SUPPORTING INFORMATION

Mono N-heterocyclic carbene amido and alkyl complexes. Cobalt mediated C-H activation and C-C coupling reactions involving benzyl ligands on a 3-coordinate intermediate

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References for the experimental part

1.1 General methods

Elemental analyses were carried out by the London Metropolitan University microanalytical laboratory. All manipulations were performed under N_2 in a Braun glovebox or under Ar using standard Schlenk techniques, unless stated otherwise. Solvents were dried by passing through alumina columns (pentane, toluene) or by distillation from sodium benzophenone ketyl (ether, THF) and kept under Ar over carefully activated sieves or K mirror until use. NMR solvents were dried and distilled from KH and stored in the glove box over activated molecular sieves. The starting materials were prepared according to the following procedures: [Co{N(SiMe$_3$)$_2$}$_2$],[1] [Co(SImes){N(SiMe$_3$)$_2$}Cl],[2] Imes, SImes, and IPr[3] [Mg(CH$_2$C$_6$H$_5$)$_2$(THF)$_2$].[4] The N, N'-dicyclohexyl acetamidine was prepared by the reaction of N, N'-dicyclohexylcarbodiimide with MeLi followed by aqueous work-up. It was purified by vacuum sublimation and stored in the glove box.

Synthetic procedures :

[Co(SIMes)Cl(μ-Cl)]$_2$: In toluene (10 ml) a mixture of $CoCl_2$ (0.12 g, 0.92 mmol) and SImes (0.28 g, 0.92 mmol) was stirred at 80 °C for 12 h. The blue green suspension was filtered and the product was crystallised by layering the toluene solution with pentane. Blue crystals were obtained in low yield that were characterised crystallographically as described below.

[Co(SIPr)Cl(μ-Cl)]$_2$: Prepared in an analogous way to **[Co(SIMes)Cl(μ-Cl)]$_2$.** The blue green crystals were characterised crystallographically as described below.

Complex 2b: In the glove box, a mixture of [Co(SImes){N(SiMe$_3$)$_2$}Cl] (0.55 g, 0.99 mmol) and the amidine (0.21 g, 0.99 mmol) were dissolved in toluene in a

Schlenk tube. The tube was taken out and heated at 90 °C for 2 h when the colour changed from emerald green to yellow green and a precipitate of the same colour started appearing. Additional toluene was added and the mixture was heated to reflux until all solids went into solution. The yellow-green solution was allowed to cool down to room temperature very slowly affording long olive green air sensitive needles. Yield: 0.45 g, (*ca.* 72%). Analysis: Calcd. for $C_{35}H_{51}ClCoN_4$·toluene: C, 70.26; H, 8.33; N, 7.84. Found: C, 69.32; H, 8.10; N, 7.38.

Complex 3b: In the glove box, to a solution of [Co(SImes){N(SiMe$_3$)$_2$}Cl] (0.61 g, 1.0 mmol) in toluene (20 ml) was added di*iso*propylaniline (0.16 g, 0.9 mmol). The green solution turned gradually purple and was stirred at room temperature for 36 h. To the reaction mixture was added an equal volume of pentane and left standing. After 24 h a small quantity of green crystals was formed (excess of Co staring material) and removed by filtration. The volatiles from the filtrate were removed under vacuum and the solid residue was extracted in ether (*ca*. 10 ml). To the filtered ether extracts was added pentane (*ca.* 10 ml) and the mixture was cooled at 4 °C for 5 days to give purple, very air sensitive crystals. Yield: 0.32 g, *ca.* 52%. Analysis: Calcd. for $C_{66}H_{88}Cl_2Co_2N_6\cdot C_4H_9O$: C, 68.45; Cl, 5.77; Co, 9.47; H, 8.04; N, 6.84. Found: C, 67.82; H, 7.95; N, 6.58.

Complex 4: To a mixture of [CoBr$_2$(THF)$_2$] (0.36 g, 1.0 mmol) and IPr (0.35 g, 0.9 mmol) at -78 °C was added precooled THF (*ca*. 40 ml). To the green-blue reaction mixture was added dropwise a solution of Mg(benzyl)$_2$(THF)$_2$ (0.44 g, 1.25 mmol) in THF (10 ml) and dioxan (2 ml). After completion of the addition the reaction mixture was allowed to reach room temperature slowly over 12 h. The colour of the reaction solution turned from torquoise-green to brown within the temperature range -20 – 0 °C. Evaporation of the volatiles, extraction of the residue into pentane (*ca*. 100ml), filtration of the brown extracts through Celite, concentration to *ca.* 5 ml under reduced pressure and cooling (-35 °C) for 48 h gave red-brown air sensitive blocks of **4** as dioxane solvate. Yield: 0.22 – 0.27 g. 35 – 42 %. Analysis: Calcd. for $C_{41}H_{49}CoN_2 \cdot C_4H_8O_2$: C, 75.39; Co, 8.22; H, 8.01; N, 3.91; O, 4.46. Found: C, 75.11; H, 7.95 ; N, 3.85. ^{1}H-NMR (toluene-d^8) 22 °C: 7.50 (1H, br d) 7.20 (t, 2H, J = 7.2 Hz), 7.15 (d, 4H, J = 7.2 Hz), 6.85 (d, 1H, J = 7.5 Hz)), 6.83 (br t, 1H), 6.81 (br t, 1H), 6.51 (br, s, 2H), 5.48 (t, 2H, J = 5.8 Hz), 5.29 (d, 2H, J = 5.8 HZ), 3.30 (br m 4H, Pr^i partially overlapping with the dioxane CH_2 signals at δ 3.33), 3.10 (t, 1H, J = 4.1 Hz), 1.29 (d, 12H, J = 6.5 Hz), 1.17 (d, 2H, J = 6.4 = Hz), 1.01 (d, 12H, J = 6.4 Hz), 0.90 (t, 2H, J = 6.0 Hz)**.** The ^{1}H-NMR assignment is shown in Figure S1:

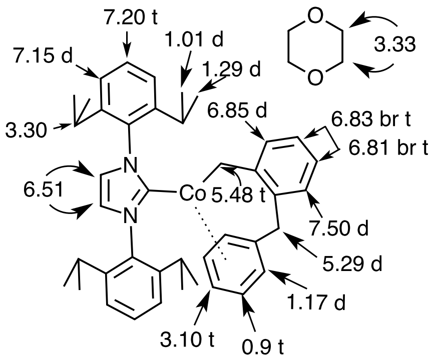

Figure S1. Assignment of the peaks in the ^{1}H-NMR spectrum of **4**.

$^{13}C\{^1H\}$-NMR (toluene-d^8): δ -12.39 (*ipso*-CH_2), 22.21 (CH*Me*$_2$), 25.49 (CH*Me*$_2$), 28.64 (*C*HMe$_2$), 38.02 (*C*H$_2$-linker), 67.17 (*C*H$_2$–dioxane), 68.15, 89.90, 90.25, 90.94, 120.95, 122.91, 123.62, 125.81, 125.87, 129.06, 138.41, 139.98, 146.10. 155.94, 195.10 (C_{NHC}).

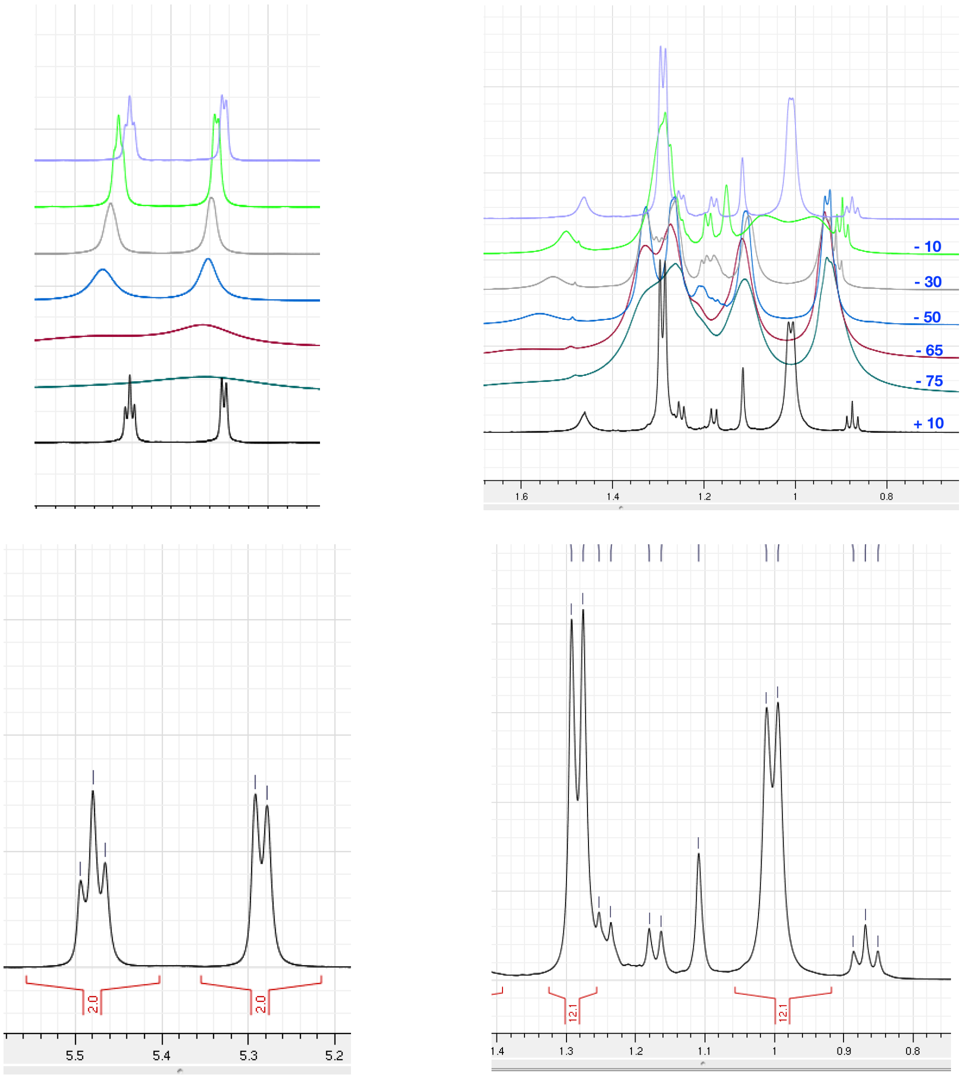

Figure S2. The appearance of the benzylic CH$_2$ and the *iso*propyl methyl regions in the VT ^{1}H-NMR spectrum of **4**: Left, benzylic region (top) and room temperature (bottom) ; right, isopropyl methyl region (top) and room temperature (bottom).

Crystallographic data

Summary of the crystal data, data collection and refinement for complexes **1a,** [Co(SIMes)Cl(μ-Cl)]$_2$, [Co(SIPr)Cl(μ-Cl)]$_2$, **2b, 3b** and **4** are given in Table S1. The crystals were mounted on a glass fiber with grease, from Fomblin vacuum oil.

Data sets for **1a**, [Co(SIMes)Cl(μ-Cl)]$_2$, [Co(SIPr)Cl(μ-Cl)]$_2$ were collected on a Enraf-Nonius Kappa CCD area detector diffractometer with an FR591 rotating anode (MoK$_a$ irradiation, λ = 0.71073 Å) and an Oxford Cryosystems low temperature device operating in ω scanning mode with ψ and ω scans to fill the Ewald sphere. Data for **2**, **4b** and **5a** were collected on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N$_2$ device, using Mo-Kα radiation (λ = 0.71073 Å). The programs used for control and integration of the data sets for **1a**, [Co(SIMes)Cl(μ-Cl)]$_2$, [Co(SIPr)Cl(μ-Cl)]$_2$ were Collect, Scalepack, and Denzo[5] while for **2b, 3b** and **4** was used the Bruker suite. All solutions and refinements were performed using the WinGX package[6] and all software packages within. The refinement and all further calculations were carried out using SHELXL-97.[7] The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2.

The crystals of **1a** and [Co(SIMes)Cl(μ-Cl)]$_2$ gave rise to a weak diffraction, especially at high angles and as a result the data quality suffered; initial collection as orthorhombic (*a* = 15.5266, *b* = 25.4401, *c* = 12.2303, α = 89.996, β = 89.985, γ = 90.008) did not provide a solution and another collection as monoclinic gave a useful data set. Although the data quality was not good, the models obtained showed adequately the atom connectivity within the asymmetric unit and provided a reasonable set of metrical data. In the structures of [Co(SIMes)Cl(μ-Cl)]$_2$ and **2b** residual electron density due to solvent in the asymmetric unit was impossible to model and therefore the PLATON SQUEEZE[8] algorithm was applied.

Table S1 X-ray data collection and refinement parameters for complexes **1a,** $[Co(SIMes)Cl(\mu\text{-}Cl)]_2$, $[Co(SIPr)Cl(\mu\text{-}Cl)]_2$, **2b, 3b** and **4**

	1a	$[Co(SIMes)Cl(\mu\text{-}Cl)]_2$	$[Co(SIPr)Cl(\mu\text{-}Cl)]_2$	**2b**	**3b**	**4**
Chemical formula	$C_{27}H_{42}ClCoN_3Si_2$	$C_{42}H_{52}Cl_4Co_2N_4$	$C_{54}H_{76}Cl_4Co_2N_4$	$C_{35}H_{51}ClCoN_4$	$C_{70}H_{96}Cl_2Co_2N_6$	$C_{43}H_5CoN_2O$
CCDC Number	918511	918512	918513	918514	918515	918516
Formula Mass	559.20	872.54	1040.85	622.18	1226.29	672.80
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	orthorhombic	Triclinic
a/Å	9.0310(4)	14.9613(4)	12.4957(5)	16.017(3)	17.3027(10)	10.8147(10)
b/Å	10.5956(5)	12.2767(3)	13.9842(8)	8.3798(15)	23.6427(14)	12.4360(12)
c/Å	16.4793(5)	14.9613(4)	16.6676(8)	28.990(6)	16.8268(10)	15.3783(15)
α/°	89.090(2)	90.00	90.00	90.00	90.00	73.166(2)
β/°	82.464(2)	117.21	95.676(3)	97.102(4)	90.00	82.284(2)
γ/°	85.249(2)	90.00	90.00	90.00	90.00	66.698(2)
Unit cell volume/Å^3	1557.87(11)	2443.94(11)	2898.3(2)	3861.2(13)	6883.6(7)	1817.7(3)
Temperature/K	120(2)	120(2)	120(2)	120(2)	120(2)	173(2)
Space group	*P-1*	*P 21/n*	*P21/n*	*P21/n*	*Pbcn*	*P -1*
Formula units / unit cell, Z	2	2	2	4	4	2
Absorption coefficient, μ/mm^{-1}	0.732	0.927	0.792	0.539	0.604	0.507
No. of reflections measured	14105	22146	15312	21869	72419	31806
No. of independent reflections	6842	4888	6615	5957	5251	7000
R_{int}	0.0853	0.0815	0.1392	0.0443	0.0782	0.0579
Final R_1 values ($I > 2\sigma(I)$)	0.0822	0.0729	0.0969	0.0773	0.0502	0.0581
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2579	0.2243	0.1702	0.2023	0.1080	0.1293
Final R_1 values (all data)	0.1010	0.0994	0.2580	0.1139	0.1015	0.1226
Final $wR(F^2)$ values (all data)	0.2768	0.2455	0.2519	0.2184	0.1331	0.1535
Goodness of fit on F^2	1.136	0.868	1.096	1.035	1.040	1.017

The Structure of 1a

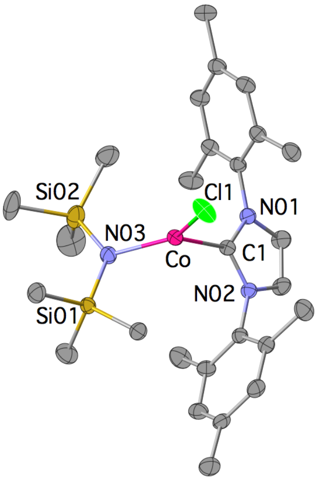

Figure S3 The structure of **1a**; ellipsoids are at 30% probability level. Selected bond lengths (Å) and angles [°]: C1 - N02 = 1.354(6), C1 - N01 = 1.360(6), C1 - Co = 2.054(4), Cl1 – Co = 1 2.2224(15), N03 - Co = 1.900(4), N03 - Co - C1 = 126.61(19), N03 - Co - Cl1 = 119.40(15), C1 - Co - Cl1 = 113.58(13), Si02 - N03 - Co = 112.7(2), Si01 - N03 - Co - 119.6(2).

The structure of [Co(SIMes)Cl(μ-Cl)]$_2$

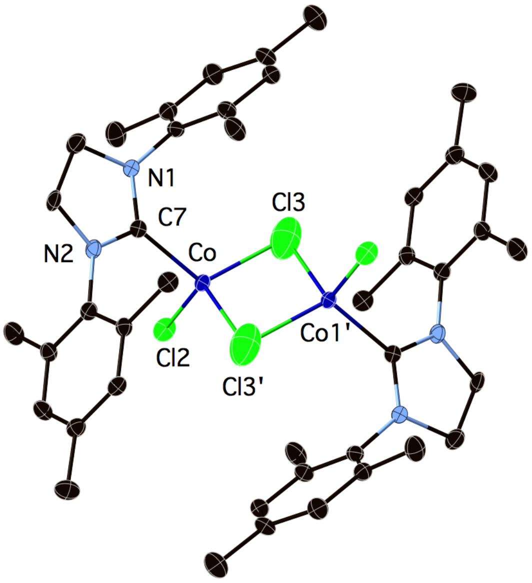

Figure S4 The structure of [Co(SIMes)Cl(μ-Cl)]$_2$; ellipsoids are at 30% probability level. Selected bond lengths (Å) and angles [°]: Co1 - C7 = 2.035(4), Co1 - Cl3 = 2.080(4), Co1 - Cl3' = 2.094(4), Co1 - Cl2 = 2.2553(13), Co1 - Co1' = 2.9513(11), C7 - Co1 - Cl3 = 113.00(15), C7 - Co1 - Cl3' = 113.83(14), Cl3 - Co1 - Cl3' = 90.01(17), C7 - Co1 - Cl2 = 111.57(12), Cl3 - Co1 - Cl2 = 114.58(10), Cl3' - Co1 - Cl2 = 112.30(10).

The structure of $[Co(SIPr)Cl(\mu\text{-}Cl)]_2$

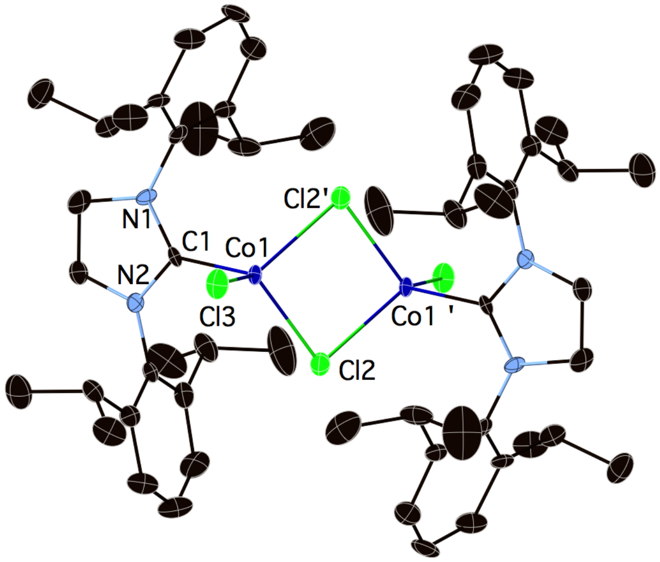

Figure S5 The structure of $[Co(SIPr)Cl(\mu\text{-}Cl)]_2$; ellipsoids are at 30% probability level. Selected bond lengths (Å) and angles [°]: C1 - Co1 = 2.041(6), Cl2 - Co1 = 2.306(2), Cl2’ - Co1 = 2.319(2), Cl3 - Co1 = 2.219(2), N2 - C1 - Co1 = 126.1(5), N1 - C1 - Co1 = 124.9(5), Co1 - Cl2 - Co1’ = 85.49(7), C1 - Co1 - Cl3 = 107.40(19), C1 - Co1 - Cl2’ = 115.24(19), Cl3 - Co1 - Cl2 = 112.50(8), C1 - Co1 - Cl2 = 115.55(18), Cl3 - Co1 - Cl2’ = 111.41(8), Cl2 - Co1 - Cl2’ = 94.51(7).

The structure of 2b

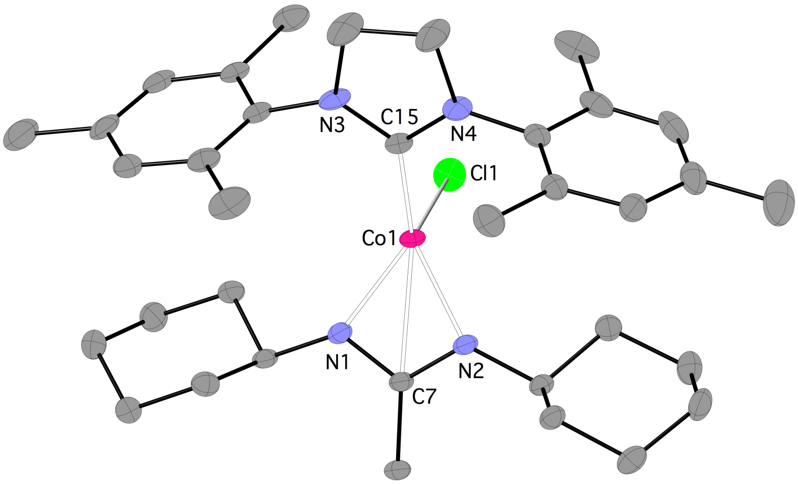

Figure S6 The structure of **2b**; ellipsoids are at 30% probability level. Selected bond lengths (Å) and angles [°]: Co1 - N1 = 2.033(3), Co1 - N2 = 2.039(3), Co1 -C15 = 2.054(4), Co1 - Cl1 = 2.2670(11), Co1 - C7 = 2.433(3), N1 - Co1 - N2 = 65.77(13), N1 - Co1 - C15 = 128.60(15), N2 - Co1 - C15 = 129.77(14), N1 - Co1 - Cl1 = 116.32(11), C15 - Co1 - Cl1 = 99.58(10), N1 - Co1 - C7 = 33.27(12), N2 - Co1 - C7 = 32.86(12), C15 - Co1 - C7 = 142.43(13), Cl1 - Co1 - C7 = 117.98(10), N2 - C7 - N1 = 112.7(3).

The structure of 3b

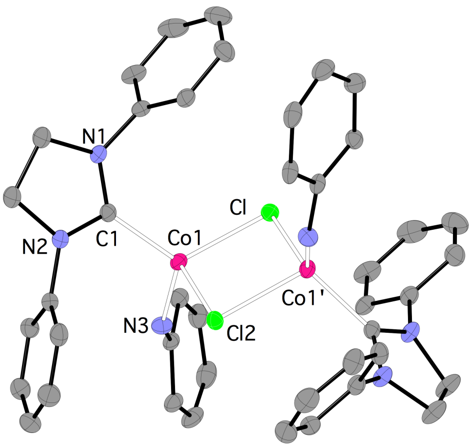

Figure S7 The structure of **3b**; ellipsoids are at 30% probability level. The methyl groups of the mesityl substituents of the SImes, the Pr^i groups of the arylamido bridges and one ether molecule of crystallisation in the asymmetric unit are omitted for clarity. Selected bond lengths (Å) and angles [°]: Co1 - N3 = 1.910(2), Co1 - C1 = 2.059(3), Co1 - Cl1 = 2.3435(8), Co1 - Cl2 = 2.3921(8), N3 - Co1 - C1 = 117.34(11), N3 - Co1 - Cl1 = 119.94(8), C1 - Co1 - Cl1 = 116.32(8), N3 - Co1 - Cl2 = 97.44(7), C1 - Co1 - Cl2 = 108.09(8), Cl1 - Co1 - Cl2 = 89.96(3).

The structure of 4

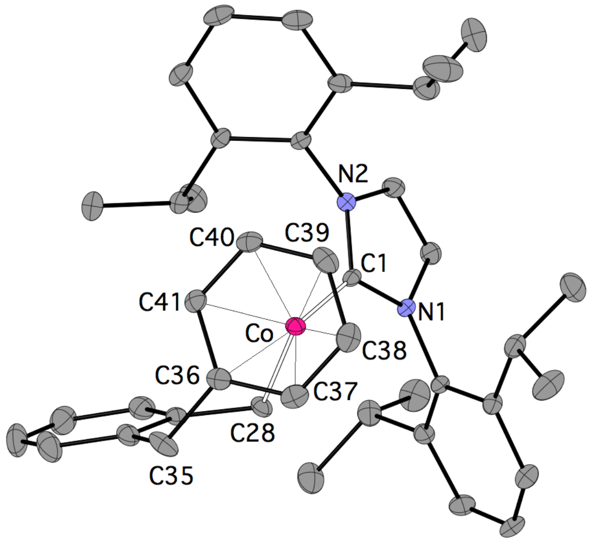

Figure S8 The molecular structure of **4**; ellipsoids are at 30% probability level; one molecule of crystallisation solvent dioxan in the asymmetric unit is omitted for clarity. Selected bond lengths (Å) and angles [°]; C1 - Co1 = 1.873(3), C28 - Co1 = 2.015(2), C36 - Co1 = 2.076(3), C37 - Co1 = 2.135(3), C38 - Co1 = 2.165(3), C39 - Co1 = 2.135(3), C40 - Co1 = 2.131(3), C41 - Co1 = 2.112(3), C1 - Co1 - C28 = 88.93(10), C1 - Co1 - C36 = 171.45(10), C28 - Co1 - C36 = 85.94(10), C1 - Co1 - C41 = 136.48(10), C28 - Co1 - C41 = 105.06(10), C36 - Co1 - C41 = 39.51(11), C1 - Co1 - C40 = 110.15(10), C28 - Co1 - C40 = 141.14(11), C36 - Co1 - C40 = 70.43(11), C41 - Co1 - C40 = 38.45(10), C1 - Co1 - C39 = 102.94(10), C28 - Co1 - C39 = 167.16(11), C36 - Co1 - C39 = 82.84(11), C41 - Co1 - C39 = 69.67(11), C40 - Co1 - C39 = 38.53(11), C1 - Co1 - C37 = 148.94(11), C28 - Co1 - C37 = 98.43(11), C36 - Co1 - C37 = 39.10(11), C41 - Co1 - C37 = 70.59(11), C40 - Co1 - C37 = 82.56(11), C39 - Co1 - C37 = 68.86(11), C1 - Co1 - C38 = 118.45(10), C28 - Co1 - C38 = 130.99(12), C36 - Co1 - C38 = 69.97(11), C41 - Co1 - C38 = 82.99(11), C40 - Co1 - C38 = 69.74(11), C39 - Co1 - C38 = 38.27(11), C37 - Co1 - C38 = 37.84(11).

References

(1) Andersen, R. A.; Faegri, K.; Green, J. C.; Haaland, A.; Lappert, M. F.; Leung, W. P.; Rypdal, K. *Inorg. Chem.* 1988, **27**, 1782.

(2) Danopoulos, A. A.; Braunstein, P.; Stylianides, N.; Wesolek, M. *Organometallics* 2011, **30**, 6514.

(3) Arduengo III, A. J.; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* 1999, **55**, 14523.

(4) Schrock, R. R. *J. Organomet. Chem.* 1976, **122**, 209.

(5) Otwinowski, Z.; Minor, W. In *Methods Enzymol.*; Charles W. Carter, Jr., Ed.; Academic Press: 1997; Vol. 276, p 307.

(6) Farrugia, L. *J. Appl. Crystallogr.* 1999, **32**, 837.

(7) Sheldrick, G. M.; University of Göttingen: Göttingen, 1999.

(8) Spek, A. *J. Appl. Crystallogr.* 2003, **36**, 7.