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DALTON COMMUNICATION

High-nuclearity cobaltadendrimers

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New dendritic polyalkynes have been prepared and reacted with $[Co_2(CO)_8]$ to give cobaltadendrimers containing up to 40 cobalt atoms.

Metalladendrimers are of intrinsic structural and synthetic interest[1–3] and offer potential applications as light-collecting devices, information storage devices and polyfunctional catalysts. We have prepared compounds in which the metals are part of the backbone dendritic connectivity,[1] or in which they decorate the dendrimer.[4] The generation of $C_2Co_2(CO)_6$ clusters from alkynes is a facile method for the introduction of multiple metal centres which has not been widely used in metalladendrimer chemistry.[5] We now report an extension of our previous work (which led to a starburst decorated with $C_2Co_2(CO)_6$ through to the third generation)[6] to genuinely dendritic systems.

Our synthetic strategy involves the preparation of a starburst or dendritic polyalkyne and post-functionalization with $[Co_2(CO)_8]$.[6] The doubly-protected compound **1** was prepared in 53% yield † by the sequential reaction of 1,3,5-tribromobenzene with two equivalents of (TIPS)C≡CH (TIPS = triisopropylsilyl) and a three-fold excess of (TMS)C≡CH (TMS = trimethylsilyl) in each case in the presence of $[(Ph_3P)_2PdCl_2]$, CuI and NEt_3, followed by alkaline cleavage of the TMS group. The use of the base-stable TIPS protecting group is critical to the success of this strategy and allows the preparation of asymmetrically substituted derivatives. The reaction of $C(p\text{-}C_6H_4I)_4$[7] with an excess of **1** under similar palladium(II)-catalysed coupling conditions followed by deprotection of **2** with $[^nBu_4N]F$ in THF yielded the intensely luminescent (λ_{max} 352 nm) dendritic dodecaalkyne **3** as white crystals.‡ Upon stirring **3** with $[Co_2(CO)_8]$ in CH_2Cl_2, a dark coloured solution was obtained from which the dendritic tetracosacobalt complex **4** was isolated as deep red crystals in 28% yield.§

Linear extension of these systems proved to be facile. The reaction of the polyalkyne **3** with $p\text{-}IC_6H_4C{\equiv}C(TMS)$ under standard Pd-coupling conditions yielded the protected dendritic icosaalkyne **5** as yellow crystals. Subsequent basic deprotection gave icosaalkyne **6**, the reaction of which with an excess of $[Co_2(CO)_8]$ produced the deep red crystalline tetracontacobalt compound **7**¶ (Fig. 1). This latter compound and all others described were characterized by the normal spectroscopic and analytical methods adopted for 'small molecules' even though modelling indicates that **7** has a diameter of ≈35 nm.

We are currently investigating the chemical and structural aspects of these novel high-nuclearity species.

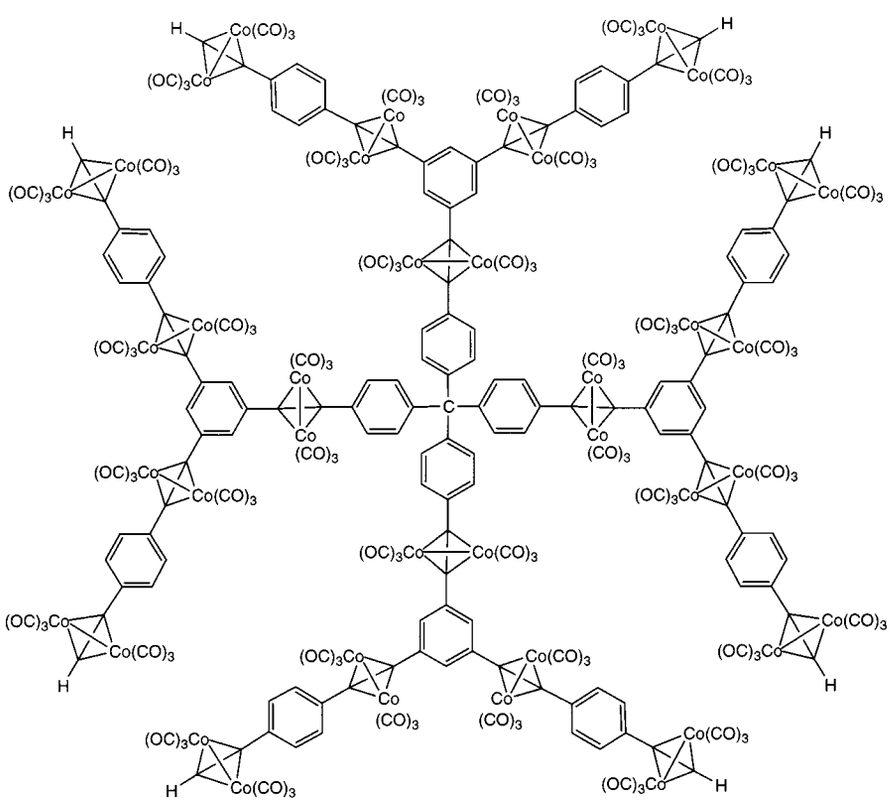

Fig. 1 Proposed structure of compound **7**.

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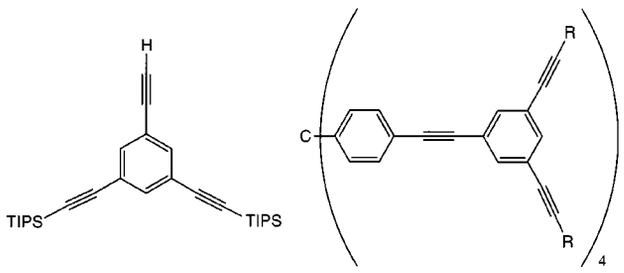


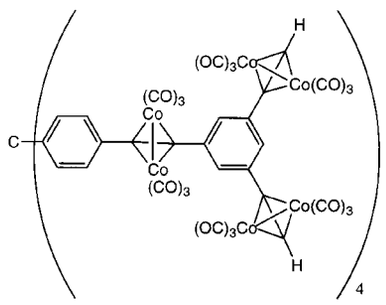
1

2 R = TIPS

3 R = H

5 R = 4-$C_6H_4C{\equiv}C$(TMS)

6 R = 4-$C_6H_4C{\equiv}CH$



4

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Notes and references

† **1**: 1,3,5-$Br_3C_6H_3$ (1.35 g, 4.28 mmol), (TIPS)C≡CH (1.64 g, 8.99 mmol), CuI (81.5 mg, 0.43 mmol) and $[(PPh_3)_2PdCl_2]$ (300 mg, 0.43 mmol) were stirred in NEt_3 (50 ml) for 4 h at 35 °C. Treatment with (TMS)C≡CH (1.26 g, 12.8 mmol) under analogous conditions to those described above (reaction time 12 h), followed by chromatographic work-up gave the protected intermediate; this was dissolved in THF (120 ml) and 1 M NaOH (150 ml) added; the solution stirred for 3.5 h. After extraction, the residue was purified by column chromatography to give a colourless oil (1.06 g; 53%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.52–7.50 (m, 3H, Ar), 3.08 (s, 1H, CC*H*), 1.12 (s, 42H, TIPS); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.2, 124.2, 122.6, 105.1, 92.4, 82.0, 78.3, 18.7 (TIPS), 11.3 (TIPS); MS (MALDI-TOF) *m/z* 502 $[M + K]^+$, 486 $[M + Na]^+$.

‡ **3**: compound **1** (0.37 g, 0.80 mmol), C(*p*-$C_6H_4I)_4$ (0.16 g, 0.19 mmol), CuI (10.8 mg, 0.06 mmol) and $[(Ph_3P)_2PdCl_2]$ (40.0 mg, 0.06 mmol) were stirred in NEt_3 (10 ml) and DMF (20 ml) for 70 h at 35 °C. Chromatographic work-up gave **2** as yellow crystals (0.35 g, 84.5%). Deprotection using $[^nBu_4N]F$ (1.60 mmol) in THF (50 ml, room temperature, 4 h) yielded **3** as white crystals (62 mg, 42%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* 1.4 Hz, 8H), 7.56 (t, *J* 1.5 Hz, 4H), 7.45 (d, *J* 8.6 Hz, 8H), 7.21 (d, *J* 8.5 Hz, 8H), 3.11 (s, 8H, CC*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 135.1, 131.3, 130.9, 124.0, 122.9, 120.8, 90.3, 87.9, 81.8, 78.5, 48.4; MS (MALDI-TOF) *m/z* 1828 $[2M]^+$, 914 $[M]^+$.

§ **4**: alkyne **3** (54.3 mg, 0.06 mmol) and $Co_2(CO)_8$ (0.49 g, 1.43 mmol) were stirred in CH_2Cl_2 (10 ml) for 1.5 h at room temperature, the solvent removed, and the residue purified by column chromatography to give a deep red crystalline solid (71.9 mg, 28%). IR (KBr disc, cm^{-1}) ν_{CO} 2093 s, 2055 vs, 2020 vs; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.67 (d, *J* 2.0 Hz, 8H), 7.57 (d, *J* 8.3 Hz, 8H), 7.50 (t, *J* 1.7 Hz, 4H), 7.18 (d, *J* 8.8 Hz, 8H), 6.37 (s, 8H, $H_{cluster}$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0 (CO), 145.7, 140.4, 139.3, 135.9, 131.7, 130.4, 129.2, 128.3, 91.4, 90.3, 88.5, 72.8, 64.8; MS (MALDI-TOF) *m/z* 4317 $[M - CO]^+$.

¶ **6** and **7**: alkyne **3** (62 mg, 68 μmol), *p*-$IC_6H_4C{\equiv}C$(TMS) (0.24 g, 0.82 mmol), CuI (10.4 mg, 0.05 mmol) and $[(PPh_3)_2PdCl_2]$ (38.1 mg, 0.05 mmol) were stirred in dry NEt_3 (5 ml) for 100 h at 39 °C. Chromatographic work-up gave compound **5** as yellow crystals (67 mg, 43%); it was dissolved in THF (30 ml), and 1 M NaOH (30 ml) added; the solution was stirred for 4 h. Water was added and after extraction with CH_2Cl_2, the residue was purified by column chromatography to give **6** as white crystals (21.3 mg, 43%). Reaction of **6** (15.4 mg, 8.98 μmol) with $[Co_2(CO)_8]$ under the same conditions as for **4** gave **7** as deep red crystals (27 mg, 41%). **6**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (br s, 12H), 7.48–7.46 (m, 40H), 7.24 (d, *J* 8.6 Hz, 8H), 3.19 (s, 8H, CC*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 134.3, 132.1, 131.5, 131.3, 130.9, 124.0, 123.8, 123.1, 122.3, 120.9, 90.3, 90.1, 89.6, 88.1, 83.1, 79.2; MS (MALDI-TOF) *m/z* 1713 $[M]^+$. **7**: IR (KBr disc, cm^{-1}) ν_{CO} 2091 s, 2055 vs, 2020 vs; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.79 (d, *J* 1.6 Hz, 8H), 7.72 (t, *J* 1.7 Hz, 4H), 7.62 (d, *J* 8.6 Hz, 8H), 7.56 (d, *J* 8.4 Hz, 16H), 7.48 (d, *J* 8.5 Hz, 16H), 7.24 (d, *J* 8.6 Hz, 8H), 6.46 (s, 8H, CC*H*); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 199.8 (CO), 199.4 (CO), 199.2 (CO), 146.2, 140.9, 140.6, 138.4, 137.9, 136.3, 131.9, 131.2, 129.9, 129.4, 128.8, 91.8, 91.7, 90.9, 90.8, 89.6, 73.4, 69.5; MS (MALDI-TOF) *m/z* 7298 $[M - 5CO]^+$, 7144 $[M - 10\ CO]^+$.

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