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Supplementary Information

Low-coordinate cobalt(II) terphenyl complexes: precursors to sterically encumbered ketones

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Supporting Information (7 pages)

Details of Synthesis and Characterising Data for 1, 3 and 4 and Refinement Details for 1, 3-2OEt2 and 4-0.75C6H14.

Synthesis and characterisation of 1, 3 and 4. S2
Refinement details for 1, 3-2OEt2 and 4-0.75C6H14. S5
References S7
Synthesis and Characterisation of 1, 3 and 4

General Procedures
All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk line or glove box techniques. Diethyl ether and THF were pre-dried over Na wire prior to distillation from Na/K alloy (diethyl ether) or sodium-benzophenone ketyl (THF). Diethyl ether was stored over a potassium mirror, THF was stored over activated 4 Å molecular sieves and both solvents were degassed prior to use. Benzene-$d_6$ was dried over potassium and degassed with three freeze-pump-thaw cycles prior to use. 2,6-Naph$_2$C$_6$H$_3$Li and CoBr$_2$(DME) were prepared by minor modification of literature methods.$^{1,2}$ All other reagents were used as received. Elemental microanalyses were performed by Mr Stephen Boyer at the Microanalysis Service, London Metropolitan University, UK. $^1$H and $^{13}$C($^1$H) NMR spectra were collected on Bruker AV3400 and AV3500 spectrometers. Chemical shifts are quoted in ppm relative to TMS. The magnetic moment for 1 was ascertained using Evans’ method at 298 K in benzene-$d_6$.\textsuperscript{3,4}

Synthesis and Characterisation of 1
A solution of 2,6-Naph$_2$C$_6$H$_3$Li (200 mg, 0.6 mmol) in diethyl ether (15 cm$^3$) was added dropwise to a stirred suspension of CoBr$_2$(DME) (92 mg, 0.3 mmol) in diethyl ether (15 cm$^3$) at $-78$ °C. The resulting mixture was stirred at this temperature for 3 hours during which a colour change from bright blue to green was observed. Slow warming of the solution to $-30$ °C and storage at this temperature yielded green crystals of 1 suitable for X-ray diffraction (179 mg, 83%). $^1$H NMR (400 MHz, C$_6$D$_6$, 298 K) $\delta = 1.28$ (s, br, $\Delta v_{1/2} = 32$ Hz), 2.17 (s, br, $\Delta v_{1/2} = 75$ Hz), 4.37 (s, br, $\Delta v_{1/2} = 179$ Hz). Elemental analysis calc’d for C$_{56}$H$_{44}$CoO: C 84.93, H 5.60; found 84.75, H 5.47. $\mu_{\text{eff}} = 4.35 \mu_B$. UV/vis (THF): strong absorption below 400 nm with peaks at $\lambda_{\text{max}}$/nm ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 478 (71), 560 (47), 616 (62) with shoulder at 628 (59), 726 (132) with shoulders at 761 (65).
Synthesis and Characterisation of 3

Numbering scheme for 3:

A green solution of 1 (40 mg, 0.5 mmol) in diethyl ether (20 cm$^3$) was exposed to an atmosphere of CO, whereupon an immediate color change to orange/red was observed. The solution was stirred at room temperature for a further 16 h, followed by controlled cooling to −30 °C, yielding colorless crystals of (2,6-Naph$_2$C$_6$H$_3$)$_2$CO (3) suitable for X-ray diffraction (23 mg, 67%). The formation of metal-containing by-product Co$_2$(CO)$_8$ was confirmed by $^{13}$C{$_1^H$} NMR and IR spectroscopy. $^1$H NMR (500 MHz, CDCl$_3$, 298 K) $\delta$ = 4.34 (d, $J$ = 6.95 Hz, 2H, H$_r$), 6.35 (t, $J$ = 7.55 Hz, 2H, H$_s$), 6.73 (d, $J$ = 7.45 Hz, 2H, H$_c$), 7.11 (d, $J$ = 8.2 Hz, 2H, H$_y$), 7.14-7.18 (m, 4H, H$_o$ + H$_x$), 7.19-7.28 (m, 6H, H$_w$ + H$_e$ + H$_i$), 7.32-7.39 (m, 8H, H$_n$ + H$_t$ + H$_h$ + H$_d$), 7.55 (d, $J$ = 8.00 Hz, 2H, H$_v$), 7.59 (t, $J$ = 7.40 Hz, 2H, H$_m$), 7.80 (d, $J$ = 8.20 Hz, 2H, H$_j$), 7.99 (d, $J$ = 8.05 Hz, 2H, H$_l$). $^{13}$C{$_1^H$} NMR (126 MHz, CDCl$_3$, 298 K) $\delta$ = 123.7 (C$_r$), 124.1 (C$_s$), 124.8 (C$_w$), 125.0 (C$_t$), 125.2 (C$_x$), 125.7 (C$_h$), 126.0 (C$_m$), 126.4 (C$_y$), 126.5 (C$_o$ + C$_i$), 126.7 (C$_a$), 127.3 (C$_j$), 127.7 (C$_v$), 128.2 (C$_l$), 129.4 (C$_d$), 131.8 (C$_c$ and C$_e$), 132.7 (C$_u$), 133.4 (C$_k$), 133.8 (C$_z$), 134.0 (C$_p$), 138.2 (C$_q$), 138.6 (C$_p$), 139.0 (C$_f$), 140.7 (C$_b$), 141.6 (C$_a$), 193.2 (C=O). Elemental analysis calc’d for C$_{53}$H$_{34}$O: C 92.68, H 4.99; found 92.77, H 4.77. IR (ATR) $\nu$/cm$^{-1}$: 2963 (wk), 1710 (wk, C=O stretch), 1670 (wk), 1390 (wk), 1260 (st), 1235 (md br), 1087 (st), 1019 (st), 920 (wk), 847 (wk), 796 (st), 775 (md). EI-MS:
M⁺ = 686 (13%), fragment ion peaks at m/z 357 [(M – 2,6-Naph₂C₆H₃)⁺, 11], 341 [(M – 2,6-Naph₂C₆H₃O)⁺, 100], 326 [(2,6-Naph₂C₆H₃)⁺, 6%]; exact mass: calc. 686.2604, found 686.2592.

**Synthesis and Characterisation of 4**

Numbering scheme for 4:

A claret red solution of (2,6-Mes₂C₆H₃)₂Co (2) (30 mg, 0.44 mmol) in hexane (20 cm³) was exposed to an atmosphere of dry CO at room temperature, causing an immediate colour change to deep orange. After stirring at room temperature for a further 16 h, controlled cooling of a saturated hexane solution to -30 °C afforded colourless X-ray quality crystals of 4 (21 mg, 72 %). Formation of the metal-containing by-product Co₂(CO)₈ was confirmed by ¹³C{¹H} NMR and MS analysis. ¹H NMR (400 MHz, CDCl₃, 298 K) δ = 1.80 (s, 3H, Me₉), 1.82 (s, 3H, Me₈), 2.11 (br s, 3H, Me₇), 2.18 (s, 6H, Me₆), 2.22 (br s, 3H, Me₅), 2.29 (s, 12H, Me₄), 2.31 (s, 6H, Me₃), 3.36 (s, 1H, H₉), 5.75 (s, 1H, H₈), 6.89 (s, 2H, H₇), 6.93 (s, 4H, H₆), 7.03 (d, J = 7.30 Hz, 1H, H₅), 7.13 (d, J = 7.70 Hz, 2H, H₄), 7.44 (t, J = 7.60 Hz, 1H, H₃), 7.56 (dd, J = 7.90 Hz, 1H, H₂), 7.63 (d, J = 7.90 Hz, 1H, H₁). ¹³C{¹H} NMR (100 MHz,
Refinement Details and Structural Data for 1, 3-2OEt₂ and 4·0.75C₆H₁₄

Crystals of 1, 3-2OEt₂ and 4·0.75C₆H₁₄ were mounted on a dual-stage glass fibre using YR-1800 perfluoropolyether oil and cooled rapidly to 90 K in a stream of cold nitrogen using an Oxford Cryosystems low-temperature device. Data for compounds 1, 3-2OEt₂ and 4·0.75C₆H₁₄ were collected on a SMART APEX diffractometer equipped with a graphite-monochromated Mo-Κα radiation source (λ = 0.71073 Å). Absorption corrections were applied using a multiscan method (SADABS). All non-H atoms were located using direct methods and difference Fourier syntheses. All fully occupied non-H atoms were refined with anisotropic displacement parameters. In the case of 1 the diethyl ether ligand was disordered over two positions; the occupancies were competitively refined to a 58:42 ratio, and chemically equivalent bond geometries were restrained to be approximately equal. A global rigid bond restraint was applied to the anisotropic displacement parameters of all atoms. In the case of 3-2OEt₂ the C(58) C(59) O(3) C(60) C(61) atoms of the diethyl ether lattice molecule were disordered over two positions; the occupancies were competitively refined to a 61:39 ratio, chemically equivalent bond geometries were restrained to be approximately equal and rigid bond restraints were applied to the displacement parameters of these atoms. Furthermore, the displacement parameters for atoms C(58) C(59) C(58a) C(59a) C(60a) and C(61a) were refined isotropically as sensible anisotropic displacement parameters could not be attained. For 4·0.75C₆H₁₄, the solvent region could not be modelled in terms of discrete

CDCl₃, 298 K) δ = 20.2 (Me₆), 20.4 (Me₆), 20.8 (Me₆), 20.9 (Me₆), 20.9 (Me₆), 22.6 (Me₆), 24.7 (Me₆), 55.4 (C₆), 58.9 (C₆), 126.0 (C₆), 127.1 (C₆), 127.7 (C₆), 127.8 (C₆), 127.9 (C₂), 128.3 (C₆), 128.3 (C₂), 129.2 (C₂), 130.0 (C₂), 131.3 (C₂), 132.3 (C₂), 132.5 (C₂), 132.8 (C₂), 133.5 (C₂), 133.9 (C₂), 134.5 (C₂), 136.0 (C₂), 137.1 (C₂), 137.8 (C₂), 140.6 (C₂), 188.9 (C₆=O), 191.4 (C=O). Elemental analysis calc’d for C₅₀H₅₀O₂: C 87.93, H 7.38; found 87.71, H 7.23. IR (nujol mull) ν/cm⁻¹: 2726 (wk), 1717 (wk, C=O stretch), 1673 (wk, C=O stretch), 1261 (wk), 1094 (wk br), 1020 (wk br), 797 (wk), 786 (wk), 771 (md), 722 (md), 690 (wk), 668 (wk). EI-MS: M⁺ = 682 (2%), fragment ion peaks at m/z 654 [(M – 2Me)⁺, 3%], 636 [(M – 3Me)⁺, 4%], 626 [(M – 4Me)⁺, 30%], 341 [(2,6-Mes₂C₆H₄CO)⁺, 90%], 207 [(M - Mes₂C₆H₄CO – Mes – Me)⁺, 10%], 341 [Mes⁺, 9%]; exact mass: calc. 682.3811, found 682.3988.
atomic sites, so PLATON SQUEEZE was used to model the contribution of the diffuse hexane solvent to the diffraction pattern and thereby produce a set of solvent-free diffraction intensities which were used for all subsequent refinement. The analysis gave a solvent volume of 427 cubic Angstroms and the electron count/cell was 75. The number of molecules of hexane per cell was calculated to be 1.5 and these are included in the chemical formula and in all quantities calculated from it. CCDC-861639, -861640 and -XXXXXX contain the supplementary data for 1, 3·2OEt₂ and 4·0.75C₆H₁₄, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for 1, 3·2OEt₂ and 4·0.75C₆H₁₄

Crystal data for 1: C₅₆H₄₄CoO, \(M_r = 791.84\), orthorhombic, space group \(Pbca\), \(a = 18.633(6)\), \(b = 17.515(5)\), \(c = 25.292(8)\), \(V = 8255(4) \text{ Å}^3\), \(Z = 8\), \(\rho_{\text{calcd}} = 1.274 \text{ g cm}^{-3}\), \(\mu = 0.457 \text{ mm}^{-1}\), \(T = 90 \text{ K}\), crystal size 0.19 x 0.13 x 0.06 mm³. 40556 reflections measured (7259 unique, \(R_{\text{int}} = 0.083\)), refinement by full-matrix least-squares on \(F^2\), data / parameters = 5060 / 573, GOF on \(F^2 = 1.05\), final \(R_1\) \([I > 2\sigma(I)] = 0.0627\), \(wR_2\) (all data) = 0.128, difference Fourier extrema ±0.52 eÅ⁻³.

Crystal data for 3·2OEt₂: C₅₃H₃₄O·2C₄H₁₀O, \(M_r = 835.04\), monoclinic, space group \(P2_1/c\), \(a = 13.933(3)\), \(b = 18.322(4)\), \(c = 19.888(4)\), \(\beta = 104.637(4)\)°, \(V = 4912.4(17) \text{ Å}^3\), \(Z = 4\), \(\rho_{\text{calcd}} = 1.129 \text{ g cm}^{-3}\), \(\mu = 0.068 \text{ mm}^{-1}\), \(T = 90 \text{ K}\), crystal size 0.2 x 0.17 x 0.1 mm³. 22879 reflections measured (8569 unique, \(R_{\text{int}} = 0.093\)), refinement by full-matrix least-squares on \(F^2\), data / parameters = 5115 / 599, GOF on \(F^2 = 1.13\), final \(R_1\) \([I > 2\sigma(I)] = 0.107\), \(wR_2\) (all data) = 0.240, difference Fourier extrema ±0.41 eÅ⁻³.

Crystal data for 4·0.75C₆H₁₄: C₅₄.5H₆₀.5O₂, \(M_r = 747.53\), triclinic, space group \(P-1\), \(a = 12.8018(9)\), \(b = 13.2388(9)\), \(c = 13.6583(10)\), \(V = 2217.8(3) \text{ Å}^3\), \(Z = 2\), \(\rho_{\text{calcd}} = 1.023 \text{ g cm}^{-3}\), \(\mu = 0.061 \text{ mm}^{-1}\), \(T = 90 \text{ K}\), crystal size 0.12 x 0.10 x 0.06 mm³. 19501 reflections measured (9934 unique, \(R_{\text{int}} = 0.0695\)), refinement by full-matrix least-squares on \(F^2\), data / parameters = 9934 / 481, GOF on \(F^2 = 1.070\), final \(R_1\) \([I > 2\sigma(I)] = 0.0695\), \(wR_2\) (all data) = 0.1793, difference Fourier extrema ±0.53 eÅ⁻³.
References