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A simple synthesis of tetraethynylethenes and representative molecular structures of some dicobalt derivatives

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Abstract

Palladium–copper catalysed cross-coupling reactions of tetracholoroethene with terminal acetylenes RC≡CH (R = $SiMe_3$, C_6H_5, C_6H_4CN-4) in refluxing triethylamine afford the corresponding tetraethynylethenes in 30–60% isolated yields. The reaction of 1,6-bis(trimethylsilyl)-3,4-bis(trimethylsilylethynyl)-hex-3-ene-1,5-diyne with $[Co_2(CO)_6(L_2)]$ [$L_2 = (CO)_2$ or μ-dppm] affords complexes in which one or two (*trans*) acetylene moieties are coordinated by a dicobalt fragment.

Keywords: Alkyne; Tetraethynylethene; Cobalt carbonyl complexes

1. Introduction

Substituted derivatives of 3,4-bis(ethynyl)-hex-3-ene-1,5-diyne (tetraethynylethene, TEE, **1**) have been the subject of a great deal of recent attention on the basis of the large non-linear optical response which they have been shown to offer [1–9], their potential for use as building blocks in the preparation of more extended conjugated systems [10–14], and as π-electron donors [15,16]. The reversible photoisomerism of the TEE framework also lends itself to the construction of molecular scale switching components, which have proved to be remarkably resistant to photo fatigue [17–19].

Early synthetic methods to substituted TEE's included dimerisation of bis(ethynyl)methylene carbenes [20,21] and the reductive dimerisation of 3-bromopenta-1,4-diynes [22,23]. More recently, Jones and co-workers have devised routes to tetraethynylethenes via a carbenoid coupling protocol [24,25], while the Diederich group have devised elegant, multi-step synthetic methodologies which allow the regio-specific synthesis of many of the isomers of substituted TEE's using palladium catalysed coupling reactions of terminal alkynes with 3-(dibromomethylidene)penta-1,4-diynes, and also through a multi-step sequence beginning with the cross-coupling alkynes with dimethyl 2,3-dibromofumarate, and subsequent elaboration (Schemes 1 and 2) [4,26,27].

To date, our own work with highly ethynylated compounds has focussed on the synthesis, structure and properties of organometallic species derived from linear conjugated polyynes [28–31]. In seeking to extend these studies to cross-conjugated polycarbon ligands we were drawn to the TEE framework. Given the demonstrated utility of dichloroethenes in the preparation of ene-ynes via palladium–copper catalysed cross-coupling reactions [32,33], we decided to investigate tetrachloroethene as a reagent in the synthesis of tetraethynylethenes. Here we report the initial results of these investigations.

2. Results and discussion

2.1. Cross-coupling reactions with tetrachloroethene

The $Pd(PPh_3)_4$ (2.5%)–CuI (2.5%) catalysed cross-coupling reaction of $Me_3SiC≡CH$ with tetrachlor-

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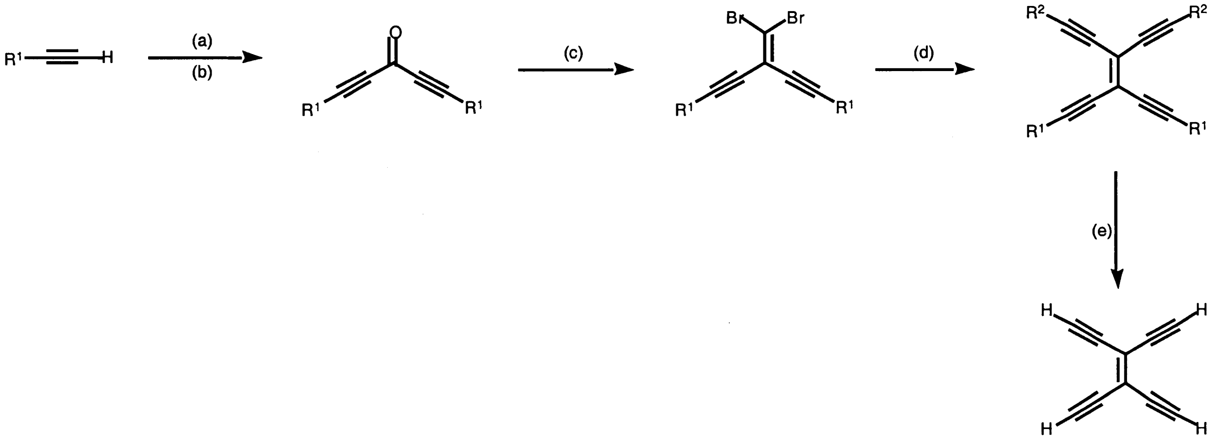
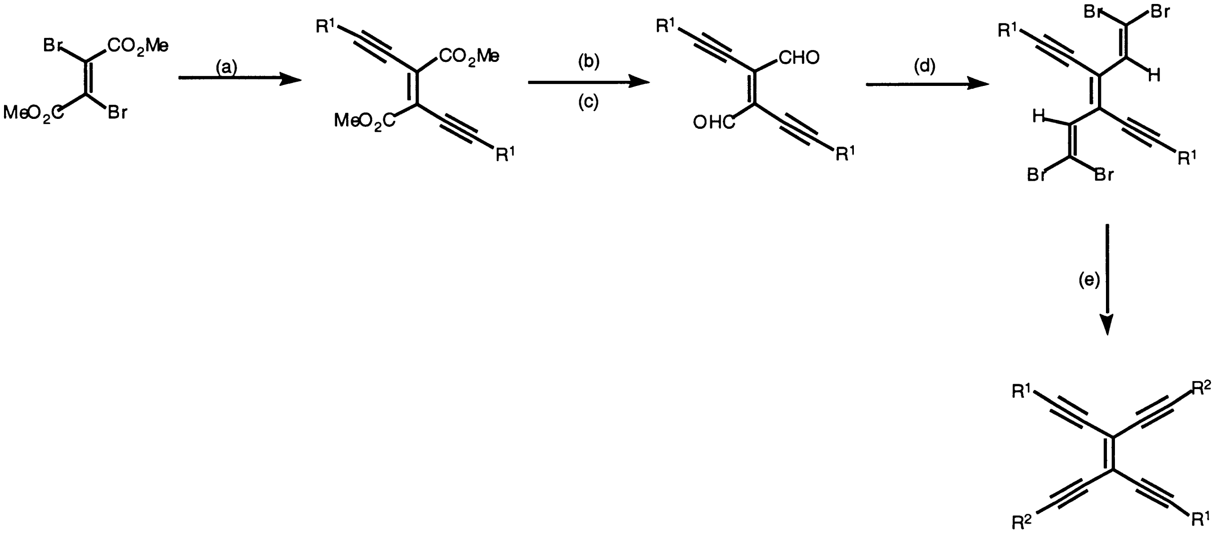


Scheme 1. Synthesis of *cis* tetraethynylethenes. (a) (i) BuLi (ii) HCO_2Et (iii) H^+. (b) $BaMnO_4$ (c) CBr_4, PPh_3 (d) $R^2C{\equiv}CH$, $Pd(PPh_3)_4$, CuI, $BuNH_2$ (e) K_2CO_3, MeOH.

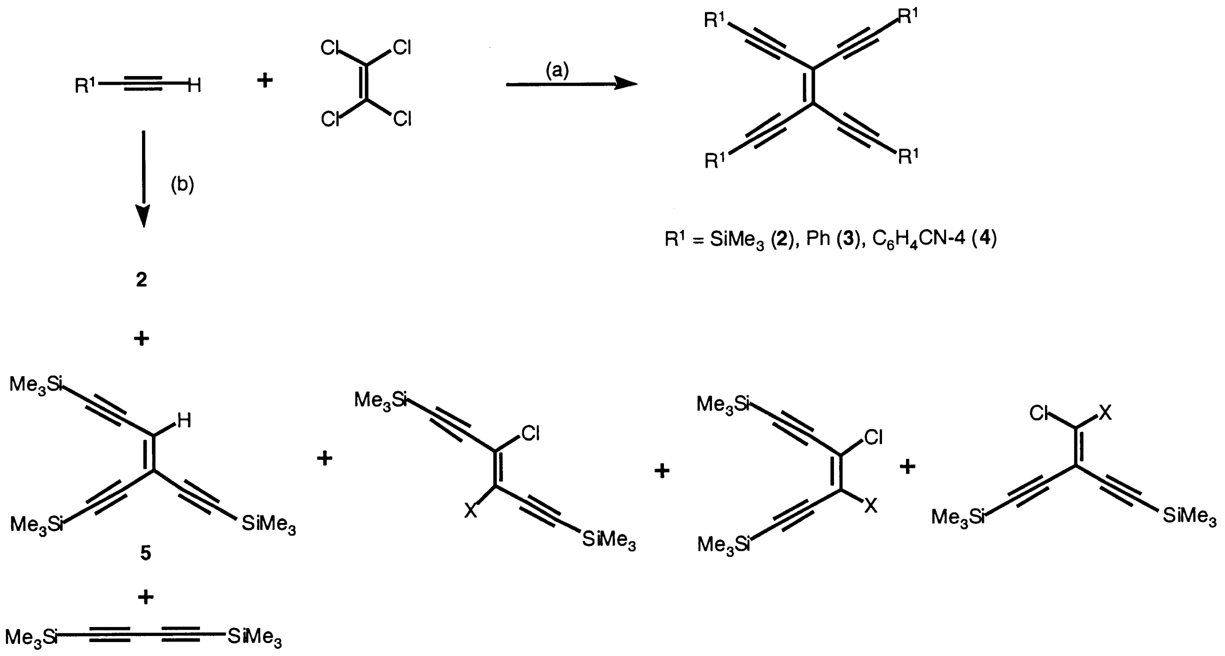
oethene in refluxing NH^iPr_2 afforded a mixture of products, the major components of which were identified by GC-MS as the desired 1,6-bis(trimethylsilyl)-3-4-bis[(trimethylsilyl)ethynyl]hex-3-ene-1,5-diyne (**2**) (ca. 40%), dichloro-bis(trimethylsilyl)-hexenediyne (three isomers, ca. 23%), chloro-bis(trimethylsilyl)-hexenediyne (one isomer, ca. 6%), 1,6-bis(trimethylsilyl)-3-(trimethylsilylethynyl)-hex-3-ene-1,5-diyne (**5**, ca. 11%) and the diyne $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ (ca. 14%), with yields estimated from the integrated area of each peak in the GC trace (Scheme 3).

Extensive extraction and chromatography procedures failed to adequately separate the partially coupled and hydrodehalogenated compounds from **2** and so in an attempt to identify conditions which would minimise the production of these by-products, we re-examined the reaction using a combinatorial array in which solvent (NEt_3, $NHEt_2$, NH^iPr_2) and source of the palladium catalyst [$Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, $Pd_2(dba)_3$–dppf, $Pd_2(dba)_3$–P^tBu_3] were varied. Analysis of the reaction mixture obtained from the NEt_3–$Pd(PPh_3)_4$ reaction by GC-MS indicated the relatively clean formation of 1,6-bis(trimethylsilyl)-3-4-bis[(trimethylsilyl)ethynyl]hex-3-ene-1,5-diyne. When these conditions were employed on preparative scale, we were pleased to find that isolation of the product (30%) could be achieved simply by filtration of the reaction mixture, to remove the precipitated trialkylammonium salts, followed by precipitation of the product in acidified MeOH and recrystallisation (Scheme 3). The isolation of gram scale quantities of **2** in this manner is competitive with the four-step method detailed by Diederich which affords **2** in 25% overall yield.

CAUTIONARY NOTE: In the presence of trace amount of the amine reaction solvent sufficient methoxide is generated during the precipitation step to desily-



Scheme 2. Synthesis of *trans* tetraethynylethenes. (a) $R^1C{\equiv}CSnBu_3$, $PdCl_2(PPh_3)_2$ (b) DIBAL-H (c) PCC (d) CBr_4, Zn, PPh_3 (e) (i) LDA (ii) R^2–X. DIBAL-H = diisobutylaluminium hydride; PCC = pyridinium chlorochromate; X = halide.



Scheme 3. Synthesis of symmetrical tetraethynylethenes from tetrachloroethene. (a) Pd(PPh$_3$)$_4$, CuI, NEt$_3$ (b) Pd(PPh$_3$)$_4$, CuI, NH^{i}Pr$_2$ (X = Cl, three isomers; X = H, one isomer).

late the highly ethynylated reaction products, which upon concentration may spontaneously detonate. It is therefore *essential* that the precipitation be carried out in MeOH acidified by addition of several drops of HCl. Any alkylammonium salt so produced is removed by recrystallisation.

The palladium–copper catalysed cross-coupling of tetrachloroethene to other terminal alkynes proceeded smoothly under similar conditions (Scheme 3). For example, the Pd(0)–Cu(I) (5%) catalysed reaction of tetrachloroethene with excess phenylacetylene in refluxing triethylamine afforded 1,6-bis(phenyl)-3,4-bis(phenylethynyl)-hex-3-ene-1,5-diyne (**3**) in 60% yield after chromatographic work-up. This compound has been prepared previously by carbenoid coupling routes, albeit in only 11% yield [20], and also by the procedure illustrated in Scheme 1 [15]. Compound **3** was identified by comparison of the spectroscopic data with that previously reported. The substituted arylalkyne 4-ethynylbenzonitrile also coupled smoothly under analogous conditions to afford **4** (42%).

Compound **4** was exceptionally insoluble in all common solvents. However, sufficient material could be dissolved in hot d_6-DMSO to permit a ^{1}H-NMR spectrum to be obtained. The expected pattern in the aromatic region was observed (δ 7.77, 7.93; 2 × d, $J_{HH} = 10$ Hz). The IR spectrum contained absorption bands at 2224 [ν(CN)] and 1600 [ν(C=C)] cm^{-1}. The parent ion was observed in the EI mass spectrum (m/z = 528).

The successful preparation of **3** and **4** by Pd–Cu catalysed coupling reactions of tetrachloroethene is in stark contrast to the failed Eglington-type coupling of tetraiodoethene with copper phenylacetylide [20]. However, attempts to cross-couple more electron-rich alkynes, including ferrocenylacetylene, with tetrachlorethylene have not yet been successful.

2.2. Reactions of 2 with $Co_2(CO)_6(L_2)$ ($L = CO$, L_2 = μ-dppm)

Dicobalt carbonyls [Co$_2$(CO)$_6$(L$_2$)] react readily with alkynes to afford complexes of general type [Co$_2$(μ–η^2-alkyne)(CO)$_4$(L$_2$)] [34]. These compounds often crystallise readily, and as such are appealing derivatives for establishing the nature of otherwise difficult to characterise acetylenes [35].

In an effort to obtain further evidence for the products formed in diisopropylamine, we allowed the crude product mixture to react with [Co$_2$(CO)$_6$(μ-dppm)] in refluxing benzene. The reaction was followed by TLC and, when adjudged complete, the solvent was removed and the residue purified by preparative TLC. The dicobalt complexes [Co$_2$(μ,η^2-Me$_3$SiC$_2$C≡CSiMe$_3$)(CO)$_4$(μ-dppm)] (29%), [{Co$_2$(CO)$_4$(μ-dppm)}$_2$-{μ,η^2:μ,η^2-(Me$_3$SiC$_2$C(H)=C(C$_2$SiMe$_3$)C≡CSiMe$_3$}] (**6**, 9%) and [Co$_2${μ,η^2-Me$_3$SiC$_2$C(C≡CSiMe$_3$)=C(C≡CSiMe$_3$)$_2$}(CO)$_4$(μ-dppm)] (**7**, 44%) were obtained. The complexes were identified by the usual spectroscopic methods and, in the case of **6** and **7**, single crystal X-ray analysis (see Section 2.3).

Identification of [Co$_2$(μ,η^2-Me$_3$SiC$_2$C≡CSiMe$_3$)(CO)$_4$(μ-dppm)] was not difficult, and the spectroscopic data collected was in good agreement with that previously reported [36,37]. The IR spectrum of **6** contained three strong ν(CO) bands (2021s, 1997vs, 1970vs cm^{-1}), as expected for a compound of the type [Co_2(alkyne)-$(CO)_4$(μ-dppm)] bearing an electron withdrawing group [38]. Three resonances of equal integrated area at −0.17, 0.13, 0.40 ppm in the ^{1}H-NMR spectrum were found for the three $SiMe_3$ groups. The methylene groups of the dppm ligands gave rise to a partially resolved doublet of triplet resonance, and an unresolved multiplet from the overlap of two protons from one CH_2 moiety and the vinyl proton. The ^{13}C-NMR spectrum gave further support for the proposed structure with three trimethylsilyl resonances at δ −0.18, 0.98 and 1.27 ppm. Only two acetylenic resonances could be detected at δ 106.04 and 106.40 ppm, while the aromatic, methylene and carbonyl resonances were all found in the expected regions of the spectrum. The FAB-MS contained the molecular ion at *m/z* 1545, confirming the coordination of two alkynyl groups by $Co_2(CO)_4$(μ-dppm) fragments.

The IR spectrum of the tetraethynyl derivative **7** contained three strong ν(CO) bands (2023s, 1999vs, 1973s cm^{-1}) and four $SiMe_3$ resonances in both the ^{1}H- and ^{13}C-NMR spectra. Only seven of the quarternary carbon resonances were observed, falling in the range δ 98.23–111.14 ppm. The FAB-MS was particularly informative, with isotopic envelopes centred at *m/z* 999 attributed to $[M-CO+H]^+$, and at *m/z* 970, 942, 914 from $[M-nCO]^+$ ($n = 2, 3, 4$).

Compound **7** was also obtained as the only product (69%) from the reaction of [$Co_2(CO)_6$(μ-dppm)] with one equivalent of a pure sample of **2**. Reaction of **7** with a further equivalent of [$Co_2(CO)_6$(μ-dppm)] afforded small amounts of [{$Co_2(CO)_4$(μ-dppm)}$_2${μ-η^2:η^2-$Me_3SiC_2C(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)C_2SiMe_3$}] (**8**), in which coordination of a second $Co_2(CO)_4$(μ-dppm) moiety to the least sterically hindered triple bond in **7** has occurred. Spectroscopic data from **8** were consistent with the proposed structure, with the expected ν(CO) band pattern, and NMR resonances at δ 0.22 and 0.55 assigned to the two distinguishable $SiMe_3$ moieties. The FAB-MS contained the molecular ion (*m/z* 1640), and fragment ions derived from carbonyl losses. The structure was confirmed crystallographically (see below).

The reactions of **2** with an excess of the less sterically demanding reagent [$Co_2(CO)_8$] were also investigated. Two complexes were obtained in good to modest yield and separated by preparative TLC. The major product formed was the dark green double adduct [{$Co_2(CO)_6$}$_2${μ,η^2-$Me_3SiC_2C(C{\equiv}CSiMe_3){=}C(C{\equiv}CSiMe_3)C_2SiMe_3$}] (**9**, 67%). While the IR spectrum contained three strong carbonyl bands (2088 s, 2056 vs, 2030 vs cm^{-1}) confirming coordination of at least one alkyne moiety, more information was contained in the ^{1}H- and ^{13}C-NMR spectra. Two resonances of equal intensity at δ 0.25 and 0.40 in the ^{1}H-NMR spectrum were matched by ^{13}C resonances (−0.39 and 1.48) for the $SiMe_3$ groups and suggested coordination of two alkyne moieties. This supposition was confirmed by the FAB-MS of the product which contained an isotopic envelope at *m/z* 872 arising from the $[M-4CO]^+$ ion, and further fragment ions corresponding to the loss of a further eight CO ligands. The compound was therefore confirmed as a bis(dicobalt) complex. Regiochemical information was contained in the ^{13}C-NMR spectrum, with the observation of five quaternary carbon resonances (δ 83.69, 105.10, 107.10, 113.34 and 127.83) indicating the formation of the *trans* disubstituted material [26].

The minor product (**10**) was obtained as a red–brown crystalline material. Again, three ν(CO) bands were found in the IR spectrum, but the ^{1}H resonances from the $SiMe_3$ groups were not fully resolved giving rise to two resonances at 0.23 and 0.39 ppm in a 1:3 ratio. The ^{13}C-NMR spectrum was better resolved and clearly indicated the presence of four distinct $SiMe_3$ groups, together with resonances from all 10 quaternary carbons (δ 84.01, 97.47, 100.73, 102.97, 104.39, 104.54, 105.55, 111.67, 112.22, 134.72 ppm) . These observations, together with the mass spectrum which contained ions corresponding to $[M-nCO]^+$ ($n = 1$–6), confirmed the product as the mono-substituted derivative [{Co_2-$(CO)_6$}(μ,η^2-$Me_3SiC_2C(C{\equiv}CSiMe_3){=}C(C{\equiv}CSiMe_3)_2$)]. In no case did we detect complexes in which three or four of the alkynyl moieties had been coordinated by dicobalt moieties.

2.3. Molecular structures

The crystal and molecular structures of many TEE derivatives have been solved [8,9,19,20,26] [39–42]. The conjugated carbon skeleton is essentially planar as a result of the extensive π-conjugation, and bond lengths of 1.34–1.37 Å for the central C=C double bond and 1.17–1.22 Å for the C≡C triple bonds are typical. The angles around the C=C carbons are rather more flexible, and in the case of **2** vary between 118.2 and 125.3° for C(8)–C(3)–C(2,4) and as little as 116.5 for C(2)–C(3)–C(4) [26]. The molecular structures of **6**, **7** and **8** were determined. Crystallographic details are summarised in Table 1, with selected bond lengths and angles contained in Tables 2 and 3, respectively.

The molecular structures of **6** (Fig. 1), **7** (Fig. 2) and **8** (Fig. 3) display a range of systematic variations which are readily attributed to the steric properties of the coordinated dicobalt fragments. The disorder in the molecular structure of **8** was modelled in terms of a 180° rotation of the uncoordinated ene–yne fragment about C2–C3, with occupancies of 75:25. The Co_2(μ–η^2-alkyne)$(CO)_4$(μ-dppm) portion(s) of each molecule (**6**–**8**) are unremarkable. The Co–Co bond lengths fall between 2.4664(4) and 2.5168(14) Å, with the longer bonds associated with **6** and **8**. The coordinated C–C bonds in **6** [1.363(10),

Table 1
Crystallographic details for **6**, **7**, **8**

	6	**7**	**8**
Empirical formula	$Co_4P_4O_8Si_3C_{75}H_{72}\cdot 2(CH_2Cl_2)\cdot 0.5(CH_3OH)$	$Co_2P_2O_4Si_4C_{51}H_{58}$	$Co_4P_4O_8Si_4C_{80}H_{80}$
Formula weight	1731.07	1027.13	1641.40
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	16.187(1)	12.846(1)	11.529(2)
b (Å)	16.160(1)	14.881(2)	18.967(2)
c (Å)	16.986(2)	17.221(1)	19.026(3)
α (°)	72.923(3)	109.391(4)	90
β (°)	89.949(4)	95.169(3)	104.118(7)
γ (°)	83.932(4)	115.508(4)	90
V (Å^3)	4221.3(6)	2695.5(4)	4034.8(10)
Z	2	2	2
μ (mm^{-1})	1.068	0.804	0.999
Crystal size	0.20 × 0.15 × 0.05	0.40 × 0.19 × 0.17	0.44 × 0.20 × 0.14
Reflections measured	46 934	22 544	45 514
Unique reflections (R_{int})	19 221 (0.1399)	13 117 (0.0190)	10 018 (0.0485)
Parameters refined	912	568	478
R, wR ($F^2 > 2\sigma$)	0.0874, 0.2239	0.0382, 0.0975	0.0569,0.1195
R, wR (all data)	0.2027, 0.2902	0.0502, 0.1054	0.0893, 0.1388

Table 2
Selected bond lengths (Å) for **6**, **7**, **8**

	6	**7**	**8**
Co(1)–Co(2)	2.4845(14)	2.4664(4)	2.4904(9)
Co(3)–Co(4)	2.5168(14)		2.4904(9) (C1′–C2′)
Co(1)–P(1)	2.220(2)	2.2205(6)	2.2052(10)
Co(2)–P(2)	2.217(2)	2.2154(6)	2.2254(11)
Co(3)–P(3)	2.241(2)		2.2052(10) (Co1′–P1′)
Co(4)–P(4)	2.207(2)		2.2254(11) (Co2′–P2′)
C(1)–C(2)	1.363(10)	1.349(3)	1.354(7)
C(2)–C(3)	1.487(9)	1.471(3)	1.475(6)
C(3)–C(4)	1.444(10)	1.448(3)	1.441(9)
C(4)–C(5)	1.201(11)	1.214(3)	1.222(11)
C(3)–C(8)	1.355(10)	1.365(3)	1.357(9) (C3–C3′)
C(6)–C(7)		1.196(3)	1.354(7) (C1′–C2′)
C(7)–C(8)		1.447(3)	1.475(6) (C2′–C3′)
C(8)–C(9)	1.455(9)	1.427(3)	1.441(9) (C3′–C4′)
C(9)–C(10)	1.369(10)	1.196(3)	1.222(11) (C4′–C5′)
C(1)–Si(1)	1.846(8)	1.854(2)	1.873(6)
C(5)–Si(2)	1.846(9)	1.844(2)	1.837(8)
C(6)–Si(3)		1.838(2)	1.873(6) (C1′–Si1′)
C(10)–Si(4)	1.846(7)	1.845(2)	1.837(8) (C5′–Si2′)
Co(1)–C(1)	1.972(7)	1.973(2)	1.909(7)
Co(1)–C(2)	1.972(7)	1.993(2)	1.914(6)
Co(2)–C(1)	1.992(8)	1.980(2)	2.034(6)
Co(2)–C(2)	1.949(7)	1.960(2)	2.021(6)
Co(3)–C(9)	1.932(7)		1.914(6) (Co1′–C2′)
Co(3)–C(10)	1.991(8)		1.909(7) (Co1′–C1′)
Co(4)–C(9)	2.020(7)		2.021(6) (Co2′–C2′)
Co(4)–C(10)	1.996(7)		2.034(6) (Co2′–C1′)

Table 3
Selected bond angles for **6**, **7**, **8**

	6	**7**	**8**
Si(1)–C(1)–C(2)	144.5(6)	146.7(2)	130.2(4)
C(1)–C(2)–C(3)	135.9(7)	141.0(2)	139.8(5)
C(2)–C(3)–C(4)	113.5(6)	118.9(2)	112.7(5)
C(3)–C(4)–C(5)	173.0(8)	174.5(2)	175.6(8)
C(2)–C(3)–C(8)	121.6(7)	124.8(2)	125.1(5) (C2–C3–C3′)
C(4)–C(3)–C(8)	124.9(6)	116.2(2)	122.2(5) (C4–C3–C3′)
C(3)–C(8)–C(7)		124.1(2)	125.1(5) (C3–C3′–C2′)
C(3)–C(8)–C(9)	127.6(7)	120.2(2)	122.2(5) (C3–C3′–C4′)
C(8)–C(9)–C(10)	139.4(7)	174.7(2)	139.8(5) (C3′–C2′–C1′)

1.369(10) Å], **7** [1.349(3) Å] and **8** [1.354(5) Å] are equal within the limits of precision. The Co–C(alkyne) bonds span the range 1.909(7)–2.034(6) Å, averaging 1.975 Å, while the coordinated C–C bond lengths [1.349(3)–1.369(10) Å] display the usual elongation relative to the uncoordinated C≡C alkynyl moieties [1.20(1)–1.22(1) Å].

The C(3)–C(8) C=C bond lengths [1.355(10)–1.365(3) Å] are similar to those normally encountered in TEE derivatives. The formal C–C single bonds C(2)–C(3) (**6**, **7**, **8**) and C(8)–C(9) (**6**) linking the cluster coordinated alkyne moieties to the central C(3)–C(8) core display a trend towards elongation relative the C(4)–C(3) and C(8)–C(7), which is attributed to the difference in hybridisation at the cluster carbon C(2), and also C(9) in the case of **6**.

The cobalt clusters and pendant ethynyl groups are found positioned around the olefinic core in a manner which reduces the steric interactions between them. In the case of the triethynyl derivative **6**, the Co–Co vectors are approximately perpendicular, with the $Si(3)Me_3$ group occupying a portion of the void space

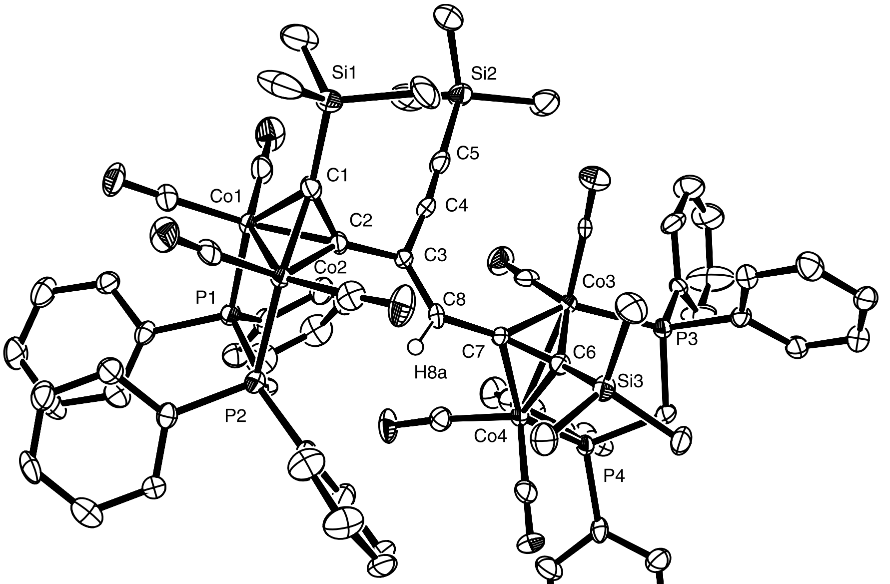


Fig. 1. An ORTEP plot of a molecule of **6**, showing the atom labelling scheme. Hydrogen atoms have been omitted for clarity.

around C(8). The Co(3)–Co(4) cluster moiety would appear to have some influence on the C(4)–C(5) alkynyl group, which bends away from the cluster giving slightly abnormal C(8)–C(3)–C(4) [124.9(6)°] and C(2)–C(3)–C(4) [113.5°] bond angles.

3. Conclusion

The Pd(0)–Cu(I) catalysed coupling reaction of terminal alkynes with tetrachloroethene in NEt_3 affords the corresponding tetraethynylethenes relatively cleanly

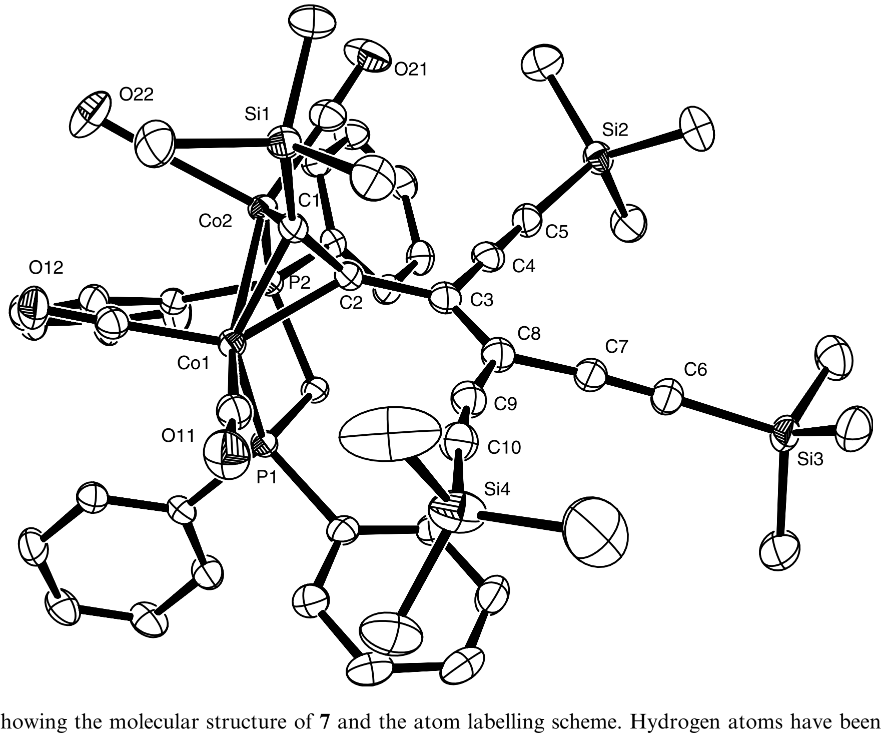


Fig. 2. A diagram showing the molecular structure of **7** and the atom labelling scheme. Hydrogen atoms have been omitted for clarity.

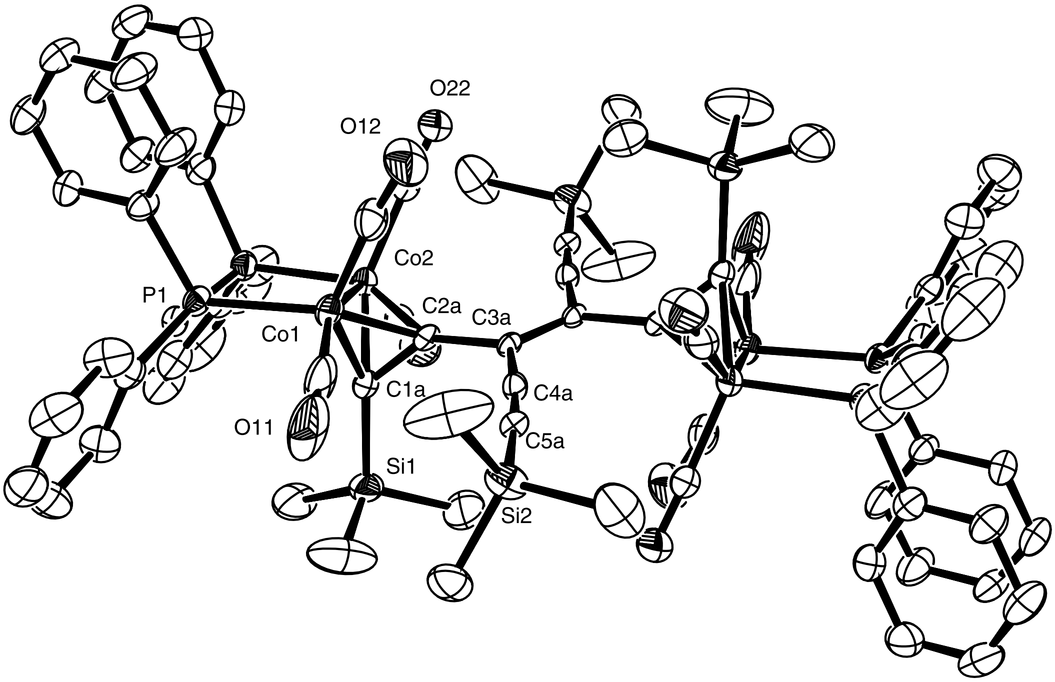


Fig. 3. The molecular structure of **8**, with hydrogen atoms omitted for clarity.

and in good yield. The alkyne moieties are available for coordination by up to two dicobalt fragments, giving the *trans* isomers as expected on steric grounds.

4. Experimental

4.1. General conditions

All reactions were carried out under dry high-purity nitrogen using standard Schlenk techniques. Solvents were dried and distilled from conventional agents prior to use. Preparative TLC was performed on 20 × 20 cm glass plates coated with silica gel (Merck GF_{254}, 0.5 mm thick). Literature methods were used to prepare trimethylsilylacetylene [43], 4-ethynylbenzonitrile [44], $Pd(PPh_3)_4$ [45], $[Co_2(CO)_6(\mu\text{-dppm})]$ [46]. All other reagents were purchased and used as received.

4.2. Instrumental measurements

Infrared spectra were recorded using calcium fluoride cells of 0.5 mm path length, or NaCl plates using a Niolet Avatar FT-IR spectrometer. NMR spectra were recorded in $CDCl_3$ and referenced against the solvent resonances using Varian Mercury 200 and 400, and Varian Inova 500 spectrometers. EI-MS were obtained on an Autospec instrument. FAB-MS were recorded at the EPSRC National Mass Spectrometry Facility, Swansea. Microanalyses were performed in house.

*4.3. 1,6-Bis(trimethylsilyl)-3-4-bis[(trimethylsilyl)ethynyl]hex-3-ene-1,5-diyne (**2**)*

Dry NEt_3 (100 ml) was introduced to an oven-dried Schlenk flask and rigorously deoxygenated by three freeze-pump-thaw sequences. Tetrachloroethylene (1.00 ml, 9.77 mmol) was added followed by trimethylsilylacetylene (7.00 ml, 49.53 mmol), $Pd(PPh_3)_4$ (0.26 g, 0.23 mmol) and CuI (0.05 g, 0.26 mmol). The solution was heated at reflux overnight forming a dark red solution and white precipitate of the alkyl ammonium salts. The precipitate was removed by filtration, and the filtrate concentrated to afford a brown semi-crystalline mass which was washed with acidified MeOH and filtered to afford a light brown solid which was recrystallised from hot EtOH to afford the title compound (1.16 g, 30 %). IR (Nujol): $\nu(C\equiv C)$ 2166 m, 2147 m; $\nu(C=C)$ 1612 w cm^{-1}. ^1H-NMR (499 MHz, $CDCl_3$): δ 0.23 ($SiMe_3$, s). ^{13}C-NMR (125 MHz, $CDCl_3$): δ −0.20 ($SiMe_3$), 100.93 ($C\equiv C$), 105.30 ($C\equiv C$), 118.78 ($C=C$). EI^+-MS (m/z): 412 $[M]^+$.

*4.4. 1,6-Bis(phenyl)-3,4-bis(phenylethynyl)-hex-3-ene-1,5-diyne (**3**)*

Dry NEt_3 (100 ml) was introduced to an oven-dried Schlenk flask and rigorously deoxygenated by three freeze-pump-thaw sequences. Tetrachloroethylene (1.0 ml, 9.8 mmol) was added followed by phenylacetylene (4.3 ml, 39 mmol), $Pd(PPh_3)_4$ (0.60 g, 0.49 mmol) and CuI (0.09 g, 0.47 mmol). The yellow mixture was heated at reflux turning red overnight. The mixture was filtered and the filtrate concentrated. The concentrated filtrate was diluted with CH_2Cl_2 and purified by column chromatography (silica, 1:1 CH_2Cl_2–C_6H_{14}). The product was contained in the bright yellow band and recrystallised from $CHCl_3$–EtOH (60 %). IR (Nujol): ν(C≡C) 2192m cm^{-1}. ^{1}H-NMR (200 MHz): 7.3–7.6 (m, Ph). ^{13}C-NMR (62.9 MHz): 87.4; 98.9; 117.2; 122.6; 128.4; 129.0; 131.7. MS (EI): *m/z* 428 [M$^+$]; 350 (M$^+$ −Ph−H); 226 [M$^+$ −2PhC≡C).

*4.5. 1,6-Bis(4′-cyanophenyl)-3-4-bis[(4′-cyanophenyl)ethynyl]hex-3-ene-1,5-diyne (**4**)*

Dry NEt_3 (100 ml) was introduced to an oven-dried Schlenk flask and rigorously deoxygenated by three freeze-pump-thaw sequences. Tetrachloroethylene (0.25 ml, 2.44 mmol) was added followed by 4-ethynylbenzonitrile (1.25 g, 9.84 mmol), $Pd(PPh_3)_4$ (0.14 g, 0.12 mmol) and CuI (0.02 g, 0.10 mmol). The solution was heated at reflux overnight forming a dark red solution with brown precipitate. The precipitate was collected by filtration, and the filtrate concentrated. The precipitate was purified by column chromatography (silica gel, C_3H_6O). The product was recrystallised from hot MeCN containing a small amount of Me_2SO (0.54 g, 42 %). IR (Nujol), ν (cm^{-1}): 2224 w (CN), 1600 w (C=C). ^{1}H-NMR (d_6-DMSO): δ 7.77, 7.93 (2 × d, $J_{HH} = 10$ Hz, 2 × 8 H, C_6H_4). EI$^+$-MS (*m/z*): 528 [M]$^+$. Anal. Calc. $C_{38}H_{16}N_4\cdot 0.5Me_2SO$ requires: C, 80.41; H, 3.26; N, 9.62. Found: C, 80.87; H: 2.89; N, 9.96%.

*4.6. [{$Co_2(CO)_4$(μ-dppm)}$_2${μ,η^2-(Me_3SiC_2C(H)=C(C≡CSiMe$_3$)$_2$}] (**6**)*

The crude product from the NH^{i}Pr$_2$ preparation of **2** (0.10 g) and [$Co_2(CO)_6$(μ-dppm)] (0.14 g, 0.23 mmol) were dissolved in dry C_6H_6 (20 ml) and the mixture stirred at reflux for 15 min after which additional [$Co_2(CO)_6$(μ-dppm)] (0.12 g, 0.19 mmol) was added and the reaction allowed to reflux for a further 20 min. The reaction was then cooled and the solvent removed in vacuo. Purification of the residue by preparative TLC (20:80 CH_2Cl_2–C_6H_{14}) afforded red, yellow–brown and green bands. These were identified as [$Co_2(CO)_4$(μ-dppm)(μ,η^2-Me_3SiC_2C≡CSiMe$_3$)] (red, 29%), [$Co_2(CO)_4$(μ-dppm)(μ,η^2-{Me_3SiC_2C(C≡CSiMe$_3$)=C(C≡CSiMe$_3$)$_2$}] (**7**) (brown, 44%), and [{$Co_2(CO)_4$(μ-dppm)}$_2${μ,η^2-(Me_3SiC_2C(H)=C(C≡CSiMe$_3$)}] (**6**) (green, 9%), respectively. All the products were crystallised from CH_2Cl_2–MeOH.

Compound **6** IR (cyclohexane): ν (CO) 2021 s, 1997 vs, 1970 vs cm^{-1}. ^{1}H-NMR (499 MHz, $CDCl_3$): δ −0.17 (s, 9H, SiMe$_3$), 0.13 (s, 9H, SiMe$_3$), 0.40 (s, 9H, SiMe$_3$), 3.26 (m, 2H, CH$_2$), 3.42 (=CH, br, 1H), 3.50 (m, 2H, CH$_2$), 6.94–7.54 (m, 20H, Ph). ^{13}C-NMR (399 MHz, $CDCl_3$): δ −0.18, 0.98, 1.27 (3 × s, 3 × SiMe$_3$), 35.82, 38.44 (2 × br, 2 × CH_2P_2), 106.04, 106.40 (2 × s, 2 × C≡C), 125.41–139.47 (m, Ph), 203.04, 204.38, 207.06, 207.61 (4 × s, 4 × CO). FAB-MS (*m/z*): 1545 [M]$^+$, 1517 [M−CO]$^+$, 1489 [M−2CO]$^+$. Anal. Calc. $Co_4P_4O_8Si_3C_{75}H_{72}$ requires: C, 58.25; H, 4.66. Found: C, 57.79; H, 4.70%.

4.7. [$Co_2(CO)_4$(μ-dppm){μ,η^2-Me_3SiC_2C(C≡CSiMe$_3$)=C(C≡CSiMe$_3$)$_2$}] (7)

A round bottomed flask was charged with **2** (0.10 g, 0.24 mmol) and [$Co_2(CO)_6$(μ-dppm)] (0.05 g, 0.08 mmol) which were dissolved in dry C_6H_6 (20 ml) and the reaction mixture heated at reflux. Three further portions of [$Co_2(CO)_6$(μ-dppm)] were added at 15 min intervals. After the final addition, the reaction was allowed to react for a further 20 min before chromatographic workup by preparative TLC (20:80 CH_2Cl_2–C_6H_{14}). The major band (brown) was crystallised (CH_2Cl_2–MeOH) to afford the title compound **7** (0.16 g, 62 %). IR (cyclohexane): ν (CO) 2023 s, 1999 vs, 1973 s cm^{-1}. ^{1}H-NMR (499 MHz, $CDCl_3$): δ 0.02 (s, 9H, SiMe$_3$), 0.09 (s, 9H, SiMe$_3$), 0.26 (s, 9H, SiMe$_3$), 0.32 (s, 9H, SiMe$_3$), 3.53, 3.73 (2 × m, 2 × 1H, CH$_2$); 7.09–7.20 (m, 20H, Ph). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 0.12, 0.41, 0.78, 2.42 (4 × s, 4 × SiMe$_3$), 36.52 (br, CH_2P_2), 98.23, 104.54, 105.47, 106.85, 107.16, 110.13, 111.14 (7 × s, 7 C≡C), 128.62–141.23 (m, Ph), 204.75, 207.09 (2 × s, CO). FAB-MS (*m/z*): 999–915 [M−*n*CO]$^+$ (*n* = 1–4). Anal. Calc. $Co_2P_2O_4Si_4C_{51}H_{58}$ requires: C, 57.83; H, 5.52. Found: C, 57.08; H, 5.93%.

*4.8. [{$Co_2(CO)_4$(μ-dppm)}$_2${μ−η^2:η^2-Me_3SiC_2C(C≡CSiMe$_3$)C(C≡CSiMe$_3$)C_2SiMe_3}] (**8**)*

A C_6H_6 solution (20 ml) of complex **7** (0.18 g, 0.17 mmol) and [$Co_2(CO)_6$(μ-dppm)] (0.40 g, 0.6 mmol) was heated at reflux for 3 h. The reaction mixture was allowed to cool, and the solvent removed in vacuo to give a residue which was purified by preparative TLC (1:1 CH_2Cl_2–C_6H_{14}). The two principal bands (brown) were crystallised (CH_2Cl_2–MeOH) to afford **7** (upper band, 10%) and the title compound **8** (lower band, 0.032 g, 11%). Compound **8** IR (cyclohexane), ν (cm^{-1}): 2127 w (C≡C), 2024 m (CO), 2001 s (CO), 1976 m (CO). ^{1}H-NMR (499 MHz, $CDCl_3$), (δ): 0.22 (SiMe$_3$, s, 9H), 0.55 (SiMe$_3$, s, 9H), 3.51 (CH$_2$, m, 2H), 7.17–7.72 (aromatic, m, 20H). FAB-MS (*m/z*): 1640 [M]$^+$, 1612–1416 [M−*n*CO]$^+$ (*n* = 1–8). Anal. Calc. $Co_4P_4O_8Si_4C_{80}H_{80}$ requires: C, 58.53; H, 4.88. Found: C, 58.79; H, 5.13%.

4.9. *Reaction of 1,6-bis(trimethylsilyl)-3-4-bis[(trimethylsilyl)ethynyl]hex-3-ene-1,5-diyne with [$Co_2(CO)_8$]*

A sample of **2** (0.05 g, 0.12 mmol) and $Co_2(CO)_8$ (0.11 g, 0.32 mmol) were dissolved in dry C_6H_6 (10 ml). The reaction was stirred for 2 h then the solvent removed in vacuo. The product was purified by preparative TLC (30:70 CH_2Cl_2–C_6H_{14}). The major green band was crystallised (CH_2Cl_2–C_6H_{14}) to afford [$\{Co_2(CO)_6\}_2$-$\{\mu,\eta^2$-$Me_3SiC_2C(C{\equiv}CSiMe_3){=}C(C{\equiv}CSiMe_3)C_2SiMe_3\}$] (**9**) (0.082 g, 67%), while the minor brown band afforded [$\{Co_2(CO)_6\}(\mu,\eta^2$-$Me_3SiC_2C(C{\equiv}CSiMe_3){=}C(C{\equiv}CSiMe_3)_2)$] (**10**) (0.011 g, 17%). Despite repeated attempts, consistent microanalytical results were not obtained.

Compound **9** IR (cyclohexane): ν (CO) 2088 s, 2056 vs, 2030 vs cm^{-1}. ^{1}H-NMR (499 MHz): δ 0.25 ($SiMe_3$, s, 18H), 0.40 ($SiMe_3$, s, 18H). ^{13}C-NMR (125 MHz): δ −0.39, 1.48 (2 × s, 2 × $SiMe_3$), 83.69, 105.10, 107.10, 113.34, 127.83 (5 × s, 5 × C≡C, C=C), 200.50 (CO). FAB-MS (m/z): 872 $[M-4CO]^+$.

10 IR (cyclohexane): ν (CO) 2089 s, 2056 vs, 2030 vs cm^{-1}. ^{1}H-NMR (499 MHz, $CDCl_3$): δ 0.23 (s, 9H, $SiMe_3$), 0.39 (s, 27H, 3 × $SiMe_3$). ^{13}C-NMR (125 MHz, $CDCl_3$): δ −0.62, −0.36, −0.18, 1.12 (4 × $SiMe_3$), 84.01, 97.47, 100.73, 102.97, 104.39, 104.54, 105.55, 111.67, 112.22, 134.72 (10 × s, 10 × C≡C, C=C), 200.24 (CO). FAB-MS (m/z): 670–530, $[M-n\text{CO}]^+$ ($n = 1$–6).

5. Crystallographic details

Single crystal diffraction data for **6**, **7** and **8** were collected at 120 K, using graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$), on a Bruker SMART CCD diffractometer equipped with a Cryostream N_2 flow cooling device [47]. Cell parameters were determined and refined using the SMART software [48] and raw frame data were integrated using the SAINT program [49]. The structures were all solved by direct methods and refined by full-matrix least-squares agains F^2 of all data, using the SHELXTL suite of programs [50]. The reflection intensities were corrected for absorption effects by numerical integration based on measurements and indexing of the crystal faces using SHELXTL software for **7** [50], and by the multi-scan method based on multiple scans of identical and Laue equivalent reflections using SADABS for **6** and **8** [51]. All non-hydrogen atoms for **6** were refined with anisotropic atomic displacement parameters (adps), except those of the disordered and/or partially occupied dichloromethane and methanol solvent molecules which were refined with isotropic adps. All non-hydrogen atoms for **7** were refined with anisotropic adps. For **8**, all non-hydrogen atoms were refined with anisotropic adps, except five carbon atoms belonging to the minor component (0.25(1) occupancy) of a modelled disorder. For the three structures, all hydrogen atoms were geometrically placed and allowed to ride on their parent C atom with U_{iso} (H) = 1.5 U_{eq}(C) for methyl groups and solvent molecules and with U_{iso} (H) = 1.2 U_{eq}(C) for all other cases. Idealized C–H distances were fixed at 0.95 Å for aromatic groups, 0.98 for CH_3 groups, 0.99 for CH_2 groups and 0.84 for the OH of a methanol. Crystal data and further experimental and refinement details are listed in Table 1.

6. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 195010–195012 for structures of **7**, **6** and **8**, respectively. Copies of this information may be obtained free of charge The Director, CCDC, 12 Union Road, Cambridge CB2 1E2, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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