Cl_2]	[Ni(**4**)Br_2]
formula	$C_{37}H_{35}Cl_3N_3S_2V$	$C_{37}H_{35}Cl_3CrN_3S_2$	$C_{37}H_{35}Cl_2MnN_3S_2$	$C_{37}H_{35}Br_2N_3NiS_2$
solvent	1.5(CH_2Cl_2)	1.5(CH_2Cl_2)	CH_2Cl_2	C_4H_8O
formula weight	870.48	871.54	796.57	876.43
temperature / K	203	203	203	203
space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	*Pbca* (no. 61)	*Pbca* (no. 61)
***a* / Å**	12.3896(16)	12.3561(14)	17.056(3)	17.540(3)
***b* / Å**	19.617(2)	19.623(2)	20.693(7)	20.405(4)
***c* / Å**	16.797(2)	16.750(2)	22.231(4)	22.230(4)
β / deg	95.449(16)	95.756(15)	—	—
***V* / Å^3**	4064.0(8)	4040.8(8)	7846(3)	7956(3)
Z	4	4	8	8
***D*$_c$ / g cm^{-3}**	1.423	1.433	1.349	1.463
radiation used	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα
μ / mm^{-1}	0.773	0.815	0.746	2.637
2θ max / deg	50	50	50	47
no. of unique reflns				
measured (Rint)	7157 (0.0382)	7085 (0.0244)	6908 (n/a)	5835 (n/a)
obs, $\|F_o\| > 4\sigma(\|F_o\|)$	4726	5317	3264	2824
no. of variables	486	486	439	457
***R*$_1$(obs), *wR*$_2$(all)** [a]	0.0545, 0.1297	0.0416, 0.1051	0.0746, 0.1495	0.0786, 0.2168

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

Table S1. Continued…

data	[Fe(**5**)Cl_2]	[Co(**5**)Cl_2]	[Fe(**6**)Cl_2]	[Co(**6**)Cl_2]
formula	$C_{43}H_{47}Cl_2FeN_3O_2$	$C_{43}H_{47}Cl_2CoN_3O_2$	$C_{43}H_{47}Cl_2FeN_3S_2$	$C_{43}H_{47}Cl_2CoN_3S_2$
solvent	1.5(CH_2Cl_2)	1.25(CH_2Cl_2)	1.5(CH_2Cl_2)	1.5(CH_2Cl_2)
formula weight	891.98	873.82	924.10	927.18
temperature / K	183	183	183	293
space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)	$C2/c$ (no. 15)
***a* / Å**	9.2178(11)	12.8687(6)	34.005(3)	34.234(6)
***b* / Å**	29.170(2)	19.6515(16)	10.0092(11)	10.0665(10)
***c* / Å**	16.7749(11)	18.0924(9)	27.105(3)	27.315(4)
β / deg	92.674(7)	90.931(4)	94.482(7)	93.888(12)
***V* / Å^3**	4505.6(7)	4574.8(5)	9197.3(17)	9392(2)
Z	4	4	8	8
***D*$_c$ / g cm^{-3}**	1.315	1.269	1.335	1.311
radiation used	Cu-Kα	Cu-Kα	Cu-Kα	Mo-Kα
μ / mm^{-1}	5.714	5.650	6.410	0.772
2θ max / deg	120	120	120	45
no. of unique reflns				
measured (Rint)	6599 (0.0672)	6320 (0.0431)	6741 (0.0358)	2339 (0.0315)
obs, $\|F_o\| > 4\sigma(\|F_o\|)$	4730	4184	4615	1576
no. of variables	491	527	514	454
***R*$_1$(obs), *wR*$_2$(all)** [a]	0.0562, 0.1567	0.0615, 0.1587	0.0594, 0.1417	0.0494, 0.1321

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

Table S1 provides a summary of the crystallographic data for the structures of [Co(**1**)Cl_2], [Fe(**2**)Cl_2], [Fe(**3**)Cl_2], [Fe(**4**)Cl_2], [V(**4**)Cl_3], [Cr(**4**)Cl_3], [Mn(**4**)Cl_2], [Ni(**4**)Br_2], [Fe(**5**)Cl_2], [Co(**5**)Cl_2], [Fe(**6**)Cl_2] and [Co(**6**)Cl_2]. Data were collected using Siemens/Bruker P4 diffractometers, and the structures were refined based on F^2 using the SHELXTL and SHELX-97 program systems.[8] The crystal used for the X-ray diffraction study of [Co(**6**)Cl_2] decomposed during the data collection, and hence the data set is very truncated. However, as the data that had been collected were sufficient to prove that the structure is isomorphous with that of the iron analogue [Fe(**6**)Cl_2] it was deemed unnecessary to make any further attempts. CCDC 253597 to 253608.

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