SUPPORTING INFORMATION

Cobalt PNC^{NHC} 'pincers': ligand dearomatisation, formation of dinuclear and N_2 complexes and promotion of C-H activation

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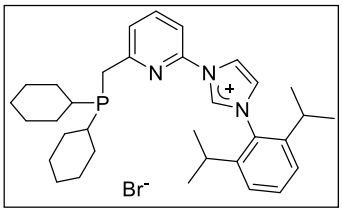
I. SYNTHESIS AND CHARACTERISATION

I.1. General considerations

All air- and moisture-sensitive manipulations were performed under dry argon atmosphere using standard Schlenk techniques or under N_2 in an MBraun glove-box, unless otherwise stated. THF and Et_2O were dried by refluxing over sodium/benzophenone ketyl and distilled under an argon atmosphere prior use. Other solvents (pentane, toluene and dichloromethane) were dried by passing through columns of activated alumina and subsequently purged with argon. The solvents used for the synthesis of the potassium and cobalt complexes were stored, after drying, over potassium mirror until use. C_6D_6 and THF-d_8 were distilled over KH, CD_2Cl_2 was dried over 4 Å molecular sieves and all were degassed by freeze-pump-thaw cycles. The imidazolium salt (^{Cy}PNC^{im})Br was dried azeotropically with a Dean-Stark apparatus using toluene or benzene under inert-atmosphere. Potassium graphite (KC_8)[1], [Co{N($SiMe_3$)$_2$}$_2$],[2] and (^{Cy}PNC^{im})Br·HBr[3] and were prepared according to literature procedures. The synthesis of K(^{Cy}P*N_aC^{NHC}) has been described previously.[3] All other chemicals were obtained from commercial sources and used without further purification.

NMR spectra were recorded on Bruker spectrometers (AVANCE I – 300 MHz, AVANCE III – 400 MHz, AVANCE III – 600 MHz or AVANCE I – 500 MHz equipped with a cryogenic probe). Downfield shifts are reported in ppm as positive and referenced using signals of the residual protio solvent (^{1}H), the solvent (^{13}C) or externally (^{31}P). All NMR spectra were measured at 298 K, unless otherwise specified. The multiplicity of the signals is indicated as s = singlet, d = doublet, t = triplet, sept = septet, m = multiplet and br = broad. Assignments were determined on the basis of unambiguous chemical shifts, coupling patterns and ^{13}C-DEPT experiments or 2D correlations (^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC). Infrared (IR) spectra were recorded in the region 4000–800 cm^{-1} on a Nicolet 6700 FT-IR spectrophotometer as a Nujol mull between KBr plates. Elemental analyses were performed by the “Service de microanalyses”, Université de Strasbourg. Electrospray mass spectra (ESI-MS) were recorded on a microTOF (Bruker Daltonics, Bremen, Germany) instrument using nitrogen as drying agent and nebulizing gas.

I.2. Synthetic procedure for (^{Cy}PNC^{im})Br



1-(6-((dicyclohexylphosphanyl)methyl)pyridin-2-yl)-3-(2,6-diisopropyl phenyl)-1*H*-imidazol-3-ium bromide (^{Cy}PNC^{im})Br

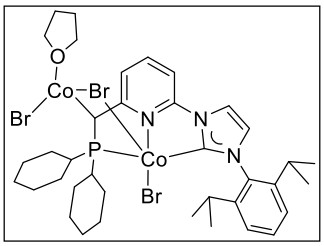
To a solution of (^{Cy}PNC^{im})Br·HBr[3] (3.45 g, 5.09 mmol) in degassed CH_2Cl_2 (15 mL) was added under argon a solution of triethylamine (2.70 mL, 2.03 g, 20.0 mmol) in CH_2Cl_2 (5 mL). After stirring the resulting solution at r.t. for 1 h, all the volatiles were evaporated. The oily residue was redissolved in CH_2Cl_2 and washed three times with degassed water to remove the triethylammonium salt. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Addition of a mixture of Et_2O and pentane precipitated (^{Cy}PNC^{im})Br as a white powder. Yield: 2.28 g (3.82 mmol), 75%.

Anal. Calcd for $C_{33}H_{47}BrN_3P$ (596.64): C, 66.43; H, 7.94; N, 7.04. Found: C, 65.64; H, 7.82; N, 6.94. No better microanalysis data could be obtained due to the air sensitivity of (^{Cy}PNC^{im})Br. The experimental values correspond to partial oxidation of the phosphine *i.e*. $C_{33}H_{47}BrN_3PO_{0.4}$: C, 65.73; H, 7.86; N, 6.97. The purity of (^{Cy}PNC^{im})Br can be assessed from its NMR spectra (see section III).

^{1}H NMR (500.13 MHz, CD_2Cl_2): δ 11.28 (t, $^4J_{HH}$ = 1.6 Hz, 1H, C$H_{imid.}$), 9.16 (t, $^3J_{HH}$ = $^4J_{HH}$ = 1.8 Hz, 1H, C$H_{imid.}$), 8.95 (d, $^3J_{HH}$ = 8.2 Hz, 1H, C$H_{pyr.}$), 7.98 (t, $^3J_{HH}$ = 7.9 Hz, 1H, C$H_{pyr.}$), 7.63 (t, $^3J_{HH}$ = 7.9 Hz, 1H, *p*-CH_{DiPP}), 7.45 (d, $^3J_{HH}$ = 7.8 Hz, 1H, C$H_{pyr.}$), 7.41 (t, $^3J_{HH}$ = $^4J_{HH}$ = 1.7 Hz, 1H, C$H_{imid.}$), 7.40 (d, $^3J_{HH}$ = 7.9 Hz, 2H, *m*-CH_{DiPP}), 3.05 (d, $^2J_{PH}$ = 1.4 Hz, 2H, CH_2P), 2.44 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, CH(CH_3)$_2$), 1.84-1.72 (m, 8H, Cy), 1.71-1.58 (m, 4H, Cy), 1.33-1.06 (m, 10H, Cy), 1.28 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.20 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (125.77 MHz, CD_2Cl_2): δ 162.4 (d, $^2J_{PC}$ = 9.5 Hz, $C_{arom.}$), 145.63 ($C_{arom.}$), 145.58 ($C_{arom.}$), 141.0 (C$H_{arom.}$), 136.2 (C$H_{arom.}$), 132.4 (C$H_{arom.}$), 130.5 ($C_{arom.}$), 125.8 (d, $^3J_{PC}$ = 5.9 Hz, C$H_{arom.}$), 125.4 (C$H_{arom.}$), 125.1 (C$H_{arom.}$), 120.8 (C$H_{arom.}$), 112.9 (d, $^5J_{PC}$ = 1.5 Hz, C$H_{arom.}$), 34.0 (d, $^1J_{PC}$ = 15.6 Hz, CH_{Cy}), 32.0 (d, $^1J_{PC}$ = 23.7 Hz, CH_2P), 30.3 (d, $^2J_{PC}$ = 13.9 Hz, C$H_{2\,Cy}$), 29.6 (d, $^3J_{PC}$ = 9.0 Hz, C$H_{2\,Cy}$), 29.2 (CH(CH_3)$_2$), 27.64 (d, $^2J_{PC}$ = 11.0 Hz, C$H_{2\,Cy}$), 27.56 (d, $^3J_{PC}$ = 7.9 Hz, C$H_{2\,Cy}$), 26.9 (d, $^4J_{PC}$ = 1.0 Hz, C$H_{2\,Cy}$), 24.4 (CH(CH_3)$_2$), 24.3 (CH(CH_3)$_2$). ^{31}P NMR (161.98 MHz, CD_2Cl_2): δ 6.4 (s).

I.3. Synthesis of [Co_2(^{Cy}PNC^{NHC})Br_3] (1)

I.3.1. By reaction with [Co{N(SiMe$_3$)$_2$}$_2$]



To a suspension of (^{Cy}PNC^{im})Br·HBr[3] (0.095 g, 0.14 mmol) in THF was added a solution of [Co{N(SiMe$_3$)$_2$}$_2$] (0.053 g, 0.14 mmol) in THF at room temperature. The resulting mixture was stirred for 1 h and briefly heated to reflux. All the volatiles were evaporated under reduced pressure and the resulting brown solid was washed with pentane and

extracted with THF. Single crystals of **1**·THF suitable for X-ray diffraction studies were obtained by slow diffusion of pentane in a THF solution of the complex at -40 °C. Yield of the crystals: 0.026 g (0.028 mmol), 20%.

No corresponding microanalysis data could be obtained due to the labile coordinated THF molecule and to the air sensitivity of **1**. The ^{1}H NMR spectrum of **1** can be found in section III.

^{1}H NMR (400.13 MHz, THF-d_8): characteristic peaks at δ 56.0 ($\Delta\nu_{1/2}$ ≈ 2000 Hz), 40.7 ($\Delta\nu_{1/2}$ = 240 Hz), 38.9 ($\Delta\nu_{1/2}$ ≈ 800 Hz), 37.6 ($\Delta\nu_{1/2}$ ≈ 700 Hz), 30.4 ($\Delta\nu_{1/2}$ = 200 Hz), 25.4 ($\Delta\nu_{1/2}$ = 300 Hz), 20.7 ($\Delta\nu_{1/2}$ = 160 Hz), 19.5 ($\Delta\nu_{1/2}$ = 150 Hz), 15.6 ($\Delta\nu_{1/2}$ = 200 Hz), 14.6 ($\Delta\nu_{1/2}$ = 180 Hz), 13.7 ($\Delta\nu_{1/2}$ = 140 Hz), 12.1 ($\Delta\nu_{1/2}$ = 320 Hz), -9.2 ($\Delta\nu_{1/2}$ = 190 Hz), -9.9 ($\Delta\nu_{1/2}$ = 190 Hz), -13.3 ($\Delta\nu_{1/2}$ = 130 Hz), -14.5 ($\Delta\nu_{1/2}$ ≈ 500 Hz), -17.1 ($\Delta\nu_{1/2}$ = 230 Hz), -24.9 ($\Delta\nu_{1/2}$ ≈ 500 Hz), -37.0 ($\Delta\nu_{1/2}$ = 250 Hz), -41.1 ($\Delta\nu_{1/2}$ = 260 Hz), -62.2 ($\Delta\nu_{1/2}$ = 600 Hz), -83.5 ($\Delta\nu_{1/2}$ = 280 Hz), -98.0 ($\Delta\nu_{1/2}$ = 150 Hz).

I.3.2. By reaction of 2 with [$CoBr_2(THF)_2$]

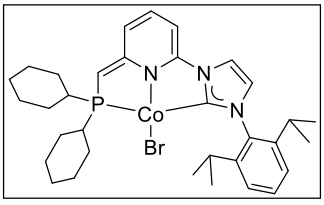
In an alternative and rational synthesis, to a solution of **2** (0.065 g, 0.10 mmol) in THF, precooled to -78 °C, was added a cold solution of [$CoBr_2(THF)_2$] (0.036 g, 0.10 mmol) in THF. The reaction mixture was allowed to warm up to room temperature and was stirred overnight. The resulting solution was concentrated to *ca*. 2-3 mL and complex **1** was precipitated by addition of pentane. Yield: 0.070 g (0.074 mmol), 74%. ^{1}H NMR data are the same as reported above (see section III).

I.3.3. Determination of the magnetic susceptibility

The determination of the magnetic susceptibility was carried out using Evans' method[4] for a THF-d_8 solution (0.80 mL) of **1** (0.0155 g, 16.4 μmol) containing hexamethyldisiloxane (HDMSO) as internal reference and using a capillary of THF-d_8/HDMSO as a diamagnetic standard. The diamagnetic corrections were calculated using Pascal's constants.[5] The ^{1}H-NMR spectrum was recorded at 400.13 MHz and 298 K. μ_{eff} = 4.8 ± 0.2 μ_B. This value is slightly lower than the effective magnetic moment corresponding to two non-interacting high-spin Co^{II} centres (spin-only moment of $\mu_{eff} = \sqrt{2}$ x 3.87 μ_B = 5.48 μ_B), suggesting some antiferromagnetic coupling between the two metal centres. Similar values have been reported for dinuclear halide-bridged Co^{II} complexes.[6]

I.4. Synthesis of [Co(^{Cy}P*N$_a$C^{NHC})Br] (2)

I.4.1. By reaction with [Co{N(SiMe$_3$)$_2$}$_2$]



To a suspension of (^{Cy}PNC^{im})Br (0.33 g, 0.55 mmol) in THF precooled at -78°C was added dropwise a cold solution of [Co{N(SiMe$_3$)$_2$}$_2$] (0.21 g, 0.55 mmol) in THF. The resulting dark-red solution was allowed to reach room temperature, stirred for 2 h and briefly heated to reflux. All the volatiles were evaporated under reduced pressure and the resulting brown-red solid was extracted

with toluene. Filtration and evaporation of the toluene solution afforded **2** as a dark purple solid. Yield: 0.27 g (0.41 mmol), 75%. Single crystals suitable for X-ray crystallography studies could be obtained by slow evaporation of a pentane solution of the complex.

Anal. Calcd for $C_{33}H_{45}BrCoN_3P$ (653.55): C, 60.65; H, 6.94; N, 6.43. Found: C, 59.31; H, 6.98; N, 6.28. No better microanalysis data could be obtained due to the high air sensitivity of **2**. The experimental values correspond tentatively to the reaction of **2** with air moisture *i.e*. $C_{33}H_{45}BrCoN_3P$ + 4/5 H_2O: C, 59.34; H, 7.03; N, 6.29. The ^{1}H NMR spectrum of **2** can be found in section III.

^{1}H NMR (400.13 MHz, C_6D_6): δ 40.8 (1H, $\Delta\nu_{1/2}$ = 200 Hz), 39.4 (4H, $\Delta\nu_{1/2}$ = 810 Hz), 30.0 (1H, $\Delta\nu_{1/2}$ = 160 Hz), 26.2 (2H, $\Delta\nu_{1/2}$ = 360 Hz), 14.0 (2H, $\Delta\nu_{1/2}$ = 65 Hz), 10.5 (8H, $\Delta\nu_{1/2}$ = 45 Hz), 8.0 (2H, $\Delta\nu_{1/2}$ = 40 Hz), 7.8 (overlapping, 2H, $\Delta\nu_{1/2}$ = 80 Hz), 7.3 (1H, $\Delta\nu_{1/2}$ = 15 Hz), 4.3 (2H, $\Delta\nu_{1/2}$ = 25 Hz), 2.7 (2H, $\Delta\nu_{1/2}$ = 50 Hz), 2.1 (1-2H, $\Delta\nu_{1/2}$ = 10 Hz), 1.4 (6H, $\Delta\nu_{1/2}$ = 60 Hz), -4.4 (2-3H, $\Delta\nu_{1/2}$ = 1000 Hz), -17.7 (6H, $\Delta\nu_{1/2}$ = 180 Hz), -38.7 (1H, $\Delta\nu_{1/2}$ = 180 Hz), -43.4 (1H, $\Delta\nu_{1/2}$ = 200 Hz), -64.8 (1H, $\Delta\nu_{1/2}$ = 550 Hz) (intensities have been estimated after baseline correction using the 'spline' mode).

I.4.2. By transmetalation from K(^{Cy}P*N$_a$C^{NHC})

To a suspension of (^{Cy}PNC^{im})Br·HBr[3] (0.460 g, 0.680 mmol) in Et_2O, precooled at –78 °C, was added a solution of KHMDS (0.407 g, 2.04 mmol) in Et_2O. The resulting suspension was allowed to reach room temperature and stirred for 1 h, giving a pink-red suspension of an off-white precipitate. Complete deprotonation could be confirmed by the disappearence of the peak at δ 1.6 in the ^{31}P{^{1}H} NMR spectrum. If needed, additional KHMDS was added to the mixture until completion of the reaction. Filtration and evaporation of the solvent gave almost quantitative yields of K(^{Cy}P*N$_a$C^{NHC}).[3]

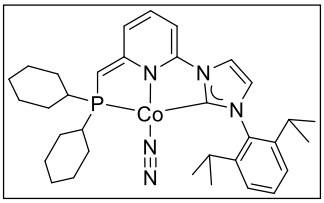
The freshly prepared K(^{Cy}P*N$_a$C^{NHC}) was dissolved in Et_2O (red solution), cooled to -78 °C and a solution of [$CoBr_2(THF)_2$] (0.247 g, 0.680 mmol) in THF (intense blue colour) was added dropwise. The resulting solution immediately turned dark brown. The reaction mixture was allowed to warm up to r.t. and was stirred for 3-4 h. All volatiles were evaporated under reduced pressure and the resulting solid was extracted with toluene (15 mL). Filtration and evaporation of the solvent afforded **2** as a dark purple solid. Yield: 0.346 g (0.530 mmol), 78%. ^{1}H NMR data are the same as reported above.

I.4.3. Determination of the magnetic susceptibility

The determination of the magnetic susceptibility was carried out using Evans' method[4] for a C_6D_6 solution of **2** (0.0066 g, 10 μmol) containing toluene as internal reference and using a capillary of toluene as a diamagnetic standard. The solvent correction was not applied[7] and the diamagnetic corrections were calculated using Pascal's constants.[5] The ^{1}H-NMR spectrum was recorded at 400.13 MHz and 298 K. μ_{eff} = 2.1±0.2 μ_B.

I.5. Synthesis of Co(I)-N_2 pincer complexes

I.5.1. Synthesis of [Co(^{Cy}P*N_aC^{NHC})(N_2)] (3)



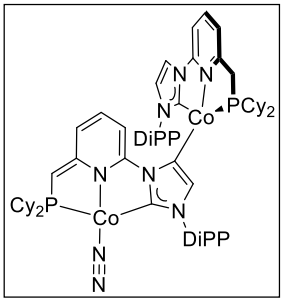
In the glovebox, a solution of **2** (0.14 g, 0.21 mmol) in a mixture of Et_2O (5 mL) and THF (1 mL) was saturated with N_2 and cooled to -78 °C. Solid KC_8 (0.029 g, 0.21 mmol) was added and the resulting mixture was allowed to warm up to room temperature and stirred for 30 min. After filtration, the dark turquoise solution was evaporated under a stream of N_2 and successively extracted with pentane and toluene. Single crystals suitable for X-ray diffraction studies could be obtained by cooling the pentane solution at -40°C. Yield: 0.096 g (0.16 mmol), 75%. No corresponding microanalysis data could be obtained due to the extreme air sensitivity of **3** but the purity of the complex can be assessed from its NMR spectra (see section III).

^{1}H NMR (500.13 MHz, C_6D_6): δ 7.21 (t, $^3J_{HH}$ = 7.8 Hz, 1H, *p*-C*H*$_{DiPP}$), 7.09 (d, $^3J_{HH}$ = 7.8 Hz, 2H, *m*-C*H*$_{DiPP}$), 6.30 (d, $^3J_{HH}$ = 1.9 Hz, 1H, C*H*$_{imid.}$), 6.22 (ddd, $^3J_{HH}$ = 9.0, 6.7 Hz, $^5J_{PH}$ = 2.1 Hz, 1H, C*H*$_{pyr.}$), 6.11 (d, $^3J_{HH}$ = 9.0, 1H, C*H*$_{pyr.}$), 6.09 (d, $^3J_{HH}$ = 1.8 Hz, 1H, C*H*$_{imid.}$), 4.83 (dd, $^3J_{HH}$ = 6.7 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, C*H*$_{pyr.}$), 3.41 (s, 1H, C*H*P), 2.95 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 2.38-2.28 (m, 2H, Cy), 2.18-2.08 (m, 2H, Cy), 1.95-1.57 (m, 12H, Cy), 1.53 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3)_2$), 1.34-1.12 (m, 6H, Cy), 1.09 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(C*H*$_3)_2$).

^{13}C{1H} NMR (125.77 MHz, C_6D_6): δ 191.8 (br d, $^2J_{P\text{-}Co\text{-}C} \approx$ 55 Hz, *C*$_{NHC}$), 171.8 (d, $^2J_{PC}$ = 22.8 Hz, N*C*$_{pyr.}$), 151.7 (d, J_{PC} = 6.2 Hz, N*C*$_{pyr.}$), 146.2 (*C*$_{DiPP}$), 135.8 (*C*$_{DiPP}$), 132.5 (d, J_{PC} = 1.8 Hz, *C*H$_{pyr.}$), 130.2 (*C*H$_{DiPP}$), 124.1 (*C*H$_{DiPP}$), 123.3 (d, J_{PC} = 2.6 Hz, *C*H$_{imid.}$), 114.0 (d, J_{PC} = 16.8 Hz, *C*H$_{pyr.}$), 113.3 (*C*H$_{imid.}$), 83.9 (*C*H$_{pyr.}$), 63.9 (d, $^1J_{PC}$ = 52.1 Hz, *C*HP), 34.5 (d, $^1J_{PC}$ = 26.2 Hz, *C*H$_{Cy}$), 29.5 (d, J_{PC} = 4.6 Hz, *C*H$_{2\ Cy}$), 28.8 (*C*H$(CH_3)_2$), 28.7 (*C*H$_{2\ Cy}$), 27.6 (d, J_{PC} = 1.2 Hz, *C*H$_{2\ Cy}$), 27.5 (d, J_{PC} = 4.5 Hz, *C*H$_{2\ Cy}$), 27.0 (d, J_{PC} = 1.1 Hz, *C*H$_{2\ Cy}$), 24.4 (CH(*C*H$_3)_2$), 24.2 (CH(*C*H$_3)_2$).

^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 46.3 (br s).

I.5.2. Synthesis of [Co{^{Cy}P*N_aC^{NHC}(Co[^{Cy}PNC^{NHC}])}(N_2)] (4)



In the glovebox, to a solution of **2** (0.13 g, 0.20 mmol) in a mixture of Et_2O (5 mL) and THF (1 mL) was added KC_8 (0.027 g, 0.20 mmol) at room temperature and the resulting mixture was stirred for 30 min. After filtration, the dark turquoise solution was evaporated under reduced pressure and the resulting solid was sequentially extracted with pentane and toluene. Single crystals suitable for X-ray diffraction studies were obtained by slow diffusion of pentane in the toluene extract at -40°C. Yield: 0.080 g (0.068 mmol), 34% No corresponding microanalysis data could be obtained due to the extreme air sensitivity of **4** but the purity of the complex can be assessed from its NMR spectra (see section III).

In the ^{1}H NMR spectrum of **4**, four non-equivalent isopropyl groups from the two DiPP substituents were observed and are referenced as a, b, c and d (based on ^{1}H-^{1}H COSY). When possible, the dearomatised (lower) ligand is designated by * (based on coupling patterns and ^{1}H-^{1}H COSY).

^{1}H NMR (500.13 MHz, C_6D_6): δ 8.64 (td, $^{3}J_{HH}$ = 7.6 Hz, $^{5}J_{PH}$ = 1.4 Hz, 1H, C$H_{pyr.}$), 7.39 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, *p*-CH_{DiPP}), 7.35 (dd, $^{3}J_{HH}$ = 7.8, $^{4}J_{HH}$ = 1.4 Hz, 1H, *m*-CH_{DiPP}), 7.26 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H, *p*-CH_{DiPP}), 7.23 (dd, $^{3}J_{HH}$ = 8.0, $^{4}J_{HH}$ = 2.1 Hz, 1H, *m*-CH_{DiPP}), 7.18-7.09 (m, 2H, *m*-CH_{DiPP}), 6.82 (d, $^{3}J_{HH}$ = 1.7 Hz, 1H, C$H_{imid.}$), 6.47 (d, $^{3}J_{HH}$ = 1.5 Hz, 1H, C$H_{imid.}$), 6.31 (d, $^{3}J_{HH}$ = 7.4 Hz, 1H, C$H_{pyr.}$), 5.87 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H, C$H_{pyr.}$*), 5.82 (ddd, $^{3}J_{HH}$ = 8.7, 6.6 Hz, $^{5}J_{PH}$ = 1.8 Hz, 1H, C$H_{pyr.}$*), 5.71 (d, $^{3}J_{HH}$ = 6.6 Hz, 1H, C$H_{pyr.}$*), 5.39 (d, $^{3}J_{HH}$ = 7.7 Hz, 1H, C$H_{pyr.}$), 5.08 (s, 1H, C$H_{imid.}$*), 3.98 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, C$^{a}H(CH_3)_2$), 3.66 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, C$^{b}H(CH_3)_2$), 3.25 (s, 1H, C*H*P*), 3.01 (dd, $^{2}J_{HH}$ = 17.5 Hz, $^{2}J_{PH}$ = 9.0 Hz, A part of ABX spin system with A = B = H and X = P, CH_2P), 2.75 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1H, C$^{c}H(CH_3)_2$), 2.73 (overlapping dd, $^{2}J_{HH}$ = 17.4 Hz, $^{2}J_{PH}$ = 9.5 Hz, B part of ABX spin system with A = B = H and X = P, CH_2P), 2.47 (br d, J_{PH} = 11.1 Hz, 1H, Cy), 2.28 (br d, J_{PH} = 12.0 Hz, 1H, Cy), 2.20 (sept, $^{3}J_{HH}$ = 6.7 Hz, 1H, C$^{d}H(CH_3)_2$), 2.21-1.55 (m, 24H, Cy), 1.85 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, C^{c}H(C$H_3)_2$), 1.79 (d, $^{3}J_{HH}$ = 6.7 Hz, 3H, C^{a}H(C$H_3)_2$), 1.76 (d, $^{3}J_{HH}$ = 6.7 Hz, 3H, C^{d}H(C$H_3)_2$), 1.53-1.20 (m, 13H, Cy), 1.35 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, C^{a}H(C$H_3)_2$), 1.32 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, C^{d}H(C$H_3)_2$), 1.30 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, C^{b}H(C$H_3)_2$ + C^{c}H(C$H_3)_2$), 1.20-1.04 (m, 2H, Cy), 1.01 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, C^{b}H(C$H_3)_2$), 0.99-0.72 (m, 3H, Cy).

^{13}C{^{1}H} NMR (125.77 MHz, C_6D_6): δ 191.5 (br d, $^{2}J_{P\text{-}Co\text{-}C}$ = *ca.* 57 Hz, C_{NHC}), 179.7 (br d, $^{2}J_{P\text{-}Co\text{-}C}$ = *ca.* 60 Hz, C_{NHC}), 172.4 (d, $^{2}J_{PC}$ = 24.1 Hz, $C_{arom.}$), 160.1 (d, $^{2}J_{PC}$ = 10.5 Hz, $C_{arom.}$), 156.4 (d, J_{PC} = 5.8 Hz, $C_{arom.}$), 146.4 (d, J_{PC} = 1.9 Hz, $C_{arom.}$), 146.1 ($C_{arom.}$), 145.19 ($C_{arom.}$), 145.18 (d, J_{PC} = 4.2 Hz, $C_{arom.}$), 138.9 ($C_{arom.}$), 138.0 ($C_{arom.}$), 131.8 (d, J_{PC} = 1.8 Hz, *C*H$_{arom.}$), 130.1 (*C*H$_{arom.}$), 129.0 (*C*H$_{arom.}$), 124.4 (*C*H$_{arom.}$), 124.3 (*C*H$_{arom.}$), 124.0 (*C*H$_{arom.}$), 122.9 (*C*H$_{arom.}$), 122.5 (br s, *C*H$_{arom.}$), 119.8 (d, J_{PC} = 10.2 Hz, *C*H$_{arom.}$), 118.5 (*C*H$_{arom.}$), 111.5 (d, J_{PC} = 17.2 Hz, *C*H$_{arom.}$), 111.0 (*C*H$_{arom.}$), 110.3 (*C*H$_{arom.}$), 86.8 (*C*H$_{arom.}$), 60.8 (d, $^{1}J_{PC}$ = 51.8 Hz, *C*HP), 37.1 (d, $^{1}J_{PC}$ = 17.3 Hz, *C*H$_2$P), 34.9 (d, J_{PC} = 24.9 Hz, *C*H$_{Cy}$), 33.8 (d, J_{PC} = 25.8 Hz, *C*H$_{Cy}$), 33.7 (d, J_{PC} = 15.8 Hz, *C*H$_{Cy}$), 30.3 (d, J_{PC} = 5.6 Hz, *C*H$_{2\ Cy}$), 29.9 (*C*H(CH$_3)_2$), 29.3 (d, J_{PC} = 18.5 Hz, *C*H$_{Cy}$), 29.2 (d, J_{PC} = 5.0 Hz, Cy), 29.1 (d, J_{PC} = 5.0 Hz, Cy), 28.6 (*C*H(CH$_3)_2$), 28.5 (d, J_{PC} = 19.9 Hz, Cy), 28.1 (*C*H(CH$_3)_2$), 27.9 (overlapping s and d, J_{PC} = 7.9 Hz, *C*H(CH$_3)_2$ + Cy), 27.8 (d, J_{PC} = 5.0 Hz, Cy), 27.72 (d, J_{PC} = 8.2 Hz, Cy), 27.65 (d, J_{PC} = 3.1 Hz, Cy), 27.57 (d, J_{PC} = 2.5 Hz, Cy), 27.4 (d, J_{PC} = 2.9 Hz, Cy), 27.3 (Cy), 27.2 (d, J_{PC} = 3.6 Hz, Cy), 27.1 (d, J_{PC} = 4.5 Hz, Cy), 26.7 (Cy), 26.5 (d, J_{PC} = 6.1 Hz, Cy), 26.4 (CH(*C*H$_3)_2$), 26.20 (CH(*C*H$_3)_2$), 26.19 (CH(*C*H$_3)_2$), 26.1 (CH(*C*H$_3)_2$), 24.9 (CH(*C*H$_3)_2$), 24.4 (CH(*C*H$_3)_2$), 24.3 (CH(*C*H$_3)_2$), 24.2 (CH(*C*H$_3)_2$).

^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6): δ 48.3, 42.3.

II. X-RAY CRYSTALLOGRAPHY

II.1. General methods

Suitable crystals for the X-ray analysis of all compounds were obtained as described above. Summary of the crystal data, data collection and refinement for compounds are given in Table S1. Data sets were collected at 173(2) K on a Bruker APEX-II CCD Duo diffractometer (graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å). Specific comments for each data set are given below.

The cell parameters were determined (APEX2 software)[8] from reflections taken from three sets of 12 frames, each at 10 s exposure. The structures were solved by direct methods using the program SHELXS-2013.[9] The refinement and all further calculations were carried out using SHELXL-2013.[9b] The H-atoms were introduced into the geometrically calculated positions (SHELXL-2013 procedures) unless stated otherwise and refined riding on the corresponding parent atoms. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2.

<u>The following special comments apply to the models of the structures:</u>

- For **1**, a squeeze procedure was applied and the residual electron density was assigned to four disordered molecules of THF.
- For **3**, thermal motions affect one cyclohexyl ring (C28-C33) on the ligand. A squeeze procedure was applied and the residual electron density was assigned to ½ disordered molecule of pentane.
- A residual electron density peak next to Co2 in the structure of **4** leads to Alerts B in the Checkcif. A squeeze procedure was applied and the residual electron density was assigned to three disordered molecules of pentane.

II.2. Summary of crystal data

Table S1. Crystal data, data collection and refinement for compounds **1**-**4.**

Compounds	**1**	**2**	**3**	**4**
Chemical formula	$C_{33}H_{45}Br_3Co_2N_3P \cdot C_4H_8O$	$C_{33}H_{45}BrCoN_3P$	$C_{33}H_{45}CoN_5P$	$C_{66}H_{90}Co_2N_8P_2$
CCDC Number	1440378	1440379	1440381	1440380
Formula Mass	944.38	653.53	601.64	1175.25
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
a/Å	14.965(5)	12.8384(8)	25.681(9)	14.8520(12)
b/Å	24.298(8)	17.0917(12)	15.695(5)	16.6741(13)
c/Å	15.796(5)	16.7231(8)	18.634(7)	18.3766(15)
α/°	90	90	90	66.340(2)
β/°	110.070(5)	116.587(4)	113.151(8)	84.429(2)
γ/°	90	90	90	66.370(2)
Unit cell volume/Å^3	5395(3)	3281.5(4)	6906(4)	3807.8(5)
Temperature/K	173(2)	173(2)	173(2)	173(2)
Space group	*P*21/*c*	*P*21/*c*	*C*2/*c*	$P\bar{1}$
No. of formula units per unit cell, *Z*	4	4	8	2
Absorption coefficient, μ/mm	2.890	1.815	0.571	0.515
No. of reflections measured	52478	31681	25053	48347
No. of independent reflections	13146	7899	8379	18344
R_{int}	0.1588	0.0896	0.0636	0.0942
Final R_1 values ($I > 2\sigma(I)$)	0.0846	0.0456	0.0569	0.0796
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2019	0.0747	0.1230	0.1847
Final R_1 values (all data)	0.2350	0.1037	0.1186	0.1670
Final $wR(F^2)$ values (all data)	0.2428	0.0884	0.1398	0.2122
Goodness of fit on F^2	0.825	1.002	0.982	0.882

II.3. Crystal structures

II.3.1. The crystal structure of 1

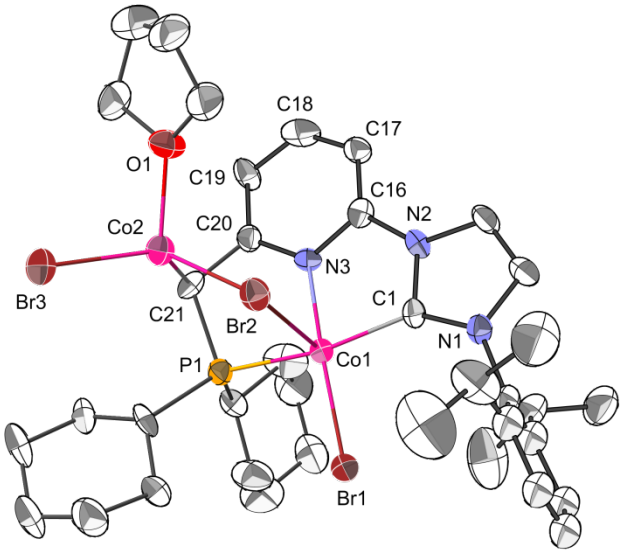


Figure S1. View of the molecular structure of **1** with thermal ellipsoids represented at the 40% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles [°]: Co1-Br1 2.348(2), Co1-Br2 2.760(2), Co1-C1 1.942(8), Co1-P1 2.251(3), Co1-N3 1.950(7), Co2-Br2 2.451(2), Co2-Br3 2.370(2), Co2-O1 2.017(7), Co2-C21 2.116(8), C16-N3 1.381(10), C16-C17 1.323(12), C17-C18 1.329(14), C18-C19 1.353(13), C19-C20 1.393(13), C20-C21 1.479(11), C21-P1 1.812(9); P1-Co1-Br1 96.2(1), C1-Co1-Br1 97.7(3), C1-Co1-N3 81.5(4), N3-Co1-P1 83.2(2), Br2-Co2-Br3 116.53(6), O1-Co2-C21 111.0(3), P1-C21-C20 110.3(6), N1-C1-N2 104.3(7).

II.3.2. The crystal structure of 2

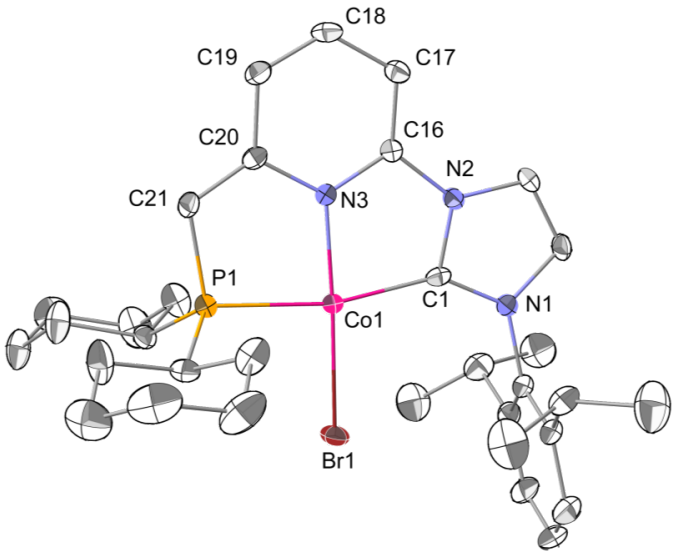


Figure S2. View of the molecular structure of **2** with thermal ellipsoids represented at the 40% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles [°]: Co1-Br1 2.3427(5), Co1-C1 1.919(3), Co1-P1 2.2179(9), Co1-N3 1.897(2), C16-N3 1.356(3), C16-C17 1.360(4), C17-C18 1.417(4), C18-C19 1.350(4), C19-C20 1.443(4), C20-C21 1.368(4), C21-P1 1.767(3); P1-Co1-Br1 93.47(3), C1-Co1-Br1 100.01(8), C1-Co1-N3 82.1(1), N3-Co1-P1 84.43(7), P1-C21-C20 113.9(2), C20-N3-Co1 122.3(2), C16-N3-Co1 117.8(2), N1-C1-N2 103.2(2); Sum of the angles around Co1: 360.0°.

II.3.3. The crystal structure of 3

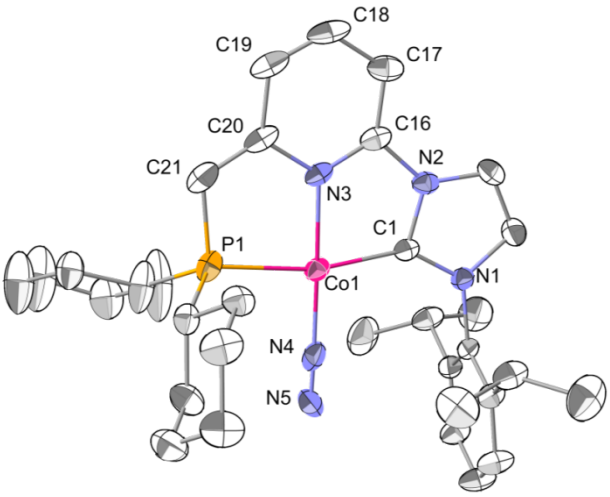


Figure S3. View of the molecular structure of **3** with thermal ellipsoids represented at the 40% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles [°]: Co1-C1 1.886(3), Co1-P1 2.225(1), Co1-N3 1.904(2), Co1-N4 1.789(3), N4-N5 0.987(3), C16-N3 1.339(4), C16-C17 1.378(4), C17-C18 1.417(5), C18-C19 1.335(5), C19-C20 1.440(5), C20-C21 1.362(5), C20-N3 1.399(4), C21-P1 1.755(3); Co1-N4-N5 178.0(3), C1-Co1-N4 98.27(12), C1-Co1-N3 81.75(11), N3-Co1-P1 84.24(8), P1-Co1-N4 95.77(9), C20-N3-Co1 122.5(2), C16-N3-Co1 118.2(2), P1-C21-C20 115.5(2), N1-C1-N2 103.2(2); Sum of the angles around Co1: 360.0°.

II.3.4. The crystal structure of 4

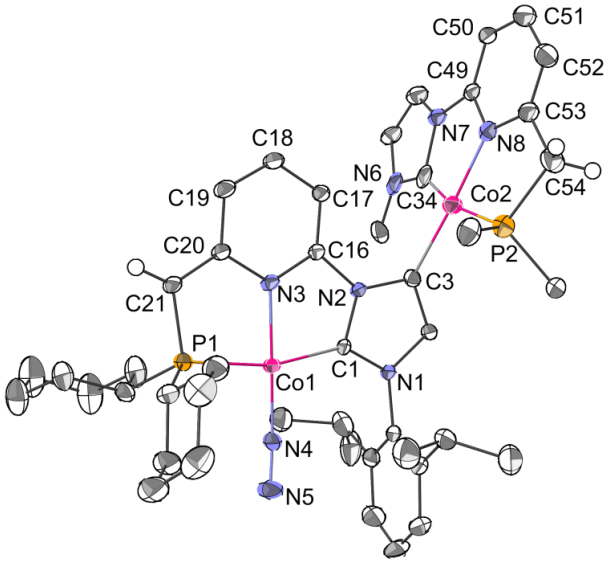


Figure S4. View of the molecular structure of **4** with thermal ellipsoids represented at the 40% probability level. H atoms except the α-C*H* and C atoms of the Cy and DiPP of the upper ligand bar those attached to P and N have been omitted for clarity. Selected bond distances (Å) and angles [°]: Co1-C1 1.914(4), Co1-N3 1.904(3), Co1-N4 1.742(4), Co1-P1 2.202(1), Co2-C3 1.960(4), Co2-C34 1.760(5), Co2-N8 1.918(4), Co2-P2 2.207(1), N4-N5 1.120(5), C16-N3 1.364(5), C16-C17 1.356(5), C17-C18 1.413(5), C18-C19 1.361(6), C19-C20 1.430(6), C20-C21 1.375(6), C20-N3 1.403(5), C49-N8 1.349(5), C49-C50 1.384(6), C50-C51 1.394(7), C51-C52 1.399(7), C52-C53 1.352(7), C53-C54 1.483(7), C53-N8 1.390(6); Co1-N4-N5 176.8(3), C1-Co1-N4 100.51(16), C1-Co1-N3 80.53(15), N3-Co1-P1 84.34(10), N4-Co1-P1 94.64(11), C20-C21-P1 114.2(3), C3-Co2-P2 94.09(12), C3-Co2-C34 98.4(2), N8-Co2-C34 83.9(2), N8-Co2-P2 83.85(11), C53-C54-P2 110.6(3), N1-C1-N2 104.0(3), N6-C34-N7 95.9(4); Sum of the angles around Co1: 360.0°, sum of the angles around Co2: 360.2°.

II.4. Comparison of metrical data in 1- 4

Table S2. Selected bond distances (Å) and angles (°) for the cobalt complexes **1**- **4**.

	1	2	3	4
Co1-N3	1.950(7)	1.897(2)	1.904(2)	1.904(3); Co2-N8 1.918(4)
Co1-C1	1.942(8)	1.919(3)	1.886(3)	1.914(4); Co2-C34 1.760(5)
Co1-P1	2.251(3)	2.218(1)	2.225(1)	2.202(1); Co2-P2 2.207(1)
C16-N3	1.381(10)	1.356(3)	1.339(4)	1.364(5); C49-N8 1.349(5)
C20-N3	1.354(11)	1.403(3)	1.399(4)	1.403(5); C53-N8 1.390(6)
C16-C17	1.323(12)	1.360(4)	1.378(4)	1.356(5); C49-C50 1.384(6)
C17-C18	1.329(14)	1.417(4)	1.417(5)	1.413(5); C50-C51 1.394(7)
C18-C19	1.353(13)	1.350(4)	1.335(5)	1.361(6); C51-C52 1.399(7)
C19-C20	1.393(13)	1.443(4)	1.440(5)	1.430(6); C52-C53 1.352(7)
C20-C21	1.479(11)	1.368(4)	1.362(5)	1.375(6); C53-C54 1.483(7)
C20-C21-P1	110.3(6)	113.9(2)	115.5(2)	114.2(3); C53-C54-P2 110.6(3)

III. NMR SPECTRA

III.1. (^{Cy}PNC^{im})Br

^{1}H NMR (500.13 MHz, CD_2Cl_2)

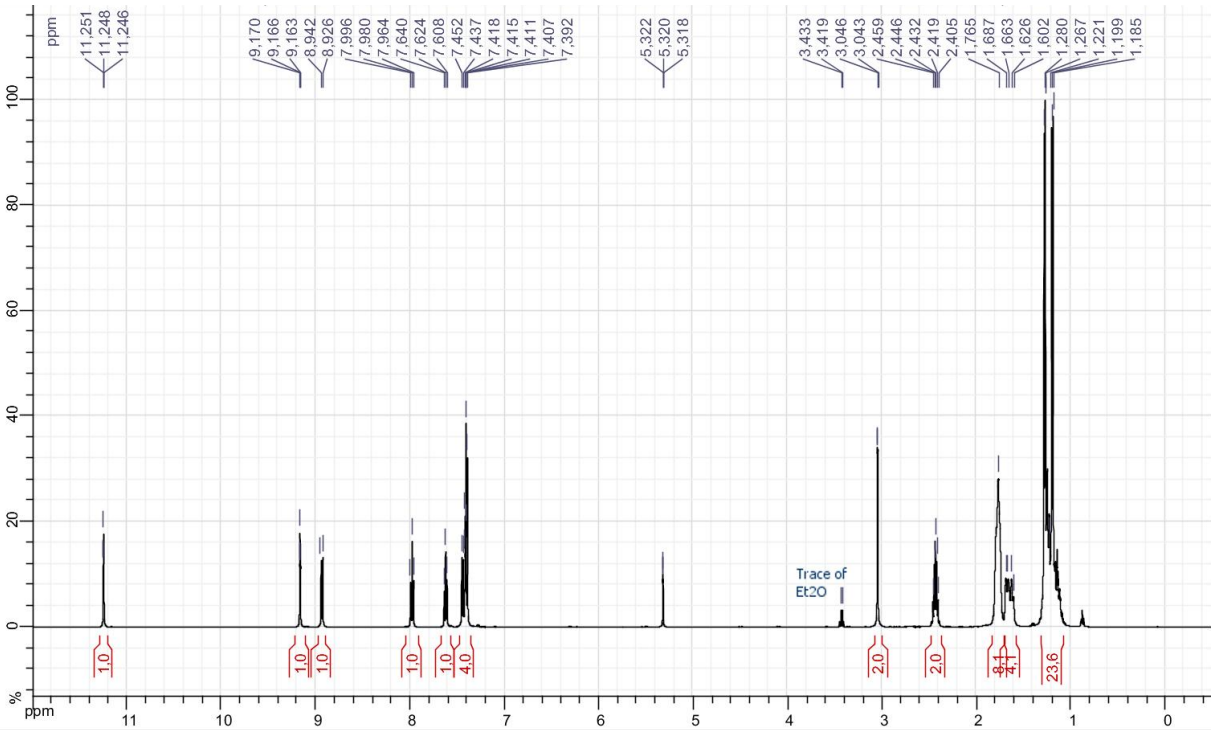


Figure S5. ^{1}H NMR spectrum of (^{Cy}PNC^{im})Br in CD_2Cl_2 (residual protio solvent from CD_2Cl_2 at δ 5.32)

$^{13}C\{^1H\}$ NMR (125.77 MHz, CD_2Cl_2)

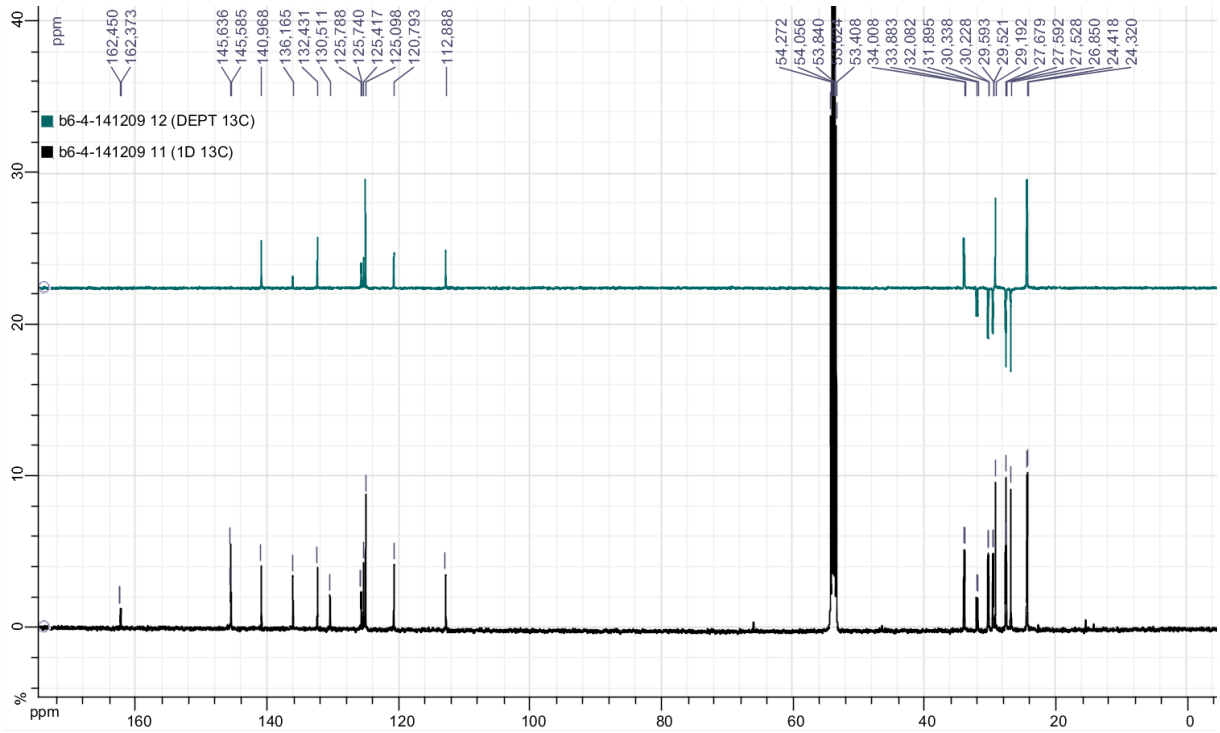


Figure S6. $^{13}C\{^1H\}$ (bottom) and ^{13}C-DEPT (top) NMR spectra of ($^{Cy}PNC^{im}$)Br in CD_2Cl_2 (solvent signals at δ 53.84).

$^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2)

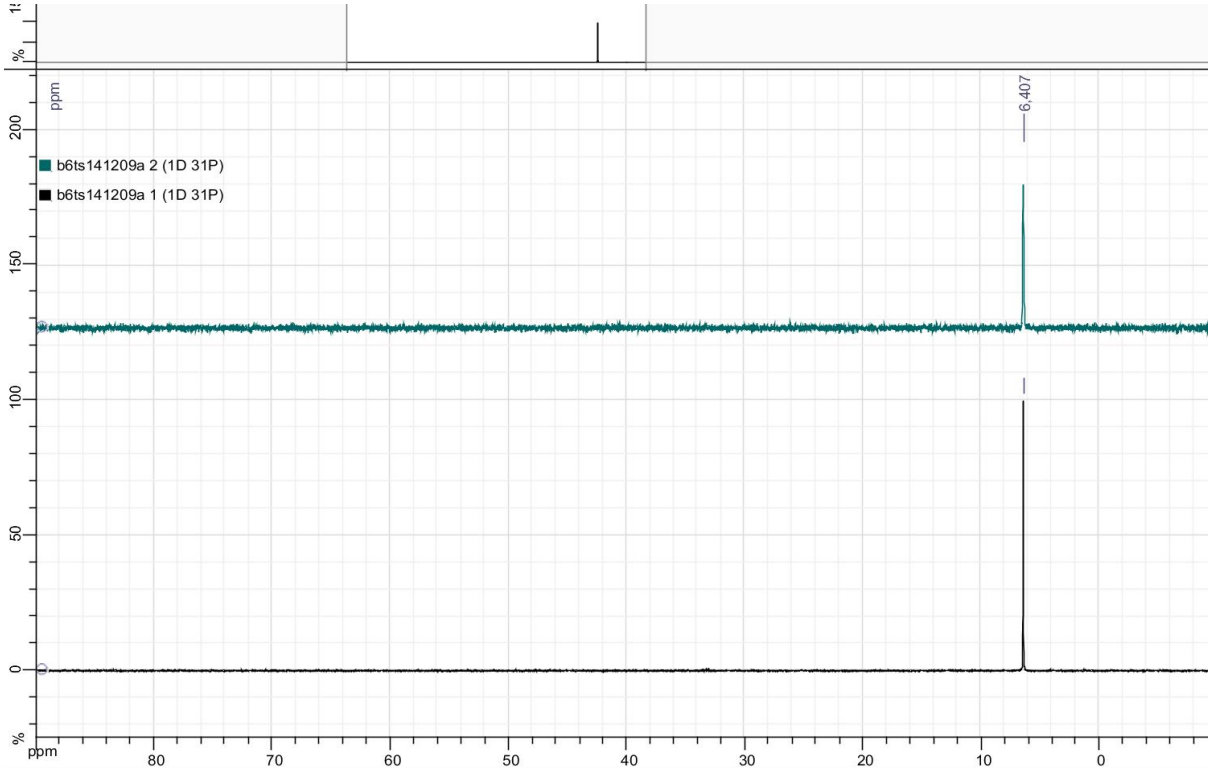


Figure S7. $^{31}P\{^1H\}$ (bottom) and ^{31}P NMR spectra of ($^{Cy}PNC^{im}$)Br in CD_2Cl_2.

III.2. $[Co_2(^{Cy}PNC^{NHC})Br_3]$ (1)

^{1}H NMR (400.13 MHz, THF-d_8)

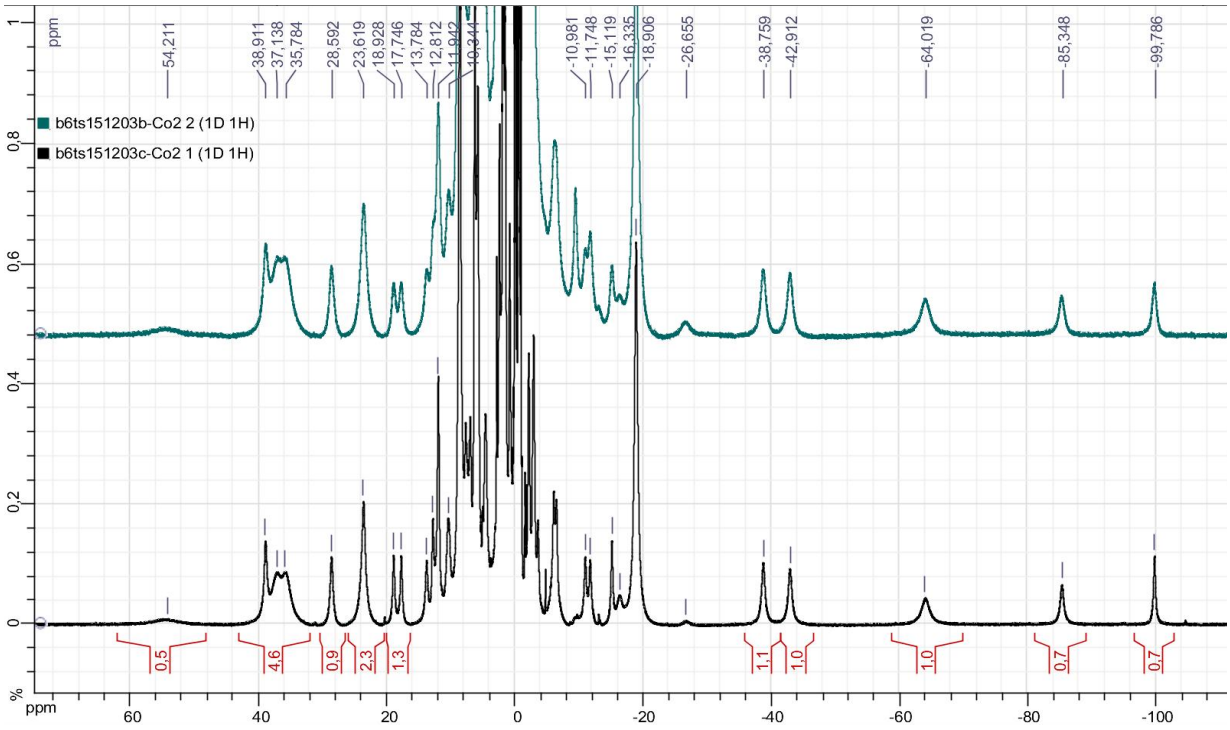


Figure S8. ^{1}H NMR spectrum of paramagnetic **1** in THF-d_8 obtained from the reaction with $[Co\{N(SiMe_3)_2\}_2]$ (bottom) and by transmetalation from $K(^{Cy}PN_aC^{NHC})$ (top) (after baseline correction using the 'spline' mode).

III.3. $[Co(^{Cy}P^*N_aC^{NHC})Br]$ (2)

^{1}H NMR (400.13 MHz, C_6D_6)

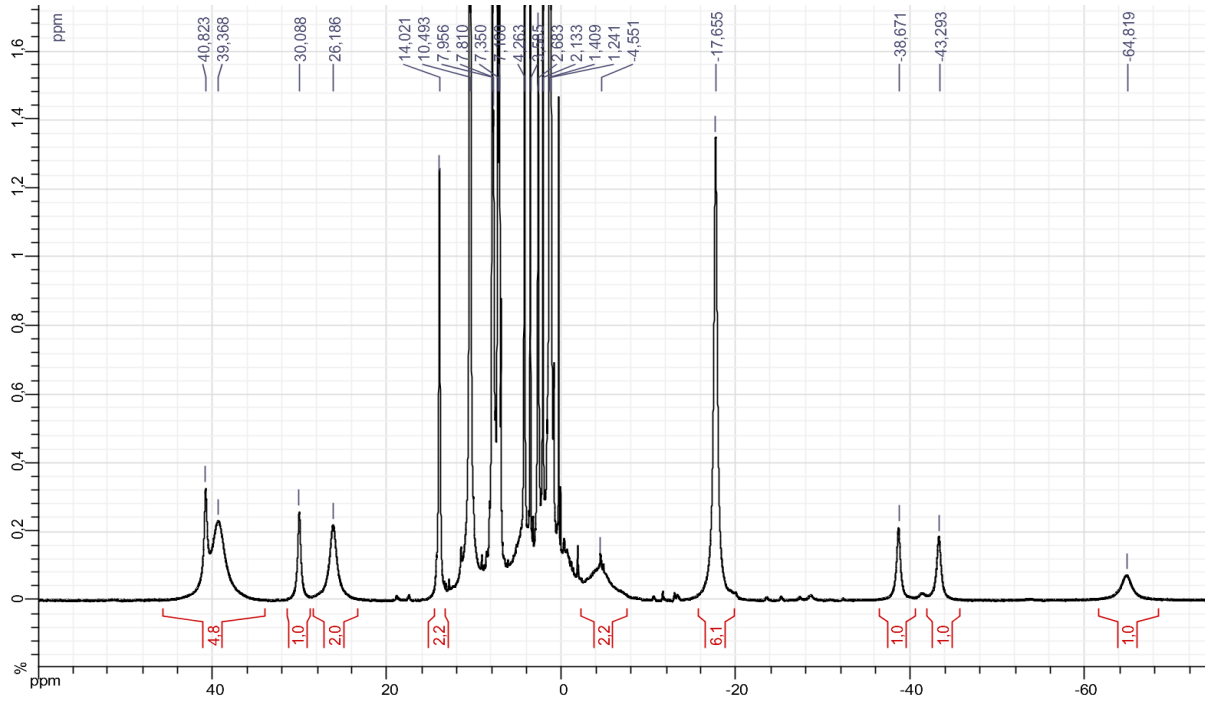


Figure S9. ^{1}H NMR spectrum of paramagnetic **2** in C_6D_6 (baseline correction using the 'spline' mode).

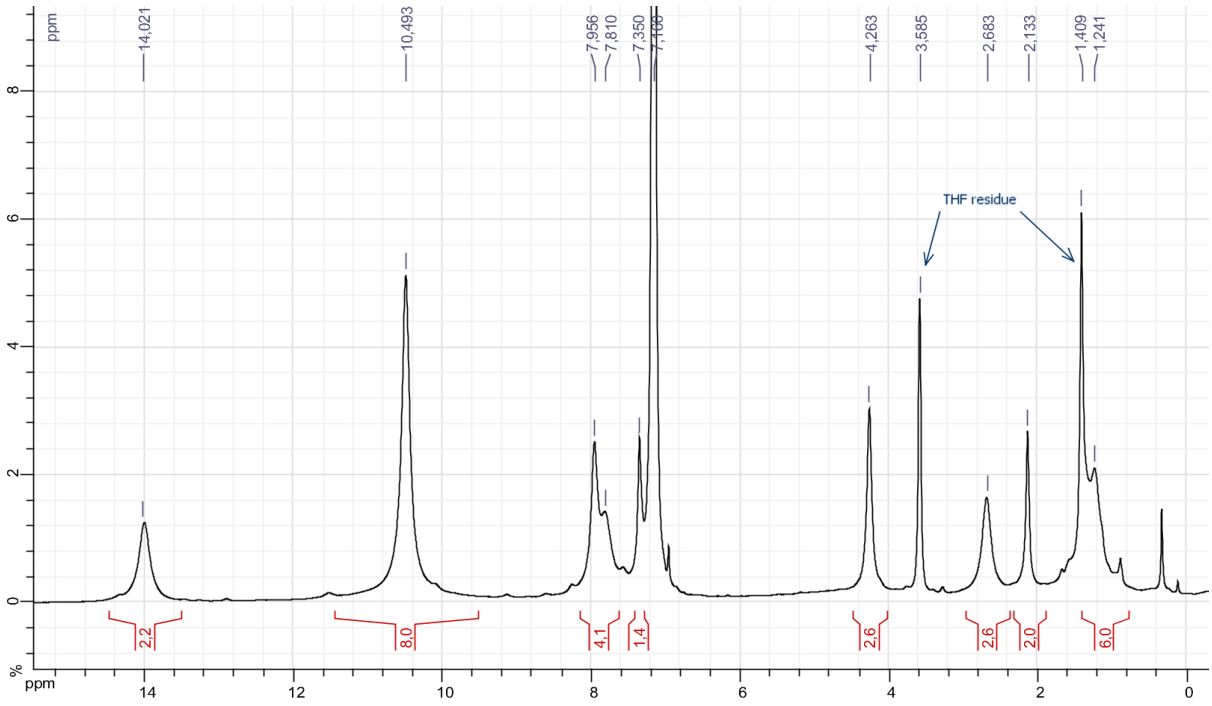


Figure S10. Detail of the region δ 15 – 0 ppm in the ^{1}H NMR spectrum of **2** in C_6D_6 after baseline correction (residual protio solvent from C_6D_6 at δ 7.16). Some residual THF is present.

III.4. [Co(^{Cy}P*N$_a$C^{NHC})(N$_2$)] (3)

^{1}H NMR (500.13 MHz, C_6D_6)

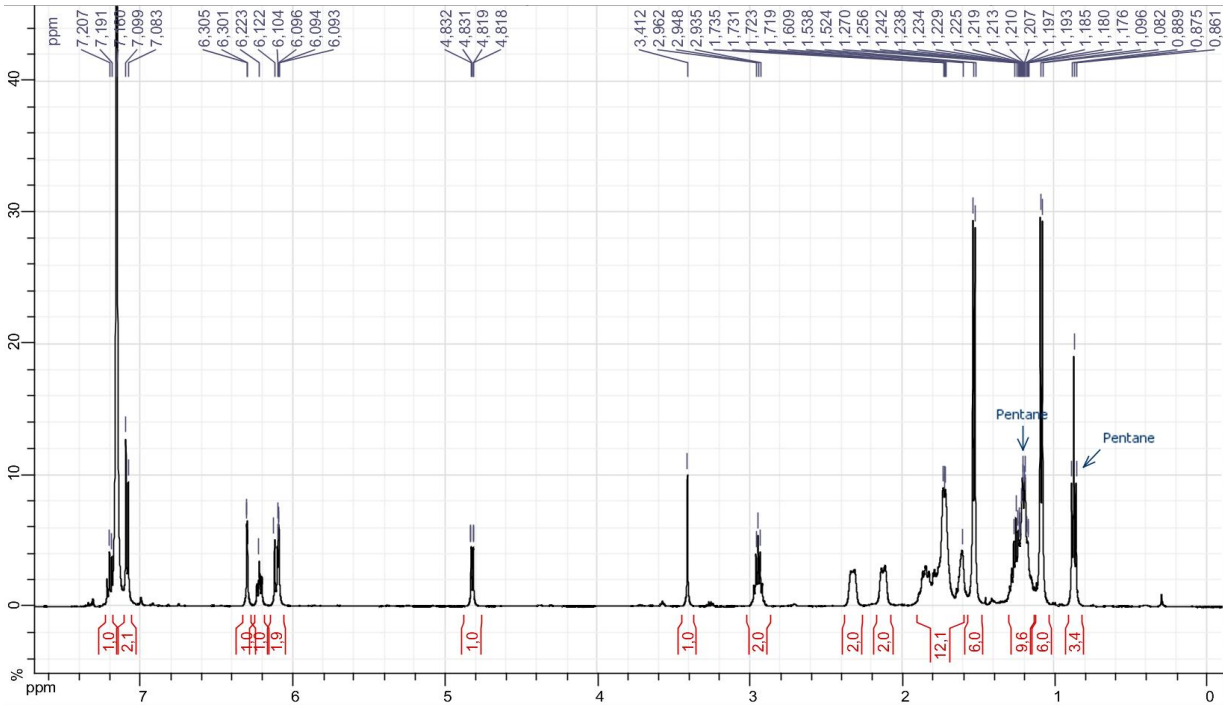


Figure S11. ^{1}H NMR spectrum of **3** in C_6D_6 (residual protio solvent from C_6D_6 at δ 7.16). Pentane originates from the crystals (half a molecule per complex, *cf*. section II.1).

$^{13}C\{^1H\}$ NMR (125.77 MHz, C_6D_6)

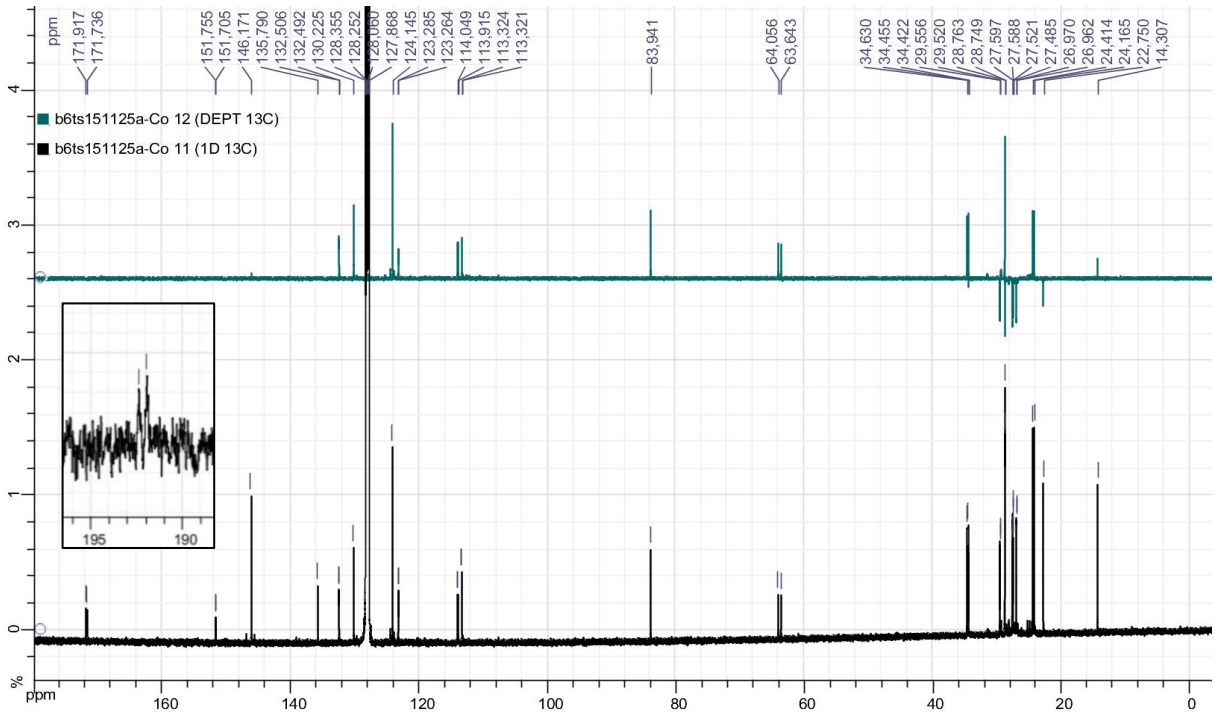


Figure S12. $^{13}C\{^1H\}$ (bottom) and ^{13}C-DEPT (top) NMR spectra of **3** in C_6D_6 (solvent signal at δ 128.06). Pentane originates from the crystals (half a molecule per complex, *cf*. section II.1). The inset shows the NHC carbene signal which is observed as a doublet due to the $^2J_{P\text{-}Co\text{-}C}$ coupling.

$^{31}P\{^1H\}$ NMR (161.98 MHz, C_6D_6)

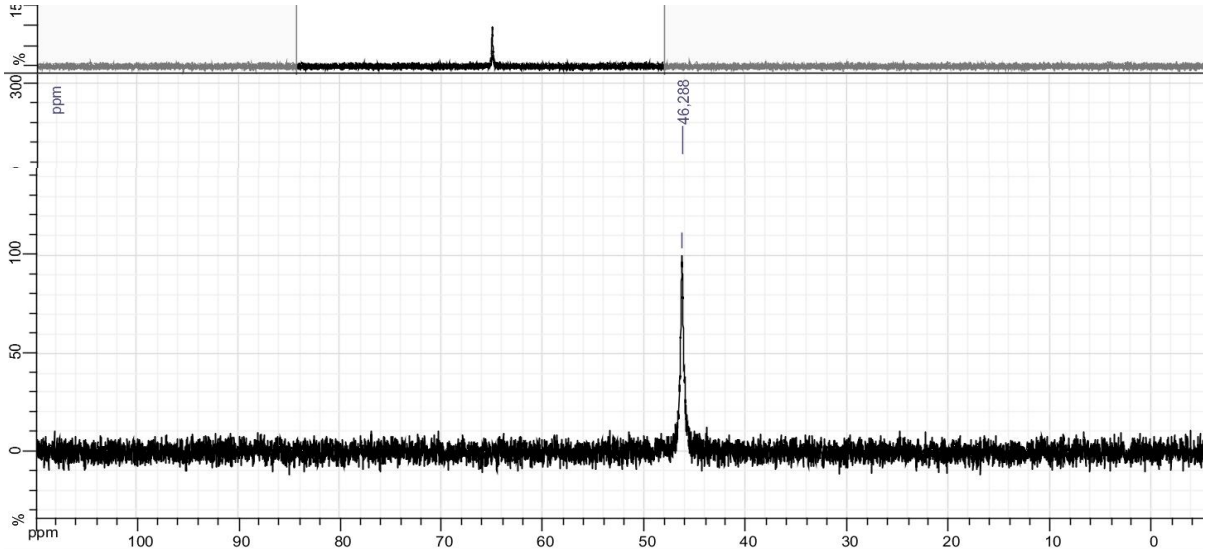


Figure S13. $^{31}P\{^1H\}$ NMR spectrum of **3** in C_6D_6.

III.5. $[Co\{^{Cy}P^*N_aC^{NHC}(Co[^{Cy}PNC^{NHC}])\}(N_2)]$ (4)

^{1}H NMR (500.13 MHz, C_6D_6)

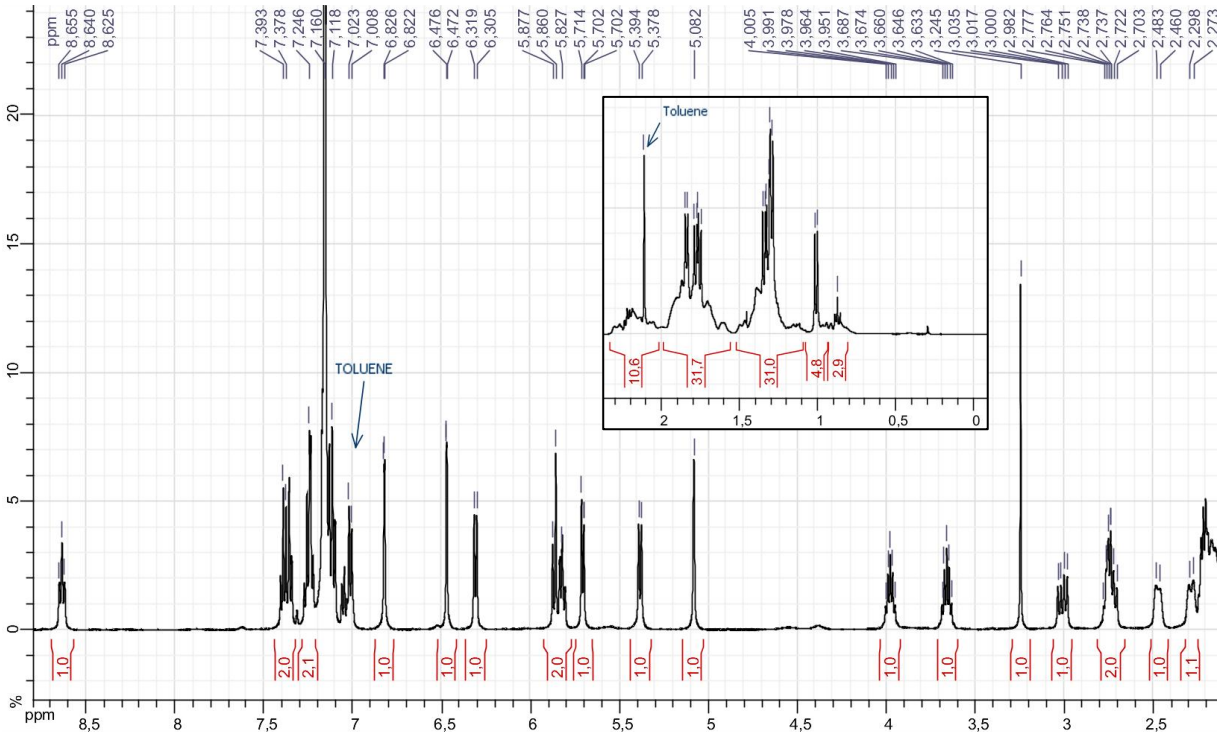


Figure S14. Detail of the region δ 8.8 – 2.2 ppm in the ^{1}H NMR spectrum of **4** in C_6D_6 (residual protio solvent from C_6D_6 at δ 7.16). The presence of toluene and pentane comes from the crystallisation solvents. The inset shows the region below 2.2 ppm.

^{13}C{^{1}H} NMR (125.77 MHz, C_6D_6)

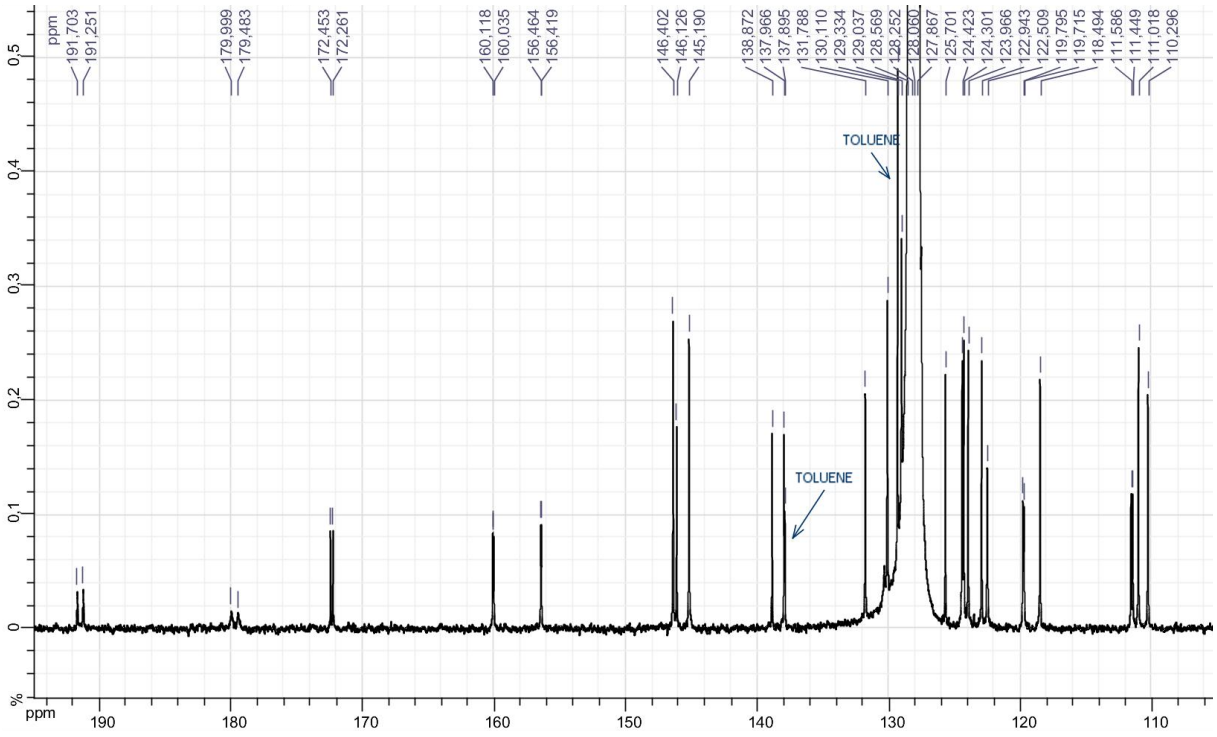


Figure S15. Detail of the region δ 195 – 105 ppm in the ^{13}C{^{1}H} NMR spectrum of **4** in C_6D_6 (solvent signal at δ 128.06). Toluene (δ 137.9, 129.3, 128.6) comes from the crystallisation solvent.

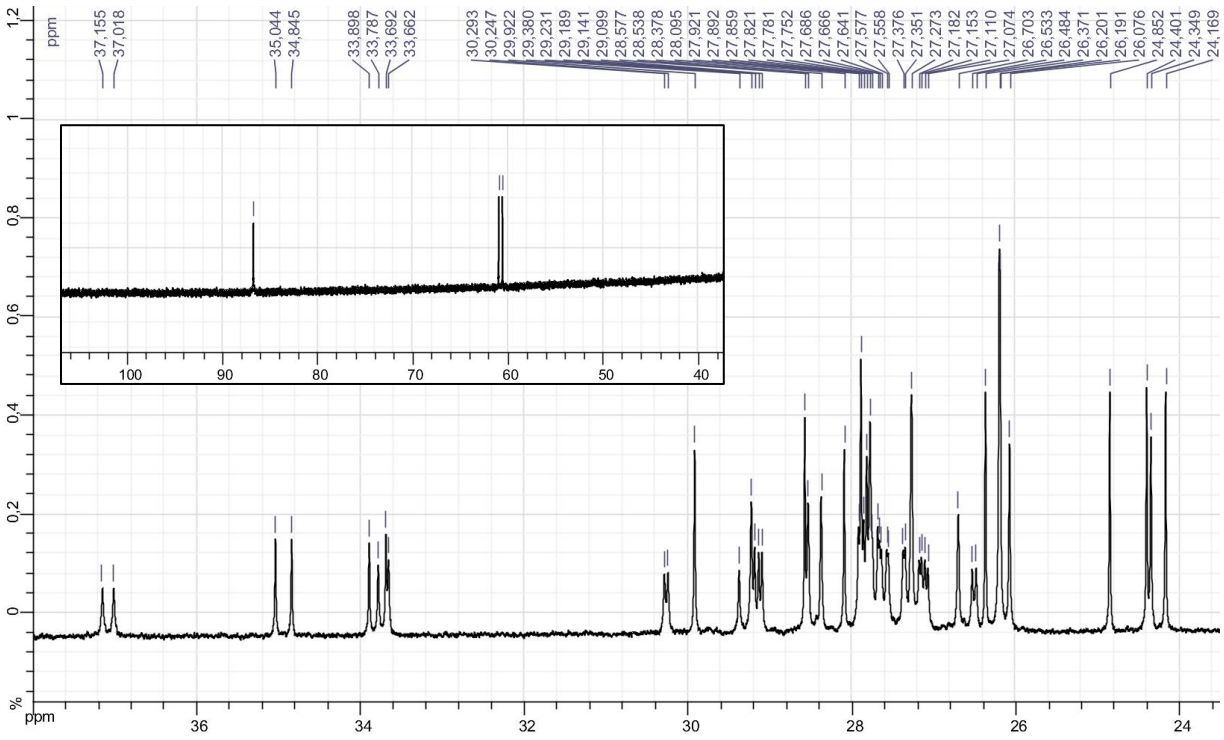


Figure S16. Detail of the region δ 38 – 22 ppm in the $^{13}C\{^1H\}$ NMR spectrum of **4** in C_6D_6. The inset shows the region δ 105 – 38 ppm.

$^{31}P\{^1H\}$ NMR (161.98 MHz, C_6D_6)

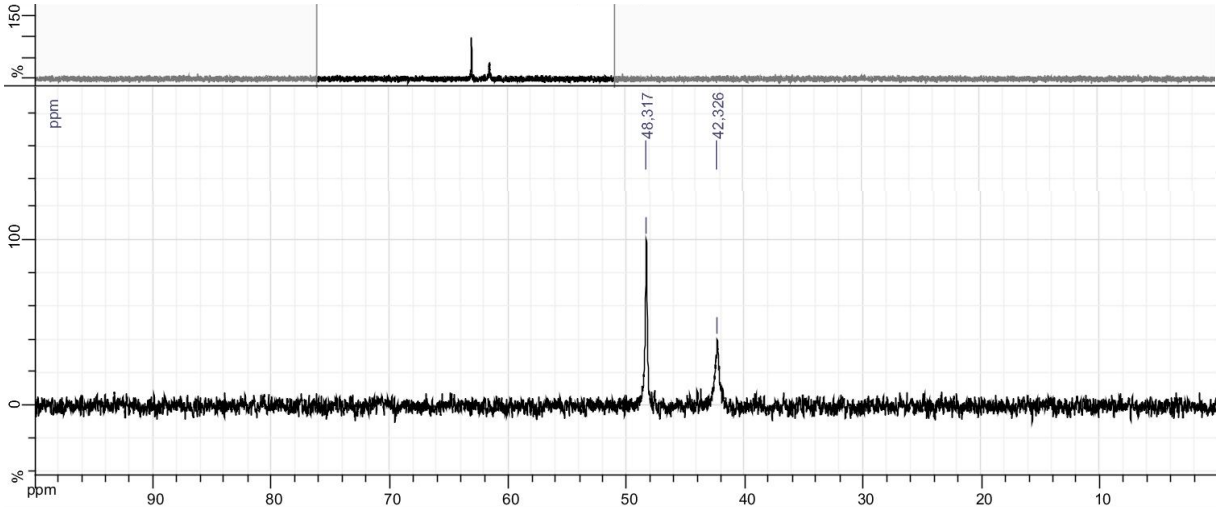


Figure S17. $^{31}P\{^1H\}$ NMR spectrum of **4** in C_6D_6.

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