Metallostars: High-Nuclearity Linearly Developed Nanostructures Containing Multiple Cluster Motifs

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Abstract: Metallostars are complexes in which a single branching site bears a number of metallated arms. Although they are related to metallodendrimers, they have the advantage of being capable of extending in an unlimited sense; in contrast to metallodendrimers, steric interactions decrease with increasing generation number. In this paper a series of polyalkyne stars with four and six arms, based upon a single tetrahedral carbon core and a benzene core, respectively, are reported and their reactions with $[Co_2(CO)_8]$ to give metallostars that contain multiple $\{C_2Co_2(CO)_6\}$ motifs are described.

Keywords: cluster compounds • cobalt • dendrimers • metallodendrimers • metallostars

Introduction

The potential application of metallostars and metallodendrimers[1–3] containing large numbers of polymetallic units as catalysts and precursors for novel materials has prompted us to develop synthetic strategies that can be applied to both these classes of compound.[4–6] Whereas metallodendrimers possess multiple branching sites and cannot be extended beyond the Gennes limit, metallostars possess a single branching site from which arms can, in principle, be extended through unlimted generations. In both cases, divergent, multiple iterative synthesis may be utilized to sequentially grow the molecules out through increasing generations.

The metallostars that we are developing arise from the reaction of polyalkyne frameworks with dicobaltoctacarbonyl to give multiple $\{C_2Co_2(CO)_6\}$ cluster sites. The area of carbon-rich molecules is already well established, with supramolecular assemblies developed from C_6 cores being of particular interest.[7] Hexaethynylbenzene, prepared by alkyne coupling to hexabromobenzene, was reported fifteen years ago by Vollhardt, along with structural details of $C_6(C{\equiv}CSiMe_3)_6$.[8] The incorporation of organometallic domains into carbon-rich frameworks has recently been exploited by a number of groups,[9–18] and includes systematic molecular construction building out from 1,3,5-triethynylbenzene cores.[9–13, 18, 19]

In this paper we describe the extension of this methodology to the formation of a series of star compounds that contain tetrahedral carbon and C_6 cores, and which possess alkyne functionalities. The reactions of these compounds with $[Co_2(CO)_8]$ lead to metallostars that contain up to 24 cobalt atoms.

Results and Discussion

Tetrahedral carbon-centred stars—the polyalkyne precursors: The compound $C(4\text{-}IC_6H_4)_4$[20] has previously been used as a starting point for the assembly of nanostructures such as organometallic tripodaphyrins.[21, 22] By using $C(4\text{-}IC_6H_4)_4$ as a central building block, our aim was to use a divergent strategy to prepare multialkyne stars which could then be functionalized by using the well-tested reaction of an alkyne with dicobalt octacarbonyl [Eq. (1)].[23–25]

$$RC{\equiv}CR + [Co_2(CO)_8] \longrightarrow [Co_2(CO)_6RCCR] + 2\,CO \qquad (1)$$

Compound **1** was prepared by a literature method,[20–22] and spectroscopic data were in accord with those published. Each of the four arms in molecule **1** can be extended systematically as summarized in Scheme 1.

Compound **2** was isolated in 66% yield, and characterized by mass spectrometric and NMR spectroscopic methods.

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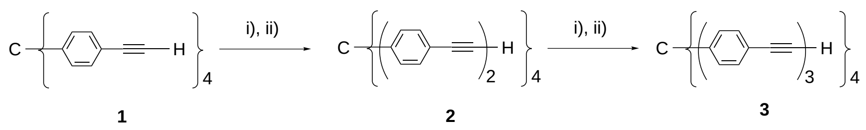
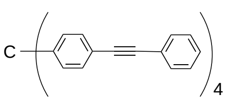


Scheme 1. i) p-$IC_6H_4C{\equiv}C(TMS)$. ii) NaOH (aq).

Spectroscopic data were consistent with the formation of a symmetrical product. This, and the observation of a parent ion in the MALDI-TOF mass spectrum at m/z 816, confirmed that all four arms of **1** had been extended to give compound **2**. A similar reaction was used to introduce another alkyne unit to each arm, converting compound **2** to **3**. A parent ion at m/z 1217 in the MALDI-TOF mass spectrum was consistent with the formation of **3**, and ^1H and ^{13}C NMR spectroscopic data were in accord with a symmetrical product.

Compounds **4** and **5** are remote functionalized first generation stars related to **1** and were both prepared from tetrakis(4-iodophenyl)methane. Coupling of $C(4\text{-}IC_6H_4)_4$ and $PhC{\equiv}CH$ in the presence of $[PdCl_2(PPh_3)_2]$, CuI and NEt_3 gave **4** in 33% yield. The MALDI-TOF mass spectrum shows a parent ion at m/z 720 consistent with the formulation of **4**. The ^{13}C and ^1H NMR spectroscopic data were also in accord with this symmetrical structure. Crystals of compound **4** suitable for X-ray diffraction were grown from CH_2Cl_2 layered with pentane. The molecular structure of one of the two independent molecules (differences between which are not chemically significant) is shown in Figure 1 and confirms the expected formulation of the tetrayne. Selected bond lengths are listed in Table 1. In each arm of the molecule, the two phenyl rings are related to one another by a twist angle of ≈51°.



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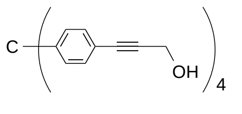

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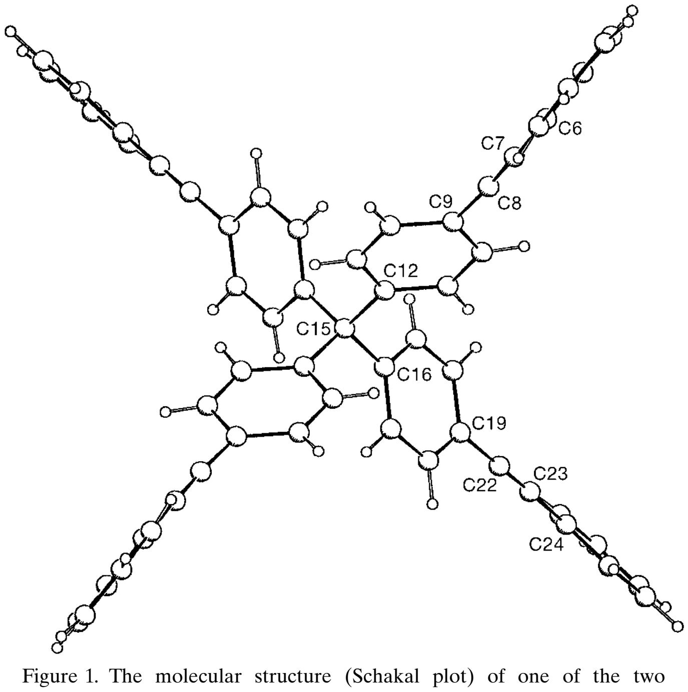


Figure 1. The molecular structure (Schakal plot) of one of the two crystallographically independent molecules of compound **4**.

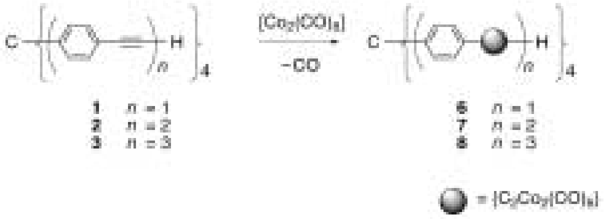
Table 1. Selected bond lengths [pm] in one of two independent molecules of compound **4**.

C15–C12	154.6(5)	C15–C16	155.6(5)
C8–C9	144.4(6)	C19–C22	145.8(7)
C7–C8	118.6(6)	C22–C23	116.9(6)
C6–C7	143.7(6)	C23–C24	144.1(7)

Coupling of $C(4\text{-}IC_6H_4)_4$ with $(TMS)OCH_2C{\equiv}CH$ followed by deprotection with base gave compound **5**, the mass spectrum of which exhibited a parent ion at m/z 536 consistent with the expected formulation. In the ^1H NMR spectrum, a triplet ($J = 6.0$ Hz) at $\delta = 5.33$ was assigned to the OH protons and a doublet ($J = 6.0$ Hz) at $\delta = 4.27$ to the methylene groups. Our interest in this tetrayne (and its organometallic derivatives) lies in its potential to form a hydrogen-bonded network although, to date, we have been unable to grow crystals of suitable quality to enable us to study the solid-state structure of compound **5**.

Compounds **1**, **2** and **3** form a series of polyalkynes that possess star motifs with linear arms, while **4** and **5** represent additional members of the first generation star family with pendant functionality. The next step in our strategy was to treat each polyalkyne with an excess of $[Co_2(CO)_8]$, thereby introducing organometallic domains into each arm of the star molecules.

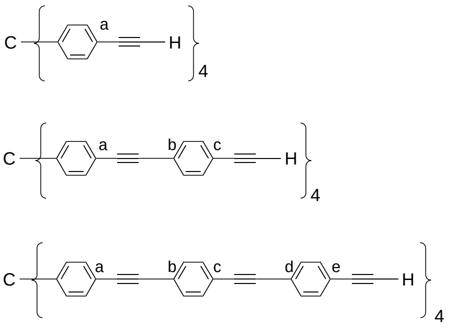
Tetrahedral carbon-centred metallostars—cobalt carbonyl derivatives: The reaction of **1** with a large excess of $[Co_2(CO)_8]$ (Scheme 2) proceeded smoothly to give **6** in 46% yield. The incorporation of the metal carbonyl units was confirmed by the appearance of strong absorptions in the IR spectrum at 2092, 2057 and 2027 cm^{-1}, typical of $[Co_2(CO)_6RCCR]$ clusters. In the ^{13}C NMR spectrum, a single signal at $\delta = 199.4$ was assigned to the carbonyl carbon atoms. That each alkyne group had been functionalized was evidenced by the appearance in the MALDI-TOF mass spectrum of a peak at m/z 1532 assigned to a parent ion with loss of one CO group. Confirmation of complete functionalization came from the ^1H and ^{13}C NMR spectroscopic data which revealed



Scheme 2.

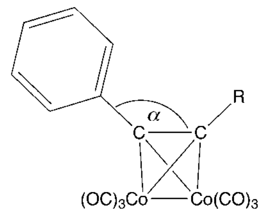
the presence in solution of a symmetrical product. In the ^{1}H NMR spectrum, a shift in the signal due to the terminal C-H proton from $\delta = 3.06$ in **1** to $\delta = 6.37$ in **8** was consistent with the coupling of the dicobalt carbonyl fragment to each alkyne moiety.

The reactions of **2** and **3** with an excess of $[Co_2(CO)_8]$ led to compounds **7** and **8** (26% and 45% yields, respectively) as shown in Scheme 2. The same characteristic pattern of IR spectroscopic bands in the carbonyl region were observed for both **7** and **8**, and a similar group of three absorptions to that described above for **6** was obtained. In the ^{13}C NMR spectra, signals assigned to the CO carbon atoms were observed at $\delta = 199.1$ both for **7** and **8**. For **7**, the ^{1}H NMR spectrum showed a singlet at $\delta = 6.39$ assigned to the terminal C-H proton of each arm; this signal had shifted from $\delta = 3.18$ in **2**. Similarly, the conversion of **3** to **8** was accompanied by a shift in this signal from $\delta = 3.18$ to 6.40. These data provided evidence that the outer generation of alkyne units in each of **2** and **3** had undergone reaction with $[Co_2(CO)_8]$. No analogous diagnostic label was available for the inner generations of alkyne. Here, the most informative data came from inspection of the ^{13}C NMR spectroscopic data. Although the shifts in the peaks assigned to the alkyne carbon atoms were too small to be useful in terms of confirming the formation of the Co_2C_2 units, those of the carbon atoms labelled Ca, Cb, Cc, Cd and Ce in Scheme 3 are highly diagnostic. On going from compound **1** to **6**, the signal for Ca shifts from $\delta = 121.3$ to 135.5. A similar shift for each of atoms Ca, Cb and Cc is observed on going from **2** to **7** ($\delta = 123.6$, 122.0 and 121.1 shift to $\delta = 138.4$, 137.3 and 136.3), and on going from **3** to **8** (the group of signals at $\delta = 123.5$, 123.3, 122.8, 122.1 and 121.2 shift to $\delta = 138.3$ (2C), 138.1, 137.4 and 136.3). These data provide good evidence for the formation of organometallic cluster units at all of the alkyne sites.



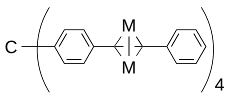
Scheme 3.

Although we have been unable to grow X-ray quality crystals of compounds **6**, **7** or **8**, it is instructive to consider one general structural change that accompanies reactions of the type shown in Equation (1). Crystallographic data for $[Co_2(CO)_6C_2Ph_2]$,[26] $[1,4\text{-}\{Co_2(CO)_6C_2H\}_2C_6H_4]$[27] and $[(CO)_6Co_2C_2H(1,4\text{-}C_6H_4)CH_2(1,4\text{-}C_6H_4)HC_2Co_2(CO)_6]$[27] (three derivatives in which the environment of the RCCR fragment is closely related to that in **6**, **7** and **8**) show that the C_{Ph}-$C_{cluster}$-$C_{cluster}$ bond angles (angle α in Scheme 4) are $\approx 140°$. This clearly means that upon conversion of each polyalkyne to its organometallic derivative, each linear arm of the star becomes kinked. By using molecular modelling, we estimate that the radius of compound **8** is in the range 1.6–2 nm.



Scheme 4.

The reaction of **4** with $[Co_2(CO)_8]$ led to the cobalt-containing derivative **9** in 76% yield. The IR spectrum provided evidence of cobalt carbonyl incorporation, giving strong absorptions at 2090, 2056 and 2027 cm^{-1}. No parent ion could be observed in the MALDI-TOF or electrospray mass spectrum; however, molecular ions corresponding to the parent ion losing 17 or more CO groups were visible. The ^{1}H and ^{13}C NMR spectroscopic data for **9** were consistent with a symmetrical product. The presence of terminal phenyl substituents in both **4** and **9** meant that we were unable to use the ^{1}H NMR spectroscopic probe for cluster formation that had been diagnostic for the conversion of **1** to **6**. However, in the ^{13}C NMR spectra, signals at $\delta = 128.3$ and 123.2, assigned to the phenyl carbon atoms attached to the alkyne groups in **4**, shifted to $\delta = 138.3$ and 136.4 upon formation of **9**. This exactly paralleled the changes in chemical shift for the carbon atoms shown in Scheme 3 for the conversions of **1** to **6**, **2** to **7**, and **3** to **8**, and thereby supported the reaction of each C≡C unit in **4** with $[Co_2(CO)_8]$ and the formation of the tetracluster product **9**.



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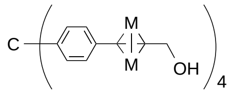

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M = Co(CO)$_3$

Compound **5** reacted smoothly with an excess of $[Co_2(CO)_8]$ to give compound **10** in reasonable yield. The reaction of all four alkyne functionalities and consequent formation of a symmetrical product was supported by the NMR spectroscopic data. In the MALDI-TOF and electrospray mass spectra, however, no parent ion could be observed, and the highest mass peak detected in the MALDI-TOF mass spectrum was at *m*/*z* 715; this corresponds to loss of 24 CO and five Co. The IR spectrum was informative in revealing the group of strong absorptions in the carbonyl region, which is diagnostic of a $[Co_2(CO)_6C_2R_2]$ cluster. Strong evidence for cluster formation also comes from the change in the ^{13}C NMR chemical shift for the alkyne-attached phenyl carbon atom; in keeping with our discussions above, this signal moved from $\delta = 120.5$ in alkyne **5** to $\delta = 137.0$ in cluster **10**. In the ^{1}H NMR spectrum of **10**, the equivalence of the four CH_2 groups was confirmed with the appearance of a single doublet at $\delta = 5.08$, shifted with respect to the corresponding signal ($\delta = 4.27$) in **5**. The OH protons are also affected by the cluster-forming reaction, and the triplet assigned to them in **5** shifts from $\delta = 5.33$ to $\delta = 4.92$ in **10**.

C_6-centred stars—the polyalkyne precursors: In the second series of compounds, the core of the star molecule is an aromatic C_6 ring. This provides a rigid, planar framework from which stepwise growth of six linear, polyalkyne arms can readily be achieved. The core building block chosen was $C_6(p\text{-}C_6H_4I)_6$.[28] The related compound $C_6(p\text{-}C_6H_4OH)_6$ has recently been reported and, in the solid state, it crystallizes to give a porous, two-dimensional hydrogen-bonded network, illustrating the potential of these systems for supramolecular assembly.[29]

Reaction of $C_6(p\text{-}C_6H_4I)_6$ with (TMS)C≡CH under standard coupling conditions (Scheme 5) gave, after deprotection with NaOH, compound **11** in good yield. Further extension of each arm of the star was then achieved by reaction with $p\text{-}IC_6H_4C{\equiv}C(TMS)$ in the presence of CuI and $[PdCl_2(Ph_3P)_2]$ in NEt_3, followed by deprotection (Scheme 5). Compound **12** was obtained in good yield as a white crystalline solid. The MALDI-TOF mass spectra of **11** and **12** showed parent ions at *m*/*z* 677 and 1279, respectively. In their ^{1}H NMR spectra, singlets due to the terminal alkyne protons was observed at $\delta = 3.02$ (**11**) and 3.22 (**12**). Signals in the aromatic region were consistent with the structures shown in Scheme 5, as were the ^{13}C NMR spectroscopic data.

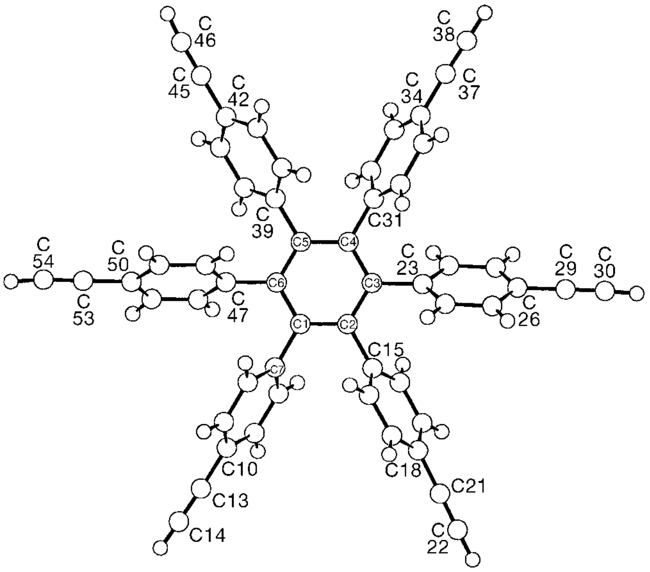
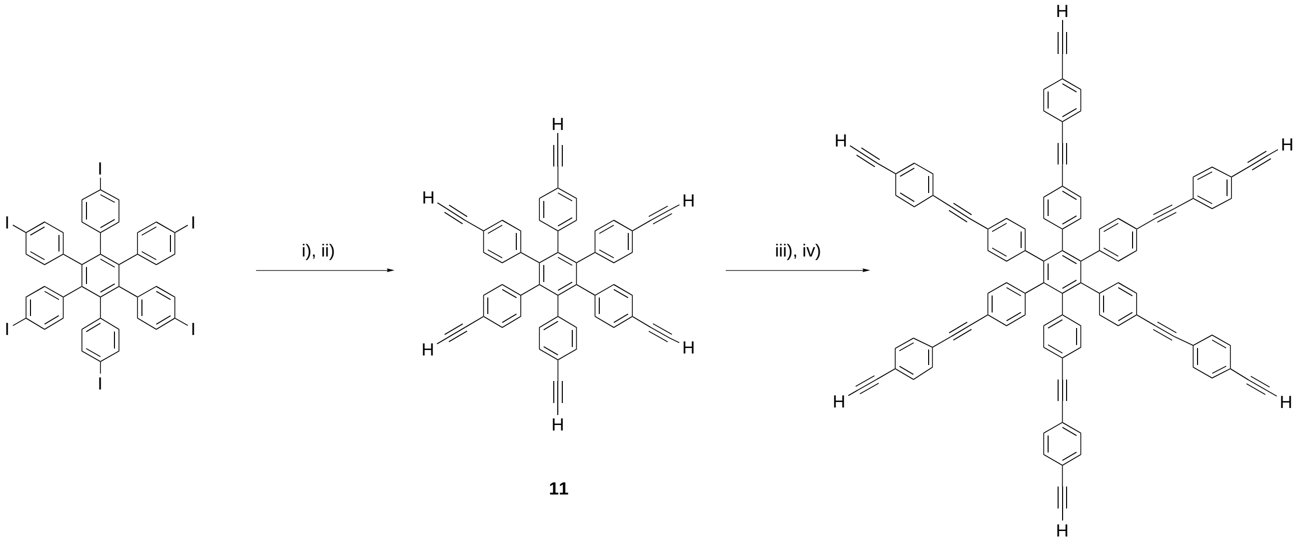


Figure 2. The molecular structure (Schakal plot) of compound **11**.

Compound **11** was further characterized by single crystal X-ray crystallography. Single crystals were grown from a mixture of CH_2Cl_2 and pentane. The molecular structure is shown in Figure 2, and selected bond lengths are listed in Table 2. The phenyl rings in the six arms of the star adopt a "paddle-wheel" configuration with an average twist angle out of the plane of the central C_6 ring of ≈67°.

Table 2. Selected bond lengths [pm] in compound **11**.

C1–C2	140.0(3)	C1–C6	141.1(3)
C2–C3	140.7(3)	C3–C4	140.9(3)
C4–C5	140.6(3)	C5–C6	140.3(3)
C1–C7	149.2(3)	C2–C15	150.1(3)
C3–C23	149.2(3)	C4–C31	149.3(3)
C5–C39	149.9(3)	C6–C47	149.6(3)
C10–C13	143.7(3)	C13–C14	117.5(4)
C18–C21	143.9(3)	C21–C22	118.2(4)
C26–C29	139.1(4)	C29–C30	117.7(4)
C34–C37	144.0(3)	C37–C38	117.8(4)
C42–C45	143.5(3)	C45–C46	117.8(4)
C50–C53	143.6(3)	C53–C54	117.7(4)



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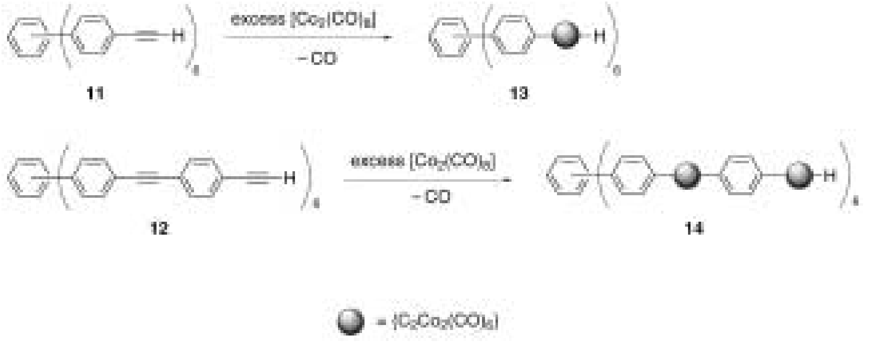
Scheme 5. i) (TMS)C≡CH, CuI, $[PdCl_2(PPh_3)_2]$, NEt_3. ii) NaOH, THF. iii) $p\text{-}IC_6H_4C{\equiv}C(TMS)$, CuI, $[PdCl_2(PPh_3)NEt_3]$, Net_3. iv) NaOH (aq).

C_6-centred metallostars—cobalt carbonyl derivatives: The structural details of hexayne **11** confirmed that the six alkyne groups were, as expected, sterically uncrowded. The reaction of **11** with an excess of $[Co_2(CO)_8]$ is facile and produces **13** (Scheme 6) almost quantitatively. The incorporation of six cluster units was clearly established from the diagnostic shift in the ^1H NMR spectrum of the alkyne proton signal from $\delta = 3.02$ in **11** to $\delta = 6.21$ in **13**. Further confirmation came from the mass spectrum, the highest mass peak in which was at *m*/*z* 2366; this corresponds to the parent ion with loss of one CO ligand. In the IR spectrum, the pattern of strong absorptions around 2000 cm^{-1} characteristic of the $\{C_2Co_2(CO)_6\}$ cluster unit were observed, and in the ^{13}C NMR spectrum of **13**, the appearance of a signal at $\delta = 200.0$ assigned to the cobalt carbonyl groups supported the formation of the cluster units. The overall spectrum was consistent with **13** retaining the high symmetry of **11**. The most diagnostic feature in terms of confirming cluster formation at each of the alkyne units was the shift of the signal assigned to the phenyl C atom adjacent to the C≡C group from 119.9 in **11** to 135.0 in **13**. This parallels the shifts which accompanied the formation of the tetrahedral carbon-centred cobalt carbonyl stars discussed above.



Scheme 6.

In polyalkyne **12**, the inner generation of alkyne functionalities is more sterically shielded than the outer generation. Nonetheless, treatment of **12** with an excess of $[Co_2(CO)_8]$ gave **14** (Scheme 6) in high yield. The MALDI-TOF mass spectrum exhibited a parent peak at *m*/*z* 4706, and IR and ^{13}C NMR spectroscopic data supported the formation of $\{C_2Co_2(CO)_6\}$ cluster units. The reaction of the outer generation of alkyne groups to form organometallic clusters was readily confirmed by the appearance in the ^1H NMR spectrum of **14** of a singlet at $\delta = 6.49$ assigned to the terminal C-H protons (shifted from $\delta = 3.22$ in **12**) and the disappearance of the $\delta = 3.22$ peak. Confirmation that the inner generation had also reacted came from a comparison of the ^{13}C NMR spectra of **12** and **14**. In **12**, signals due to the phenyl C atoms adjacent to the C≡C groups appear at $\delta = 124.0$, 122.2 and 120.6 and this set of signals shifts to $\delta = 138.9$, 137.4 and 135.8 upon the formation of **14**. This is consistent with our previous discussions, and confirms the complete cluster-functionalization of compound **14**.

Conclusion

Two new cores for the preparation of metallostars have been developed and iterative methods have been used to extend poyalkyne arms out through the third generation. Subsequent reaction with $[Co_2(CO)_8]$ resulted in the formation of metallostars in which both the surface and core alkynes have reacted to generate $\{C_2Co_2(CO)_6\}$ motifs. The use of these compounds as precursors for novel materials is currently under investigation.

Experimental Section

General: Reagents and solvents were generally purchased as reagent grade and used without further purification. Toluene and THF were distilled over sodium and benzophenone. Column chromatography: silica gel 60 (230–400 mesh, 0.040–0.063 mm, Merck). UV/Vis spectra were measured on a Varian Cary-5 spectrophotometer or on a Perkin–Elmer Lamda 19 spectrophotometer. IR spectra were measured on Perkin–Elmer 580 or Genesis Series FTIR spectrometers. NMR spectra were recorded on Bruker AM500, AM250 or Varian Gemini 300 or 200 spectrometers at 296 or 300 K, with solvent peaks as internal reference. Electrospray mass spectra (ES-MS) were recorded on a Finnigan Mat LCQ-mass spectrometer with acetone or acetonitrile as solvent; MALDI-TOF mass spectra were obtained by using a PerSeptive Biosystems Vestec spectrometer in positive linear mode at 5 kV acceleration voltage either without a matrix or with 2,5-dihydroxybenzoic acid as matrix. Compound **1** was prepared according to the literature,[20–22] spectroscopic data were in accord with those published.

Compound 2: Compound **1** (83 mg, 0.20 mmol), *p*-$IC_6H_4C{\equiv}C(TMS)$ (251 mg, 0.837 mmol), CuI (15 mg, 0.080 mmol) and $[PdCl_2(PPh_3)_2]$ (56 mg, 0.080 mmol) were stirred in dry, degassed NEt_3 (10 mL) under Ar for 42 h at 41 °C. Chromatographic workup (alumina, hexane/CH_2Cl_2 4:1) gave the TMS-protected intermediate as a yellow crystalline solid. This was dissolved in THF (30 mL), and NaOH (1 M, 30 mL) was added; the solution was stirred for 1 h at room temperature. Water was then 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, $CDCl_3$): $\delta = 7.47-7.43$ (m, 24 H), 7.20 (d, $J = 8.3$ Hz, 8 H), 3.18 (s, 4 H); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 146.1$, 132.1 (2 C), 131.5 (2 C), 131.2 (2 C), 130.9 (2 C), 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 $[M - 2\,C_6H_4CCH]^+$, 413 $[M - 4\,C_6H_4CCH]^+$.

Compound 3: Compound **2** (47 mg, 0.058 mmol), *p*-$IC_6H_4C{\equiv}C(TMS)$ (72.5 mg, 0.242 mmol), CuI (4.4 mg, 0.023 mmol) and $[PdCl_2(PPh_3)_2]$ (16.2 mg, 0.023 mmol) were stirred in dry, degassed NEt_3 (5 mL) under Ar for 12 h at 35 °C. Work-up was analogous to that for **2** and gave a white crystalline solid (37 mg, 53 %). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 7.50-7.44$ (m, 40 H), 7.22 (d, $J = 8.3$ Hz, 8 H), 3.18 (s, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 146.1$, 132.1, 131.6, 131.5, 131.2, 130.9, 123.5, 123.3, 122.8, 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): *m*/*z*: 1217 $[M]^+$, 915 $[M - (C_6H_4C_2)_3H]^+$, 613 $[M - 2\,(C_6H_4C_2)_3H]^+$; UV/Vis ($CHCl_3$): λ_{max} (ε) = 337 (139.7), 357 nm (100.0 dm^3 mol^{-1} cm^{-1}); fluorescence ($CHCl_3$, $h\tilde{\nu} = 337$ nm, 298 K): $\lambda = 370$, 394, 738, 781 nm.

Compound 4: Tetrakis(4-iodophenyl)methane[20] (200 mg, 0.24 mmol), CuI (9.3 mg, 0.049 mmol) and $[PdCl_2(PPh_3)_2]$ (34.1 mg, 0.049 mmol) were suspended in dry NEt_3 (5 mL). Phenylacetylene (104.2 mg, 1.02 mmol) was added, and the mixture was stirred under Ar for 1 h at room temperature, followed by heating for 1 h at 50 °C. The solvent was removed, and the residue extracted with toluene (20 mL) while stirring at 50 °C. The extract was filtered and the filtrate was evaporated. The residue was purified by chromatography (SiO$_2$; AcOEt/hexanes 1:11) and recrystallized from CH$_2$Cl$_2$/hexane to yield off-white crystals (58 mg, 33 %). IR (KBr disc): $\tilde{\nu} = 3053$ (w), 3031 (w, ≡C-H), 1596 (m), 1503 (s, C=C), 845 (w), 822 (s), 753 (s), 687 cm^{-1} (s, =C-H); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.55-7.52$ (m, 8H), 7.46 (d, $J = 8.7$ Hz, 8H,), 7.37–7.32 (m, 12H), 7.22 (d, $J = 8.7$ Hz, 8H); ^{13}C NMR (101 MHz, CDCl$_3$): $\delta = 145.9$, 131.7 (2C), 131.1 (2C), 130.9 (2C), 128.4 (2C), 128.3, 123.2, 121.4, 89.8 (C$_{alkyne}$), 89.0 (C$_{alkyne}$), 64.9 (C$_{quat}$); MS (MALDI-TOF): m/z: 720 $[M]^+$.

Compound 5: Tetrakis(4-iodophenyl)methane[20] (254.7 mg, 0.31 mmol), CuI (23.6 mg, 0.12 mmol) and [PdCl$_2$(PPh$_3$)$_2$] (86.8 mg, 0.12 mmol) were suspended in dry NEt$_3$ (15 mL). Then (TMS)OCH$_2$C≡CH (0.41 mL, 2.66 mmol) was added, and the mixture was stirred under Ar for 36 h at 50 °C. The solvent was removed, and the residue extracted with benzene. The mixture was then filtered, and solvent removed from the filtrate; the residue was purified by chromatography (alumina, CH$_2$Cl$_2$/MeOH 100:4). The brown solid was dissolved in THF (40 mL), and then aqueous NaOH (3 M, 30 mL) was added. The reaction mixture was stirred at room temperature for 4 h. The solution was diluted with aqueous HCl (3 M, 40 mL) to give pH ≈ 1 and extracted with AcOEt (250 mL). The combined organic phases were washed once with H$_2$O and brine and dried over MgSO$_4$. The solvents were removed and the orange oil was purified by column chromatography (SiO$_2$, AcOEt/hexane 1:1) to give white crystals of **5** (130.0 mg, 78.4 %). IR (KBr disc): $\tilde{\nu} = 2921$ (s), 2853 (m, C–H), 1499 (s, C=C), 1034 (s, C–O), 825 (s), 748 (w), 733 (s), 712 (s), 669 cm^{-1} (w); ^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 7.38$ (d, $J = 8.4$ Hz, 8H,), 7.07 (d, $J = 8.4$ Hz, 8H), 5.33 (t, $J = 6.0$ Hz, 4H; OH), 4.27 (d, $J = 6.0$ Hz, 8H); ^{13}C NMR (101 MHz, [D$_6$]DMSO): $\delta = 145.$, 130.9 (2C), 130.5 (2C), 120.5, 90.2 (C$_{alkyne}$), 83.0 (C$_{alkyne}$), 64.1 (C$_{quat}$), 49.4 (C$_{methylene}$); MS (MALDI-TOF): m/z: 536 $[M]^+$, 519 $[M - \text{OH}]^+$, 408 $[M - 4\,\text{CH}_3\text{OH}]^+$.

Compound 6: Compound **1** (19 mg, 0.046 mmol) and [Co$_2$(CO)$_8$] (94 mg, 0.27 mmol) were stirred in CH$_2$Cl$_2$ (or acetone, 6 mL) for 1 h, the solvent was removed, and the residue was purified by column chromatography (SiO$_2$, hexane:CH$_2$Cl$_2$ 1:1) to give a dark brown solid (33 mg, 46 %). IR (CHCl$_3$): $\tilde{\nu} = 2092$ (s), 2057 (vs), 2027 cm^{-1} (vs, CO); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.44$ (d, $J = 8.1$ Hz, 8H), 7.22 (d, $J = 8.1$ Hz, 8H), 6.37 (s, 4H); ^{13}C NMR (101 MHz, CDCl$_3$): $\delta = 199.4$ (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 $[M - \text{CO}]^+$.

Compound 7: Compound **2** (16 mg, 0.020 mmol) and [Co$_2$(CO)$_8$] (95 mg, 0.27 mmol) were stirred in CH$_2$Cl$_2$ (or acetone, 6 mL) for 1 h, the solvent was removed, and the residue was purified by column chromatography (SiO$_2$, hexane/CH$_2$Cl$_2$ 1:1) to give a dark brown solid (16 mg, 26 %). IR (CHCl$_3$): $\tilde{\nu} = 2089$ (s), 2057 (vs), 2028 cm^{-1} (vs, CO); ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 7.60-7.29$ (m, 32H), 6.39 (s, 4H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 199.1$ (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$_{quat}$).

Compound 8: Compound **3** (29 mg, 0.024 mmol) and [Co$_2$(CO)$_8$] (95 mg, 0.27 mmol) were stirred in CH$_2$Cl$_2$ (or acetone, 6 mL) for 1 h, the solvent was removed, and the residue was purified by column chromatography (SiO$_2$, hexane/CH$_2$Cl$_2$ 1:1) to give a dark brown solid (50 mg, 45 %). IR (KBr pellet): $\tilde{\nu} = 2090$ (s), 2052 (vs), 2020 cm^{-1} (vs, CO); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.61-7.31$ (m, 48H), 6.40 (s, 4H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 199.1$ (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 $[M]^+$.

Compound 9: Compound **4** (35.0 mg, 0.049 mmol) was dissolved in dry CH$_2$Cl$_2$ (2 mL), and [Co$_2$(CO)$_8$] (105.0 mg, 0.307 mmol) was added. The solution was stirred for 1.75 h under nitrogen at room temperature. Afterwards the solvent was removed at room temperature and the residue dried briefly under high vacuum, followed by chromatographic workup (SiO$_2$; CH$_2$Cl$_2$/hexanes 1:9) to give a black solid of **9** (69.0 mg, 76.2 %). IR (CCl$_4$ solution): $\tilde{\nu} = 2090$ (s), 2056 (vs), 2027 cm^{-1} (vs, CO); ^{1}H NMR (400 MHz, CDCl$_3$) $\delta = 7.64-7.52$ (m, 16H), 7.40–7.28 (m, 20H); ^{13}C NMR (101 MHz, CDCl$_3$) $\delta = 199.3$ (CO), 145.7 (C^2), 138.3 (C^8), 136.4 (C^5), 131.6 (C^3, 2C), 129.2 (C$^{9/10}$, 2C), 128.9 (C$^{9/10}$, 2C), 128.5 (C^4, 2C), 127.9 (C^{11}), 92.4 (C$^{6/7}$), 91.5 (C$^{6/7}$), 65.0 (C^1); MS (MALDI-TOF): m/z: 1388 $[M - 17\,\text{CO}]^+$, 1133 $[M - 24\,\text{CO}]^+$.

Compound 10: Compound **5** (14.0 mg, 0.026 mmol) was dissolved in dry acetone (1.5 mL), and [Co$_2$(CO)$_8$] (56.0 mg, 0.16 mmol) was added. The solution was stirred for 1.2 h. Solvent was removed at room temperature, and the residue dried briefly under high vacuum, followed by chromatographic workup (SiO$_2$, AcOEt/hexane 1:1) to give a red-brown solid of **10** (26.0 mg, 59.5 %). IR (KBr disc): $\tilde{\nu} = 2923$ (w), 2858 (w, C–H), 2092 (s), 2053 (s), 2030 (s), 2015 (s, CO), 1490 cm^{-1} (w, C=C); ^{1}H NMR (400 MHz, [D$_6$]acetone): $\delta = 7.62$ (d, $J = 8.4$ Hz, 8H), 7.33 (d, $J = 8.4$ Hz, 8H), 5.08 (d, $J = 6.0$ Hz, 8H), 4.92 (t, $J = 6.0$ Hz, 4H; OH); ^{13}C NMR (101 MHz, [D$_6$]acetone): $\delta = 200.7$ (CO), 146.6, 137.0, 132.1 (2C), 130.0 (2C), 100.5 (C$_{alkyne}$), 90.4 (C$_{alkyne}$), 65.8 (C$_{quat}$), 63.4 (C$_{methylene}$); MS (MALDI-TOF): m/z: 715 $[M - 24\,\text{CO} - 5\,\text{Co}]^+$, 588, 570, 553.

Compound 11: A suspension of C$_6$(p-C$_6$H$_4$I)$_6$[28] (405 mg, 0.314 mmol), (TMS)C≡CH (370 mg, 3.77 mmol), CuI (23.9 mg, 0.126 mmol) and [PdCl$_2$(PPh$_3$)$_2$] (88.1 mg, 0.126 mmol) in NEt$_3$ (20 mL) was stirred at 43 °C for 19 h. The solvent was removed, and the product was extracted with C$_6$H$_6$. After chromatographic separation, the brown solid obtained was dissolved in THF (80 mL); NaOH (1 M, 80 mL) was added, the solution stirred for 3.5 h, and water added to give a white precipitate. The mixture was extracted with CH$_2$Cl$_2$ and purified by column chromatography to yield white crystals (125.2 mg, 59 %). IR (KBr disc): $\tilde{\nu} = 3291$ (vs, ≡C-H), 3035 (w) (=C-H), 1509 (m, C=C), 870 (w), 841 (s), 795 (m), 664 (s), 641 (m), 615 cm^{-1} (s); ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 7.04$ (d, $J = 8.4$ Hz, 12H), 6.79 (d, J 8.4 Hz, 12H), 3.02 (s, 6H); ^{13}C NMR (101 MHz, CD$_2$Cl$_2$): $\delta = 140.9$, 140.2, 131.6 (2C), 131.1 (2C), 119.9, 83.7 (C$_{alkyne}$), 77.5 (C$_{alkyne}$); MS (MALDI-TOF): m/z: 677 $[M]^+$; elemental analysis calcd (%) for C$_{54}$H$_{30}$: C 95.6, H 4.5; found C 94.9, H 4.7

Compound 12: A suspension of **11** (126 mg, 0.185 mmol), p-IC$_6$H$_4$C≡C(TMS) (445 mg, 1.48 mmol), CuI (10.0 mg, 0.053 mmol) and [PdCl$_2$(PPh$_3$)$_2$] (13.0 mg, 0.019 mmol) in NEt$_3$ (15 mL) was stirred at 45 °C for 12 h, solvent was removed, and the product was purified by column-chromatography (white solid, 133.9 mg, 42.2 %). Deprotection of the TMS-protected product (274 mg, 0.160 mmol) under the same conditions as for **11**, gave **12** as white crystals (140.5 mg, 68.5 %). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 7.44-7.36$ (m, 24H), 7.13 (d, $J = 8.1$ Hz, 12H), 6.89 (d, $J = 8.1$ Hz, 12H), 3.22 (s, 6H); ^{13}C NMR (75 MHz, CD$_2$Cl$_2$): $\delta = 140.8$, 140.3, 132.4, 131.7 (two coincident signals), 130.7, 124.0, 122.2, 120.6, 91.5 (C$_{alkyne}$), 89.2 (C$_{alkyne}$), 83.4 (C$_{alkyne}$), 79.2 (C$_{alkyne}$); MS (MALDI-TOF): m/z: 1279 $[M]^+$; elemental analysis calcd (%) for C$_{102}$H$_{54}$: C 93.1, H 4.2; found C 93.5, H 4.6; UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 315 (149.1), 327 nm (136.3 dm^{3}mol^{-1}cm^{-1}); fluorescence (CH$_2$Cl$_2$, $h\tilde{\nu} = 327$ nm, 298 K): $\lambda = 370$, 730 nm.

Compound 13: [Co$_2$(CO)$_8$] (125 mg, 0.366 mmol) was added to compound **11** (33.2 mg, 0.026 mmol) dissolved in CH$_2$Cl$_2$ (3 mL), the mixture was stirred for 1.5 h, and solvent removed. After chromatographic workup, compound **13** was obtained as a red crystalline solid (46.3 mg, 95.1 %). ^{1}H NMR (250 MHz, CD$_2$Cl$_2$): $\delta = 7.08$ (d, $J = 7.9$ Hz, 12H), 6.81 (d, $J = 7.9$ Hz, 12H), 6.21 (s, 6H); ^{13}C NMR (101 MHz, CD$_2$Cl$_2$): $\delta = 200.0$ (CO), 140.7, 140.5, 135.0, 132.3 (2C), 129.3 (2C), 90.4 (C$_{cluster}$), 73.0 (C$_{cluster}$); IR (KBr): $\tilde{\nu} = 2094$, 2051, 2032, 2022, 2010 cm^{-1} (CO); MS (MALDI-TOF): m/z: 2366 $[M - \text{CO}]^+$.

Compound 14: [Co$_2$(CO)$_8$] (319 mg, 0.934 mmol) was added to compound **12** (33.2 mg, 0.026 mmol) dissolved in CH$_2$Cl$_2$ (5 mL), the mixture stirred for 1 h, and the solvent removed. After chromatographic workup, **14** was obtained as a red crystalline solid (105 mg, 85.7 %). ^{1}H NMR (250 MHz, CD$_2$Cl$_2$): $\delta = 7.49$ (d, $J = 8.1$ Hz, 12H), 7.42 (d, $J = 8.1$ Hz, 12H), 7.24 (d, $J = 8.4$ Hz, 12H), 6.94 (d, $J = 8.4$ Hz, 12H), 6.49 (s, 6H); ^{13}C NMR (75 MHz, CD$_2$Cl$_2$): $\delta = 199.6$ (CO), 140.6, 140.5, 138.9, 137.4, 135.8, 132.4 (2C), 130.9 (2C), 129.9 (2C), 128.2 (2C), 92.2 (C$_{cluster}$), 91.5 (C$_{cluster}$), 89.7 (C$_{cluster}$), 73.6 (C$_{cluster}$); IR (KBr disc): $\tilde{\nu} = 2089$, 2053, 2021 cm^{-1} (CO); MS (MALDI-TOF): m/z: 4706 $[M]^+$, 3711 $[M - 36\,\text{CO}]^+$.

Crystallography: Crystallographic parameters and details of the data collection for compounds **4** and **11** are given in Table 3. The structures were solved by routine methods as described previously.[30] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-143144 and CCDC-143145. Copies of the data can be obtained free of charge on application to CCDC, 12

Table 3. Crystallographic data and structure refinement for compounds **4** and **11**.

	4	**11**
formula	$C_{57}H_{36}$	$C_{54}H_{30}$
M_w	720.86	678.78
T [K]	183(2)	193(2)
λ [Å]	0.71073	0.71073
crystal system	tetragonal	monoclinic
space group	$I4_1/a$	$P2_1/c$
a [Å]	13.424(2)	17.933(4)
b [Å]	13.424(2)	15.039(3)
c [Å]	66.283(13)	14.939(3)
β [°]		105.12(3)
V [Å^3]	11944.0(34)	3889.5(13)
Z	12	4
ρ_{calcd} [g cm^{-3}]	1.203	1.159
μ [mm^{-1}]	0.068	0.066
$F(000)$	4536	1416
θ range [°]	2.16 to 26.07	2.47 to 28.07
reflections collected	22834	13320
independent reflections	5893 ($R_{int} = 0.1764$)	8629 ($R_{int} = 0.0508$)
observed reflections [$I > 2\sigma(I)$]	2583	5614
refinement method	full-matrix least-squares on F^2	
data/restraints/parameters	5043/0/494	8621/0/607
GOF on F^2	0.798	0.797
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0689$	$R_1 = 0.0565$
	$wR_2 = 0.1684$	$wR_2 = 0.1681$
R indices (all data)	$R_1 = 0.1696$	$R_1 = 0.0942$
	$wR_2 = 0.3298$	$wR_2 = 0.2168$
largest diff. peak/hole [e Å^{-3}]	0.245/ − 0.183	0.281/ − 0.157

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