Divergent assembly of a starburst tetracosacobalt compound

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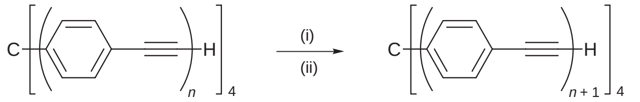
The syntheses of C[{p-$C_6H_4C{\equiv}C$}$_n$H]$_4$ (n = 1 ,2 ,3) and their reactions with $Co_2(CO)_8$ have led to the formation of starburst molecules with rigid, cluster-containing arms; up to twelve cluster units have been incorporated.

We are currently developing synthetic strategies for the preparation of monodispersed dendritic and starburst molecules containing metal centres,[1–3] with a view to developing novel materials. Here, we report initial studies on the synthesis of metal-rich species containing low oxidation state carbonyl clusters with precise spatial distribution. We hope to use molecules of this type, which exhibit distinct onion-like shells of 'organic' and 'inorganic' components, for the formation of metal oxide nanospheres with precise dimensions.

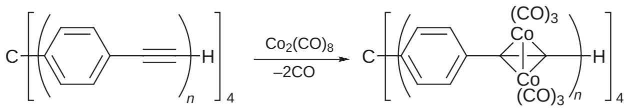
Very recently, there has been active interest in the use of multifunctional alkynes containing 1,3,5-triethynylbenzene



1 n = 1
2 n = 2

2 n = 1
3 n = 2

Scheme 1 *Reagents and conditions*: i, p-$IC_6H_4C{\equiv}CSiMe_3$; ii, NaOH (aq).



1 n = 1
2 n = 2
3 n = 3

4 n = 1
5 n = 2
6 n = 3

Scheme 2

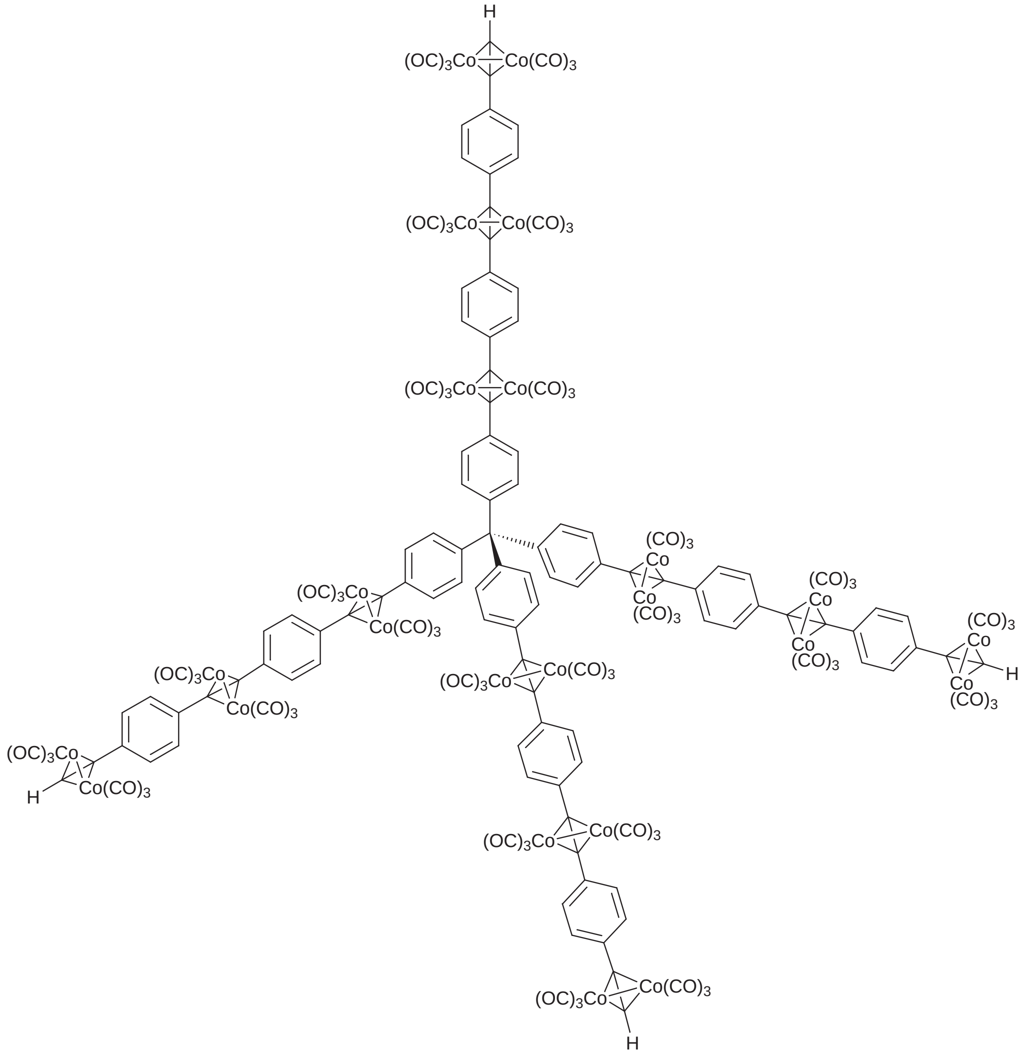


Fig. 1 Proposed structure of compound **6**.

cores as building blocks for starburst systems.[4–7] Here, we focus on multifunctional alkynes radiating from a tetrahedral carbon centre; the compound $C(p\text{-}C_6H_4I)_4$[8] has previously been recognised as a precursor for the assembly of nanostructures such as organometallic tripodaphyrins.[9,10] We report here the reaction of alkynes **1**–**3**, (prepared by a divergent strategy), with dicobalt octacarbonyl to give starburst molecules **4**–**6** which possess rigid, cluster-containing arms. The synthetic procedure may be extended to allow the incorporation of any desired number of alkyne substituents. Reactions between alkynes and $Co_2(CO)_8$ are well established, and provide a useful means of entry into this novel area.[11–13] More recently, Diederich and coworkers have shown that cyclic systems containing $\{C_2Co_2(CO)_6\}$ units are stabilised with respect to the corresponding polyalkynes.[14,15]

Compound **1** was prepared as previously reported,[8–10] and reaction of **1** with an excess of $Co_2(CO)_8$ gave **4** as a brown solid in 46% isolated yield after chromatographic purification.† The IR spectrum showed the expected absorptions in the carbonyl region. In the ^1H NMR spectrum, the change in the chemical shift of the alkyne proton from δ 3.06 in **1** to δ 6.37 in **4** was consistent with the incorporation of the RC≡CH group into a $Co_2(CO)_6(RCCH)$ cluster unit. Both the ^1H and ^{13}C NMR spectra were in accord with a symmetrical product, *i.e.* reaction of all four alkyne functionalities with $Co_2(CO)_8$ and this was supported by the observation in the MALDI-TOF mass spectrum of a parent ion corresponding to **4**.

Systematic growth of each polyyne chain from the carbon core of **1** was achieved‡ by sequential divergent reaction as shown in Scheme 1. Compounds **2** and **3** were characterised by NMR spectroscopy and mass spectrometry. Reaction of each alkyne generation with an excess of $Co_2(CO)_8$ (Scheme 2) gave moderately good yields of compounds **5** and **6**.§ The spectroscopic data for **5** and **6**, and mass spectrometric data for **6** (no parent ion could be obtained for **5**) were fully in accord with cluster formation at each of the alkyne functionalities of the respective precursors. ^{13}C NMR chemical shift correlations across the series of compounds **1**–**6** provided additional support for their formulation. A schematic representation of compound **6** is given in Fig. 1. In going from **3** to **6**, each carbon incorporated into a Co_2C_2-cluster core undergoes a change in local geometry and the C_{ring}–$C_{cluster}$–$C_{cluster}$–C_{ring} is no longer linear. Crystallographic determinations of $[1,4\text{-}\{Co_2(CO)_6CHC\}_2C_6H_4]$[16] and $[Co_2(CO)_6C_2Ph_2]$[17] show the C_{ring}–$C_{cluster}$–$C_{cluster}$ angles to be *ca.* 140°. We estimate from molecular modelling studies that the radius of compound **6** is in the range 1.6–2 nm.

We are currently extending these studies to higher generations and to the oxidative degradation of the compounds.

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Notes and references

† **4**: Alkyne **1** (19 mg, 0.046 mmol) and $Co_2(CO)_8$ (94 mg, 0.27 mmol) were stirred in CH_2Cl_2 (or acetone) for 1 h, the solvent removed, and the residue purified by column chromatography [SiO_2, hexane:CH_2Cl_2 (1 : 1)] to give a dark brown solid (33 mg, 46%). IR ($CHCl_3$, cm^{-1}) ν_{CO} 2092s, 2057vs, 2027vs. ^1H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, 8H, *J* 8.1 Hz), 7.22 (d, 8H, *J* 8.1 Hz), 6.37 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.4 (CO), 145.8, 135.5, 131.4, 129.5, 89.5 ($C_{cluster}$), 73.0 ($C_{cluster}$), 64.9 (C_{quat}); MS (MALDI-TOF) *m/z* 1532 $[M - CO]^+$.

‡ **2**: Alkyne **1** (83 mg, 0.20 mmol), $p\text{-}IC_6H_4C{\equiv}CSiMe_3$ (251 mg, 0.837 mmol), CuI (15 mg, 0.080 mmol) and $[(PPh_3)_2PdCl_2]$ (56 mg, 0.080 mmol) were stirred in dry, degassed NEt_3 (10 ml) under argon for 42 h at 41 °C. Chromatographic work-up [alumina, hexane–CH_2Cl_2 (4 : 1)] gave the TMS-protected intermediate as a yellow crystalline solid; it was dissolved in THF (30 ml), and 1 M NaOH (30 ml) added; the solution was stirred for 1 h at room temperature. Water was added and after extraction with CH_2Cl_2, the residue was purified by column chromatography [SiO_2, hexane–CH_2Cl_2 (1:1)] to give a yellow crystalline product (107 mg, 66 %). ^1H NMR (250 MHz, $CDCl_3$) δ 7.47–7.43 (m, 24H), 7.20 (d, 8H, *J* 8.3 Hz), 3.18 (s, 4H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 146.1, 132.1, 131.5, 131.2, 130.9, 123.6, 122.0, 121.1, 90.9 (C_{alkyne}), 89.3 (C_{alkyne}), 83.3 (C_{alkyne}), 78.9 (C_{alkyne}), 65.0 (C_{quat}); MS (MALDI-TOF) *m/z* 816 $[M]^+$, 614 $[M - 2C_6H_4CCH]^+$, 413 $[M - 4C_6H_4CCH]^+$.

3: Alkyne **2** (47 mg, 0.058 mmol), $p\text{-}IC_6H_4C{\equiv}CSiMe_3$ (72.5 mg, 0.242 mmol), CuI (4.4 mg, 0.023 mmol) and $[(PPh_3)_2PdCl_2]$ (16.2 mg, 0.023 mmol) were stirred in dry, degassed NEt_3 (5 ml) under argon for 12 h at 35 °C. Work-up similar to that for **2** gave a white crystalline solid (37 mg, 53 %). ^1H NMR (250 MHz, $CDCl_3$) δ 7.50–7.44 (m, 40H), 7.22 (d, 8H, *J* 8.3 Hz), 3.18 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.1, 132.1, 131.6, 131.5, 131.2, 130.9, 123.5, 123.3, 122.1, 121.2, 91.0 (C_{alkyne}), 90.9 (C_{alkyne}), 90.7 (C_{alkyne}), 89.6 (C_{alkyne}), 83.2 (C_{alkyne}), 79.0 (C_{alkyne}), 65.0 (C_{quat}); MS (MALDI-TOF) 1217 $[M]^+$, 915 $[M - \{C_6H_4C_2\}_3H]^+$, 613 $[M - 2\{C_6H_4C_2\}_3H]^+$.

§ **5** and **6**: As for **4**. Isolated yields of **5** and **6** were 26 and 45% respectively. **5**: IR ($CHCl_3$, cm^{-1}) ν_{CO} 2089s, 2057vs, 2028vs. ^1H NMR (250 MHz, $CDCl_3$) δ 7.60–7.29 (m, 32H), 6.39 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1 (CO), 145.7, 138.4, 137.3, 136.3, 131.6, 130.6, 129.6, 128.5, 91.7 ($C_{cluster}$), 91.3 ($C_{cluster}$), 89.1 ($C_{cluster}$), 72.8 ($C_{cluster}$), 65.0 (C_{quat}). **6**: IR (KBr pellet, cm^{-1}) ν_{CO} 2090s, 2052vs, 2020vs. ^1H NMR (300 MHz, $CDCl_3$) δ 7.61–7.31 (m, 48H), 6.40 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1 (CO), 145.7, 138.3, 138.1, 137.4, 136.3, 131.7, 130.7, 129.8, 129.7, 129.6, 128.6, 91.7 ($C_{cluster}$), 91.6 ($C_{cluster}$), 91.4 ($C_{cluster}$), 91.3 ($C_{cluster}$), 89.1 ($C_{cluster}$), 72.9 ($C_{cluster}$), 65.0 (C_{quat}); MS (MALDI-TOF) *m/z* 4653 $[M]^+$.

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