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Solvent-Mediated Generation of Cobalt-Cluster-Stabilised Propargyl Cations and Radicals: Allyl Migration versus Peroxide Formation

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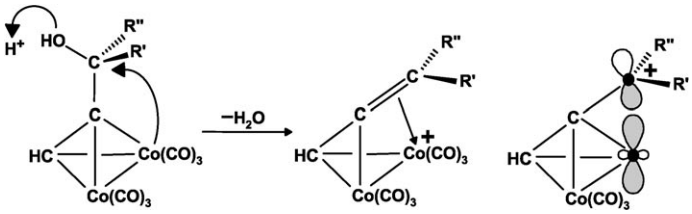
Abstract: The protonation of $[Co_2(CO)_6\{9\text{-}[(allyldimethylsilyl)ethynyl]\text{-}9H\text{-}fluoren\text{-}9\text{-}ol\}]$ (**4**), with HBF_4 in CH_2Cl_2 led to migration of the allyl group from silicon to the cobalt-stabilised cationic site to furnish $[Co_2(CO)_6\{9\text{-}allyl\text{-}9\text{-}[(dimethylfluorosilyl)ethynyl]\text{-}9H\text{-}fluorene\}]$ (**17**). However, under the same conditions, $[Co_2(CO)_6\{9\text{-}[(benzyldimethylsilyl)ethynyl]\text{-}9H\text{-}fluoren\text{-}9\text{-}ol\}]$ (**5**) underwent desilylation and rearrangement of the resulting terminal alkyne–dicobalt complex to give $[Co_3(CO)_9(9H\text{-}fluorenylmethylcarbynyl)]$ (**24**); moreover, dimerisation of the (benzyldimethylsilyl)ethynyl-9*H*-fluorenyl moiety led to the propargyl–allene **26**. In contrast, protonation of **5** in THF yielded $[\{Co_2(CO)_6\{[(benzyldimethylsilyl)ethynyl\text{-}9H\text{-}fluorenyl]\}\}_2peroxide]$ (**27**) through a radical coupling process. Analogously, protonation of $[Co_2(CO)_6\{9\text{-}[(vinyldimethylsilyl)ethynyl]\text{-}9H\text{-}fluoren\text{-}9\text{-}ol\}]$ (**6**) yields the corresponding peroxide **28**. X-ray crystallographic data are reported for, among others, complexes **17**, **24**, **26**, **27** and **28**.

Keywords: allylsilanes · benzylsilanes · cluster compounds · cobalt · peroxides

Introduction

The ability of alkyne–dicobalt clusters to stabilise an α-cationic site is the basis of the Nicholas reaction[1]—a synthetically valuable procedure used, for example, in the preparation of enediynes,[2a] (+)-begamide E,[2b] blastinomycine,[2c] cyclocolorenone,[2d] tetrapyrroles,[2e] insect pheromones,[2f] vitamin A derivatives,[2g] carotenes,[2h] pyrones[2i] and benzofurans.[2j] This stabilisation can be attributed to partial delocalisation of the charge onto a cobalt atom through overlap of a filled metal d orbital with the vacant p orbital on the electron-deficient α-carbon atom,[3] and is facilitated by a structural perturbation such that the carbocationic centre leans toward a metal vertex as illustrated in Scheme 1. This geometric distortion is evident in a variety of crystallographic determinations, whereby the α-carbon atom is clearly bonded to a cobalt,[4] iron,[5] or molybdenum[6] cluster vertex. Moreover, such stabilisation by a metal allows the convenient generation of otherwise inaccessible species such as the non-classical bornyl or fenchyl cations,[7,8] or the antiaromatic indenyl or fluorenyl cations.[9]



Scheme 1. Cobalt-stabilised propargyl cations.

This phenomenon, together with the known enhanced stabilisation of β-silyl cations,[10] has been elegantly exploited by Schreiber in a number of cyclisations,[11] as depicted in Scheme 2. An additional factor in this process is the bending of the alkyne upon complexation to a $\{Co_2(CO)_6\}$ moiety such that the originally linear C–C≡C–C unit now makes angles of approximately 135–145° at the central carbon atoms, thus permitting the formation of cycloalkynes containing as few as six ring carbon atoms.[12] More recently, Green has used this approach to synthesise a series of cyclophanes.[13]

Although nucleophilic attack at the α-cationic site has been extensively exploited for synthetic purposes, studies on the development of radical character at the α-carbon are of

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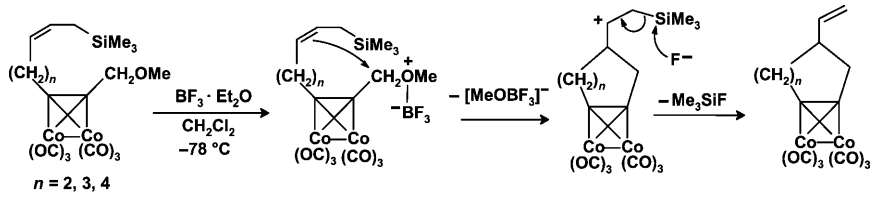
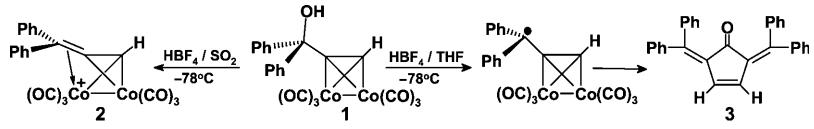


Scheme 2. Metal-cluster-mediated cyclisations of allylsilanes.

much more recent vintage.[14] Pioneering studies by Nicholas and Melikyan initially focussed on the deliberate reduction of the cations by use of zinc dust,[15] but subsequently it became evident that in certain solvents, notably diethyl ether or tetrahydrofuran, electron-transfer processes led directly to metal-cluster-complexed propargylic radicals without the need to add an extra reducing agent.[16] For example, as depicted in Scheme 3, treatment of $[Co_2(CO)_6(HC{\equiv}C{-}CPh_2OH)]$ (**1**) with HBF_4 in SO_2 yields the isolable cation $[Co_2(CO)_6(HC{\equiv}C{-}CPh_2)]^+$ (**2**);[17] however, in THF as the solvent, the reaction takes an entirely different course and the major product is 2,5-bis(diphenylmethylene)-3-cyclopentenone (**3**).[18] Although the mechanistic details have not yet been fully elucidated, the formation of **3** is believed to proceed through dimerisation of $[Co_2(CO)_6(HC{\equiv}C{-}CPh_2)]^{\bullet}$ radicals, such that coupling occurs at the less sterically hindered termini of the complexed alkynes to form a diallene–cobalt complex, which, after a carbonyl migration and reductive elimination, ultimately yields the cyclopentenone **3**.



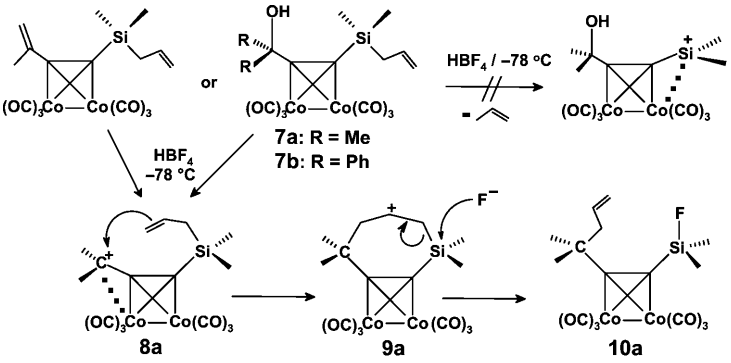
Scheme 3. Reactions of cobalt-complexed propargyl cations and radicals.

Herein we describe the reactions of $[Co_2(CO)_6\{9\text{-}[(allyldimethylsilyl)ethynyl]\text{-}9H\text{-}fluoren\text{-}9\text{-}ol\}]$ (**4**), $[Co_2(CO)_6\{9\text{-}[(benzyldimethylsilyl)ethynyl]\text{-}9H\text{-}fluoren\text{-}9\text{-}ol\}]$ (**5**) and $[Co_2(CO)_6\{9\text{-}[(vinyldimethylsilyl)ethynyl]\text{-}9H\text{-}fluoren\text{-}9\text{-}ol\}]$ (**6**) with fluoroboric acid in dichloromethane and in tetrahydrofuran, yielding products that clearly involve both cationic and radical intermediates.

Results and Discussion

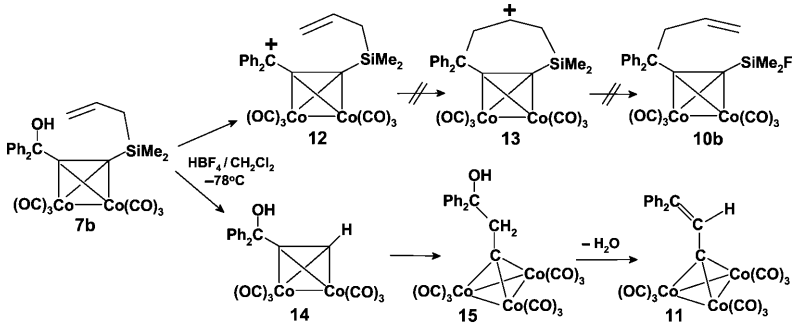
Our involvement in this area arose as the result of an attempt to study the relative ease of generation of metal-cluster-stabilised silylium ions versus carbocations from the bifunctional starting material **7**. The former were potentially preparable by elimination of propene from an allyl–silane,[19] while the latter could be generated through protonation of an alcohol or an alkene, as shown in Scheme 4. In the case of **7a** (R = Me), the observed outcome of the experiment involved initial formation of the carbocation **8a**, which underwent intramolecular nucleophilic attack by the terminus of the allyl group thus furnishing the β-silyl cation **9a**. Subsequent formation of a thermodynamically favourable silicon–fluorine bond yielded **10a**, in which the allyl group has migrated from silicon to carbon, thereby generating a quaternary centre.[20]

In contrast, protonation of the cluster **7b** (R = Ph) led to the carbynyl–tricobalt cluster **11**, rather than the anticipated allyl migration product **10b**. One might hypothesise that the initially generated carbocation **12**, surrounded as it is by two phenyl groups and a cobalt cluster, is reluctant to undergo addition to the allyl group to produce the cation **13**, which would be stabilised only by a hyperconjugative interaction with the β-silicon. Instead, as shown in Scheme 5, desilylation[21] yields the terminal alkyne complex **14**, which undergoes the known rearrangement to a tricobalt cluster.[22] The mechanism of rearrangement of alkyne–dicobalt hexacarbonyl clusters, $[Co_2(CO)_6(RC{\equiv}CH)]$ into the corresponding carbynyl–nonacarbonyltricobalt systems, $[RCH_2{-}CCo_3(CO)_9]$, is not yet fully understood, but a proposal for the initial stages of the process has been advanced.[23] In the present case, one might have expected formation of the tertiary alcohol **15**, but elimination of water led directly to the observed product **11**, which has been unequivocally characterised by X-ray crystallography.[18]



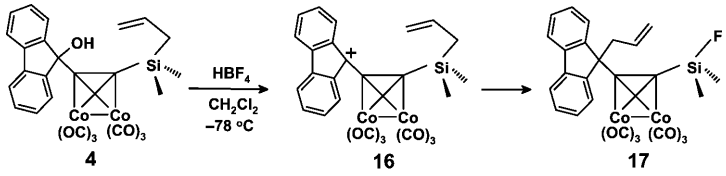
Scheme 4. A metal-cluster-mediated allyl migration.

Protonation of $[Co_2(CO)_6\{9\text{-}[(allyldimethylsilyl)ethynyl]\text{-}9H\text{-}fluoren\text{-}9\text{-}ol\}]$ in CH_2Cl_2: On the premise that allyl migration to the diphenyl-substituted cationic site in **12** is thwarted by its enhanced stability, we chose instead to link the two phenyls so as to incorporate a fluorenyl skeleton, as in complex **4**. The derived cation (**16**) not only presents a



Scheme 5. Rearrangement of **7b** to form a tricobalt cluster.

flat, less sterically demanding target for the incoming allyl group, but, as a 12π antiaromatic system, is also strongly electronically disfavoured unless the charge deficiency is alleviated by a neighbouring cobalt vertex. Gratifyingly, in this case, protonation results in efficient transfer of the allyl group from silicon to the metal-stabilised carbocationic centre of the anti-aromatic fluorenyl framework (Scheme 6); the X-ray crystal structure of the rearranged product $[Co_2(CO)_6\{9\text{-allyl-9-[(dimethylfluorosilyl)ethynyl]-9}H\text{-fluorene}\}]$ (**17**) is shown in Figure 1.



Scheme 6. Cobalt-mediated allyl migration from silicon to carbon.

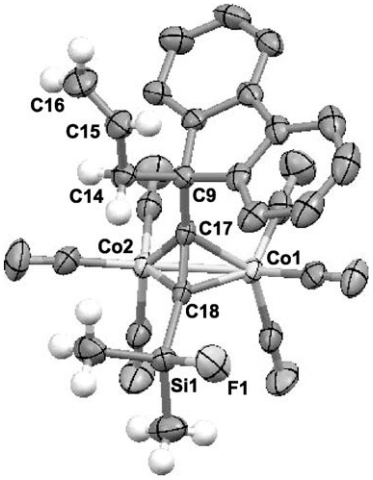
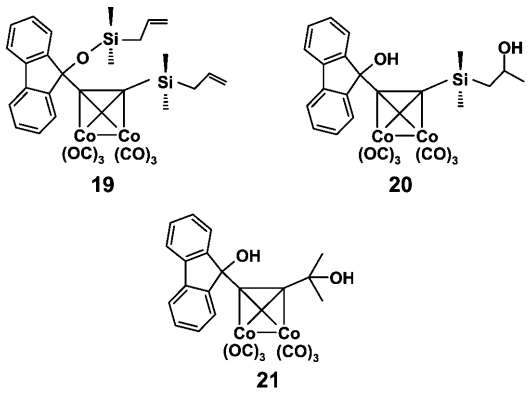


Figure 1. Mercury[24] representation of the molecular structure of complex **17**, (30% thermal ellipsoids; aromatic hydrogen atoms have been excluded for clarity.)

Interestingly, the synthesis of 9-[(allyldimethylsilyl)-ethynyl]-9*H*-fluoren-9-ol, **18**, from allylchlorodimethylsilane and the di-lithio derivative of 9-ethynylfluoren-9-ol, also yielded several minor by-products. These materials were not readily separable as free ligands but were obtained as cobalt clusters, **19**, **20** and **21**, during the subsequent chromatographic purification procedure.

The bis-silylated complex **19** evidently arises in the course of the reaction of the dilithio salt



of 9-ethynylfluoren-9-ol with two molecules of allylchlorodimethylsilane. The second product, **20**, which was characterised X-ray crystallographically (see Figure 2), presumably results from hydration of the allylsilane **18**. Although β-hydroxysilanes are normally rather susceptible to dehydration,[25] the excellent crystallinity of **20** appears to be enhanced by a combination of strong inter- and intramolecular hydrogen-bonding interactions, evident within the solid-state structure as illustrated in Figure 3. Two crystallographically independent molecules are found in the unit cell, for which

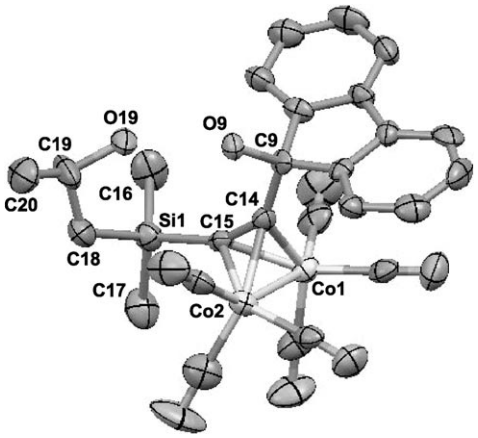


Figure 2. Molecular structure of the dicobalt cluster diol, **20**, (30% thermal ellipsoids; hydrogen atoms have been excluded for clarity.)

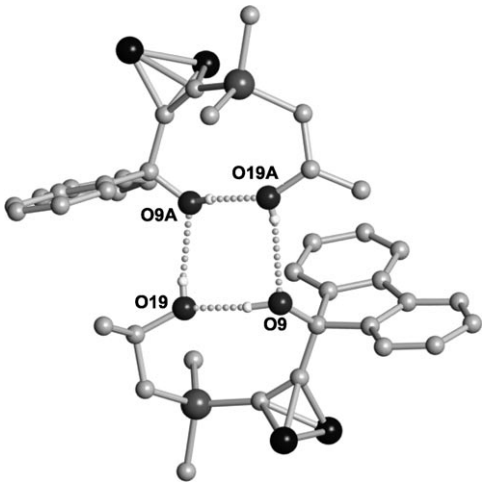


Figure 3. Inter- and intramolecular hydrogen-bonding interactions in **20**; cobalt carbonyl groups have been excluded for clarity.

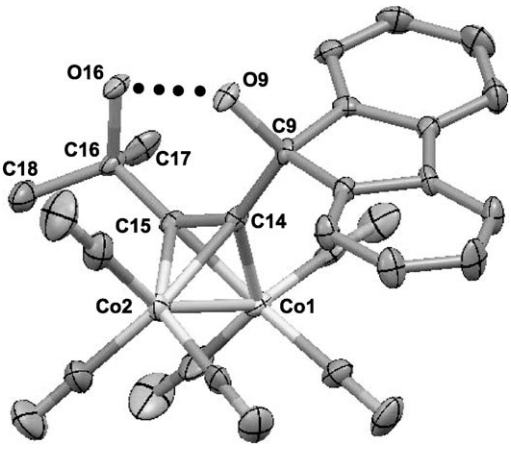


Figure 4. Mercury[24] representation of the molecular structure of **21**, excluding hydrogen atoms, with 30% thermal probability ellipsoids. The intramolecular hydrogen bond contact O9···O16 is 2.790 Å.

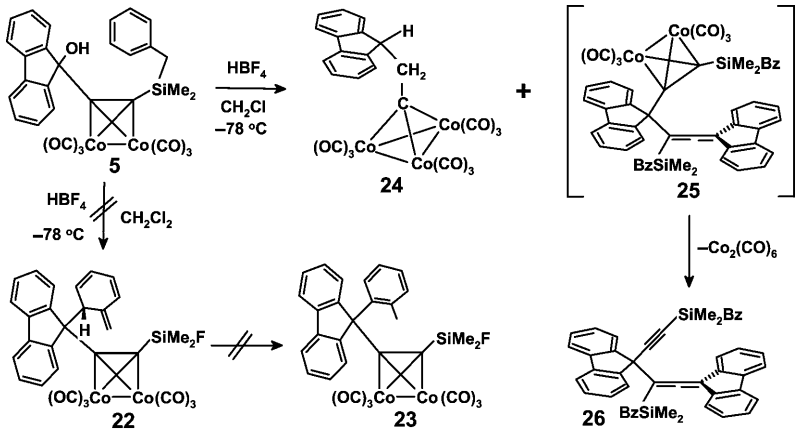
the four hydroxy groups adopt a slightly distorted square planar arrangement (see Table 1), and deviate merely 0.2 Å from planarity.[26,27] The hydrogen bonding within this species undoubtedly contributes to its stability and permits its isolation, whereas the corresponding hydroxylsilane may not be favoured in the analogous diphenyl system, because of rotational interference engendered by the aryl rings.

Table 1. Relevant distances and angles within the hydrogen bonding regime of **20**.

D−H···A	D···H [Å]	H···A [Å]	D···A [Å]	D−H···A [°]
O9−H···O19	0.87(4)	1.90(4)	2.732(6)	161(4)
O9A−H···O19A	0.84	1.91	2.691(7)	154
O19−H···O9A	0.72(5)	2.03(5)	2.740(8)	170(7)
O19A−H···O9	0.63(7)	2.22(7)	2.835(8)	166(10)

With respect to the other unexpected product (**21**), our initial thought was that it may have arisen through reaction of the fluorenyl-alkynyl anion, generated in situ, with traces of acetone left from cleaning the glassware prior to conducting the experiment. However, repetition of this reaction, taking meticulous care to avoid any possibility of contamination by acetone, still afforded small quantities of the product, which was unambiguously identified X-ray crystallographically (Figure 4). As with the hydroxysilane complex **20**, hydrogen bonding is a prominent feature of the crystal structure; however, unlike **20**, it is only manifested intramolecularly. One cannot overlook the possibility that the three-carbon unit originated on the allyl substituent attached to the silane. Nevertheless, it is not immediately evident how the allyl functionality could have migrated to the alkynyl terminus with concomitant cleavage of the dimethylsilyl fragment, but mechanistic investigations are ongoing.

Protonation of $[Co_2(CO)_6\{9\text{-}[(benzyldimethylsilyl)ethynyl]\text{-}9H\text{-}fluoren\text{-}9\text{-}ol\}]$ in CH_2Cl_2: With the aim of broadening the scope of this intramolecular rearrangement, we chose to prepare the analogous (benzyldimethylsilyl)ethynyldicobalt complex **5**, which contains an allyl subsystem. The objective was to determine whether the thermodynamic driving force provided by the formation of a silicon–fluorine bond was great enough to induce a benzyl migration. For this to happen, the aromatic character of the phenyl ring would have to be lost, albeit temporarily, as illustrated in Scheme 7. Thus, the initial result of rearrangement would be the energetically disfavoured methylene–cyclohexadiene **22**, which should rapidly re-aromatise to generate an *ortho*-tolyl substituent, as in **23**.



Scheme 7. Products from the protonation of complex **5** with HBF_4 in CH_2Cl_2.

However, **5** does not undergo this silicon–carbon migration process; instead, when protonated with HBF_4 in dichloromethane at −78 °C, it furnished the (9-fluorenyl)methylcarbynyl–tricobalt cluster **24**, the molecular structure of which is shown in Figure 5. Apparently, in the absence of an

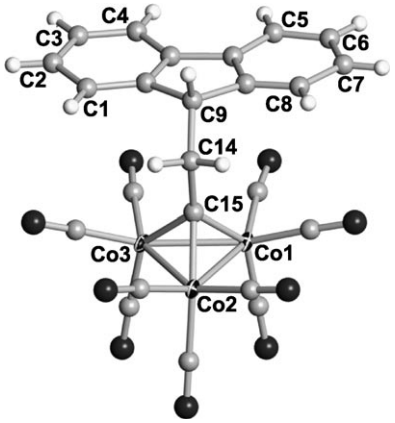


Figure 5. Molecular structure of complex **24**. Thermal parameters were established only for the cobalt atoms and are represented as 30% probability ellipsoids.[30]

energetically viable migration pathway, the system suffers desilylation to yield a terminal alkyne complex that subsequently undergoes the known rearrangement from $[Co_2(CO)_6(RC{\equiv}CH)]$ to $[Co_3(CO)_9(RCH_2{-}C)]$.[22] Intriguingly, the tricobalt cluster formed (see Scheme 7) does not correspond to the unsaturated system **11**, obtained from $[Co_2(CO)_6\{Ph_2C(OH){-}C{\equiv}CH\}]$ and HBF_4 in dichloromethane,[18] but instead follows the pattern observed by Hagihara,[28] whereby the reaction of $[Co_2(CO)_6\{Ph_2C(OH){-}C{\equiv}CH\}]$ with concentrated sulfuric acid forms the saturated molecule $[Co_3(CO)_9\{Ph_2CH{-}CH_2{-}C\}]$.[29] A possible contributory factor is the enhanced tendency of the anti-aromatic fluorenyl cation, even when complexed to the metal, to undergo reduction to the corresponding radical (and thereby initiate hydrogen abstraction) relative to that of the much more stable diphenylmethyl cation. It is also worth noting that the reaction of $[Co_2(CO)_6\{9\text{-}[(vinyl\text{dimethylsilyl})\text{ethynyl}]\text{-}9H\text{-fluoren-9-ol}\}]$ (**6**) with HBF_4 in dichloromethane likewise yields the (9-fluorenyl)methylcarbynyl–tricobalt cluster **24**.

The protonation of **5** in CH_2Cl_2 also yields a second cluster, presumably **25**, that exhibited ^{13}C NMR resonances at 206 ppm and 200 ppm—characteristic of an allene linkage and a cobalt carbonyl, respectively. However, it was rather unstable, and repeated attempts to recrystallise the crude material, led to loss of cobalt and isolation of the free ligand that was characterised by X-ray crystallography (Figure 6) as the unsymmetrical propargylallene dimer, **26**, formed by coupling of the alkynylfluorenyl radical with its fluorenylideneallenyl radical resonance form.[31] Since dichloromethane is not normally considered to be an electron-donating solvent, it is possible that radical formation was initiated by single-electron transfer from a cobalt radical fragment generated during the final step in the formation of the trinuclear complex **24**.[23] In the crystalline state, the propargyl–allene dimer exhibits a 50:50 disorder, such that the modelled overlapped molecular orientations (Figure 7) generate pseudo C_i symmetry. This same centrosymmetric disorder phenomenon is also found in the corresponding bis(trimethylsilyl)propargylallene.[32] Interestingly, a Cope rearrangement of the hexa-1,2-diene-5-yne **26** would regenerate itself, presumably through a twofold symmetric transition state.

Protonation of $[Co_2(CO)_6\{9\text{-}[(benzyldimethylsilyl)ethynyl]\text{-}9H\text{-fluoren-9-ol}\}]$ in THF: As noted above, in contrast to the well-established chemistry of $[Co_2(CO)_6(propargyl\ alcohol)]$ complexes, which, upon protonation in dichloromethane, yield metal-stabilised carbocations, it is now evident that changing to an ether-based solvent leads to the generation of the corresponding propargyl radicals. To compare the results of protonations in dichloromethane with ones carried out in a solvent known to engender radical products, the benzylsilane-dicobalt complex **5** was treated with fluoroboric acid at −78 °C in THF. The ^1H and ^{13}C NMR spectra

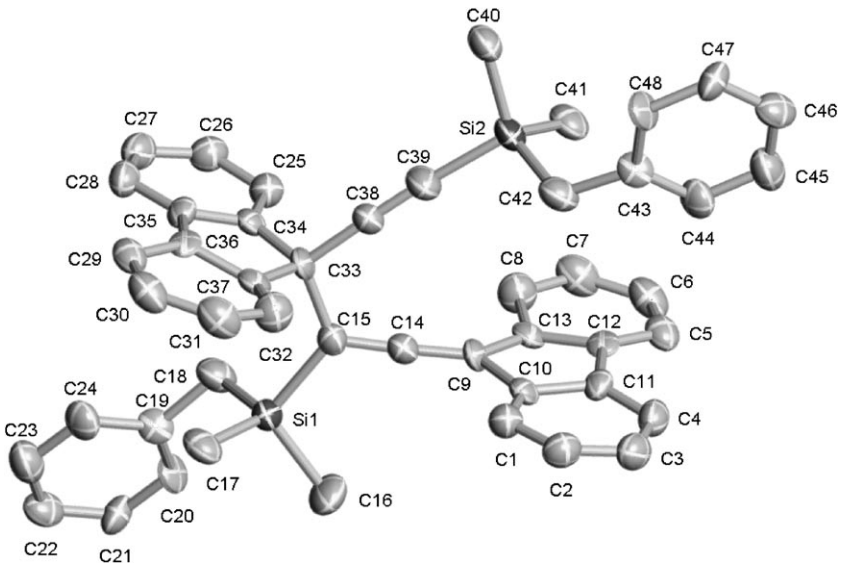


Figure 6. Molecular structure of the alkynylallene **26** (30% thermal probability ellipsoids; hydrogen atoms omitted for clarity). Selected distances (Å) and angles (°): C9−C14 1.310(15), C14−C15 1.287(9), C15−C33 1.587(18), C33−C38 1.473(12), C38−C39 1.213(10), C39−Si2 1.837(7), C9-C14-C15 177.3(10), C33-C38-C39 177.4(11), C38-C39-Si2 176.7(6).

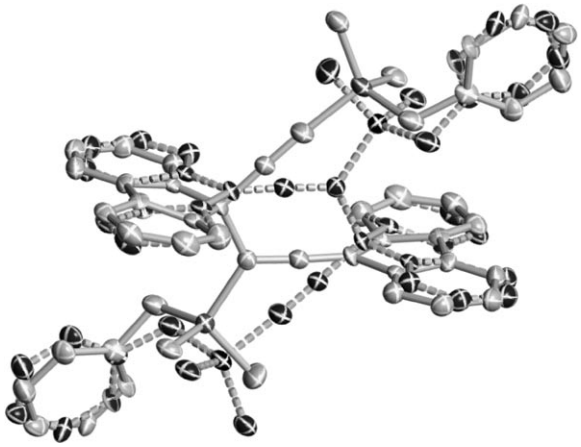


Figure 7. View showing the extensive overlap of both partially occupied models of **26**.

of the sole product (**27**) revealed resonances very similar to those of the starting material, except for the absence of the alcoholic proton signal. In the absence of a distinct molecular ion in the mass spectrum, the unequivocal identification of **27** as either an ether or a peroxide could not be made, since the first major bond cleavage would be that of the oxygen–oxygen linkage, and the fragmentation patterns would not be expected to differ significantly. However, isolation of single crystals of **27** revealed the product to be the peroxide (see Scheme 8), the molecular structure of which is shown in Figure 8. Unlike hydrogen peroxide which exhibits an "open-book" type geometry, the cluster-substituted peroxide **27** adopts a centrosymmetric (C_i) structure with a central O9–O9A distance of 1.494(3) Å and C9-O9-O9A angle of 104.5(2)°. In this respect it resembles the very bulky bis(9-*ortho*-isopropylphenyl-9-fluorenyl)peroxide, which also adopts a centrosymmetric structure with a central O–O distance of 1.496 Å, a C-O-O angle of 106°, and parallel fluorenyl planes.[33] However, as illustrated in Figure 9, the additional bulk of the dicobalt hexacarbonyl clusters in **27** results in the fluorenyl ligands being distorted such that each six-membered ring deviates from planarity by approximately 7°.

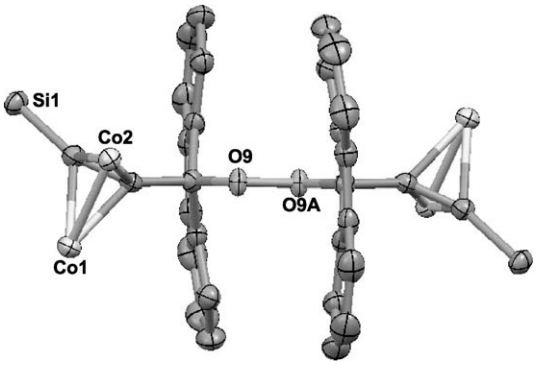
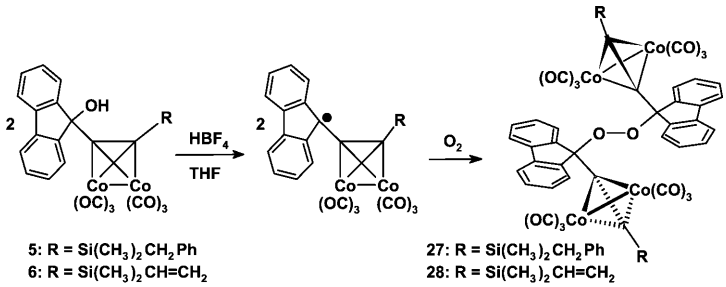


Figure 9. Perpendicular view of the benzylsilyl peroxide **27** without hydrogen atoms and carbonyl groups, emphasising the curved nature of the fluorenyl ligands.



Scheme 8. Formation of peroxides **27** and **28** upon protonation of **5** and **6**, respectively, in THF.

The vinylsilanedicobalt complex **6** was protonated under identical conditions, and also afforded the analogous peroxide **28** as the only isolable product. Although only weakly diffracting crystals were obtained for **28**, the data were sufficiently good to establish the atom connectivity of the molecule, as shown in Figure 10. In this case, the fluorenyl ligands deviate merely 3.5° from planarity, somewhat less than was seen in the benzyl analogue, possibly attributable

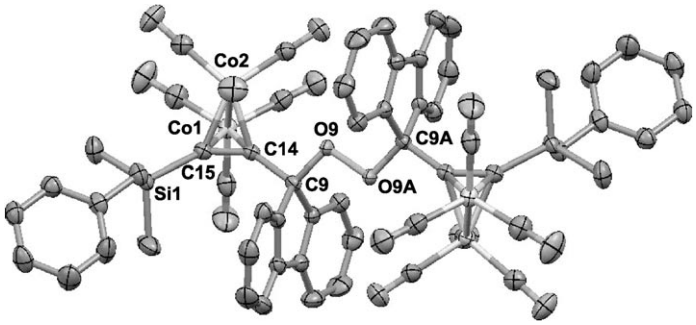


Figure 8. Mercury[24] representation of the molecular structure of the benzylsilyl peroxide **27** (30% thermal probability ellipsoids; hydrogen atoms excluded for clarity).

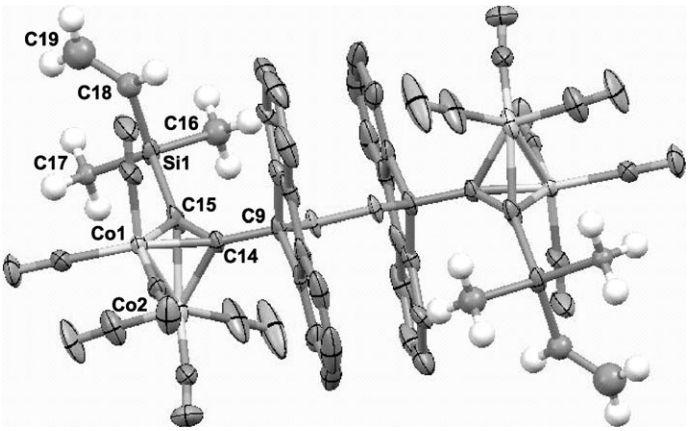


Figure 10. Mercury[24] representation of the molecular structure of the vinyl-silyl peroxide **28**; aromatic hydrogen atoms have been excluded for clarity.

to a reduction in packing influences afforded by the smaller vinyl substituent. Repetition of both protonation reactions in diethyl ether likewise yielded the peroxides **27** and **28** as the major and only identifiable products.

Conclusion

These observations confirm and extend earlier reports, notably by Melikyan,[15,16] that protonations of cobalt-complexed propargylic alcohols in either THF or diethyl ether yield radical products. The generation of peroxides is a characteristic of reasonably long-lived radicals that react with dioxygen to produce R-O-O$^{\bullet}$ intermediates. Although these are, to our knowledge, the first metal-complexed fluorenyl peroxides to have been synthesised, there are several known metal-free difluorenyl peroxides, including phenyl-, isopropyl- and benzyl- substituted systems.[33,34] It should be emphasised that organometallic peroxides are relatively uncommon: not only are preformed peroxide ligands insufficiently thermally stable to survive the conditions required for complexation by a metal, but also low-valent transition metals generally bring about cleavage of the peroxy linkage. Previously known examples include numerous mercuric peroxides[35] and transition-metal-containing porphyrins.[36] The very first organometallic peroxide was prepared by passing oxygen gas through a solution of cobaltocene in diethyl ether at −78 °C.[37] Since then, several ferrocenyl systems[38] and also a rhodocene have been reported;[39] however, these molecules were prepared either by coordination of dioxygen to cationic complexes of the metal in the absence of any known radical initiating solvents, or by nucleophilic addition of the metal complex to a preformed peroxide.

As far as we are aware, the molecules described herein are the first examples of metal-cluster-based peroxides. Moreover, the technique of initiating the formation of an organometallic radical by use of tetrahydrofuran as solvent, with subsequent exposure to atmospheric oxygen, provides a novel and efficient synthetic methodology, which has the potential to be applied to the preparation of a wide range of transition metal-containing peroxides.

Experimental Section

All syntheses were carried out under a dry nitrogen atmosphere, and solvents were dried and distilled according to standard procedures. 9-(Trimethylsilyl)ethynyl-9*H*-fluoren-9-ol was prepared as previously described.[32] ^{1}H and ^{13}C NMR spectra were acquired on Bruker DRX-500 or AC-200 spectrometers; assignments were based on standard 2D NMR techniques (^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC and HMBC). Mass spectra were acquired with a Finnigan EI/CI mass spectrometer system, using direct electron impact and chemical ionisation methods. Chemical ionisation was induced using NH_3 as the collision gas. High-resolution mass spectra (HRMS) were obtained using a Micromass GCT, GC Time-of-Flight mass spectrometer. Silica gel, 230–400 mesh, was used for flash column chromatography. Elemental analyses are from Guelph Chemical Laboratories, Guelph, Ontario, or from the Microanalytical Laboratory at University College Dublin.

Syntheses of 4, 17, 18, 19, 20 and 21: 9-(Trimethylsilyl)ethynyl-9*H*-fluoren-9-ol[32] (2.45 g, 8.8 mmol) was treated with two equivalents of *n*BuLi (11.0 mL of a 1.6 M hexanes solution, 17.6 mmol) at −78 °C and left to react for 4 h at low temperature. A solution of allyldimethylchlorosilane (1.1 mL, 8.8 mmol) in anhydrous diethyl ether (20 mL) was then added dropwise and the solution allowed to warm gradually to room temperature. The mixture was quenched with aqueous $NaHCO_3$, and the product was extracted with diethyl ether, dried using $MgSO_4$, and filtered to furnish 9-[(allyldimethylsilyl)ethynyl]-9*H*-fluoren-9-ol (**18**) as a yellow oil that was subjected to chromatography on a silica gel column with a 50:50 mixture of CH_2Cl_2/hexanes; the isolated yield was 74 %. Subsequent treatment of the alkynol **18** with an equimolar quantity of $[Co_2(CO)_8]$ in THF at room temperature for 12 h, removal of solvent and chromatographic separation with hexanes gave complex **4** as a dark red oily solid (86 %). In the preparation of **18**, several other oily products were also formed, but were not separable at this stage; however, treatment of the mixture with dicobalt octacarbonyl yielded complexes **19**, **20** and **21** after chromatographic separation. X-ray diffraction quality crystals of **17**, **20** and **21** were obtained by recrystallisation from CH_2Cl_2/hexanes.

Protonation of 4 in CH_2Cl_2: Treatment of **4** (600 mg, 1.02 mmol) with an equimolar amount of HBF_4 in dichloromethane at −78 °C yielded, after hydrolysis and column chromatography, complex **17** in 60 % yield. X-ray diffraction quality crystals of **17** were obtained by recrystallisation from CH_2Cl_2/hexanes.

Data for 18: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.97$–7.25 (m, 1H; fluorenyl), 5.79 (m, 1H; CH=C), 4.90 (m, 2H; C=CH_2), 2.79 (s, 1H; OH), 1.64 (d, $J = 7.3$ Hz, 2H; CH_2), 0.17 ppm (s, 6H; $Si(CH_3)_2$); ^{13}C NMR (50 MHz): $\delta = 146.9$, 139.1 (Ar C's), 133.7 (*C*H=CH_2), 129.5, 128.4, 124.3, 120.1 (Ar C's), 113.9 (CH=*C*H_2), 105.8 (*C*CSi), 86.6 (*C*CSi), 74.9 (C-OH), 23.7 (CH_2), −2.5 ppm ($Si(CH_3)_2$); MS (DEI): *m*/*z* (%): 304 (15) $[M]^+$, 287 (30) $[M-OH]^+$, 263 (76) $[M-C_3H_5]^+$; MS (CI, NH_3): *m*/*z* (%): 304 (43) $[M]^+$, 287 (100) $[M-OH]^+$, 263 (24) $[M-C_3H_5]^+$, 247 (6) $[M-OH-C_3H_5]^+$.

Data for 4: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.60$–7.53 (m, 4H; fluorenyl), 7.35–7.24 (m, 4H; fluorenyl), 5.65 (m, 1H; CH=C), 4.84 (m, 2H; C=CH_2), 2.57 (s, 1H; OH), 1.46 (d, $J = 7.2$ Hz, 2H; CH_2), 0.00 ppm (s, 6H; $Si(CH_3)_2$); ^{13}C NMR (50 MHz): $\delta = 199.9$ (CO's), 150.3, 138.8 (Ar C's), 134.2 (*C*H=CH_2), 129.5, 127.6, 124.3, 120.2 (Ar C's), 117.8 (*C*CSi), 114.0 (CH=*C*H_2), 83.3 (C-OH), 24.6 (CH_2), −1.7 ppm ($Si(CH_3)_2$); MS (DEI): *m*/*z* (%): 534 (21) $[M-2CO]^+$, 506 (10) $[M-3CO]^+$, 478 (43) $[M-4CO]^+$, 450 (42) $[M-5CO]^+$, 422 (100) $[M-6CO]^+$, 380 (30) $[M+H-C_3H_5-6CO]^+$; MS (CI, NH_3): *m*/*z* (%): 573 (100) $[M-OH]^+$, 545 (60) $[M-OH-CO]^+$, 517 (48) $[M-OH-2CO]^+$, 489 (13) $[M-OH-3CO]^+$, 478 (7) $[M-4CO]^+$, 450 (6) $[M-5CO]^+$, 422 (7) $[M-6CO]^+$, 304 (10) $[M-Co_2(CO)_6]^+$, 287 (13) $[M-OH-Co_2(CO)_6]^+$, 181 (12) $[C_{13}H_8OH]^+$; HRMS: *m*/*z* calcd for $C_{24}H_{20}Co_2O_5Si$ ($[M-2CO]^+$): 533.9744; found: 533.9739.

Data for 17: Dark red solid, m.p. 96 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta =$ 7.72 (m, 2H; fluorenyl), 7.58 (m, 2H; fluorenyl), 7.42–7.29 (m, 4H; fluorenyl), 5.10–4.65 (m, 3H; CH=CH_2), 3.17 (d, $J = 6.6$ Hz, 2H; CH_2), 0.57 ppm (d, $^3J_{H\text{-}F} = 6.9$ Hz, 6H; $Si(CH_3)_2$); ^{13}C NMR (50 MHz): $\delta = 199.0$ (CO's), 149.9, 140.2 (Ar C's), 132.9 (*C*H=CH_2), 128.3, 127.3, 124.3, 119.6 (Ar C's), 118.2 (CH=*C*H_2), 57.8 (C-9), 45.0 (CH_2), 0.9 ppm ($^2J_{C\text{-}F} =$ 16.8 Hz, $Si(CH_3)_2$); MS (DEI): *m*/*z* (%): 536 (10) $[M-2CO]^+$, 508 (18) $[M-3CO]^+$, 452 (26) $[M-5CO]^+$, 424 (25) $[M-6CO]^+$, 265 (32) $[M-C_3H_5-Co_2(CO)_6]^+$; MS (DCI, NH_3): *m*/*z* (%): 610 (25) $[M+NH_4]^+$, 582 (56) $[M+NH_4-CO]^+$, 554 (24) $[M+NH_4-2CO]^+$, 537 (34) $[M+NH_4-OH-2CO]^+$, 509 (12) $[M+NH_4-OH-3CO]^+$, 469 (44) $[M+NH_4-H-5CO]^+$, 424 (100) $[M-6CO]^+$, 324 (30) $[M-C_3H_5-Co-6CO]^+$, 265 (12) $[M-C_3H_5-Co_2(CO)_6]^+$; elemental analysis calcd (%) for $C_{26}H_{19}Co_2FO_6Si$: C 52.72 H 3.23; found: C 52.97, H 3.46.

Data for 19: Dark red oily solid (55 mg); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.66$–7.53 (m, 4H; fluorenyl), 7.42–7.27 (m, 4H; fluorenyl), 5.63 (m, 2H; CH=C), 4.82 (m, 4H; C=CH_2), 1.46 and 1.36 (d, $J = 7.8$ Hz, each 2H; CH_2), 0.01 and −0.25 ppm (s, each 6H; $Si(CH_3)_2$); ^{13}C NMR (50 MHz): $\delta = 200.2$ (CO's), 150.2, 138.9 (Ar C's), 134.1 and 133.9 (*C*H=CH_2), 129.5, 127.4, 125.2, 120.2 (Ar C's), 113.9 and 113.6 (CH=*C*H_2), 85.0

(*C*CSi), 25.6 and 24.6 (CH_2), −1.1 and −1.8 ppm ($Si(CH_3)_2$); MS (DEI): *m/z* (%): 632 (5) $[M-2CO]^+$, 576 (10) $[M-4CO]^+$, 548 (14)$[M-5CO]^+$, 520 (100) $[M-6CO]^+$, 478 (10) $[M-C_3H_5-H-6CO]^+$; MS (DCI, NH_3): *m/z* (%): 573 (100) $[M-OSi(CH_3)_2(C_3H_5)]^+$, 548 (60) $[M-5CO]^+$, 520 (85) $[M-6CO]^+$; HRMS: *m/z* calcd for $C_{29}H_{30}Co_2O_5Si_2$ ($[M-2CO]^+$): 632.0296; found: 632.0284.

Data for 20: Dark red solid (30 mg), m.p. 132–133 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=7.72$–7.65 (m, 4H; fluorenyl), 7.40–7.32 (m, 4H; fluorenyl), 4.10 (s, 1H; SiOH), 2.63 (s, 1H; OH), 1.36 (br, 2H; CH_2), 1.20 (s, 3H; CH_3), 0.19 and 0.15 ppm (s, 3H; $Si(CH_3)$); ^{13}C NMR (50 MHz): $\delta=199.4$ (CO's), 150.6, 139.2, 129.2, 127.4, 124.2, 120.0 (Ar C's), 117.8 (*C*CSi), 83.4 (C*C*Si), 66.5 (C-OH), 37.2 28.3, 27.6, 0.9 and −0.1 ppm ($Si(CH_3)_2$); MS (DEI): *m/z* (%): 608 (3) $[M]^+$, 552 (10) $[M-2CO]^+$, 496 (12) $[M-4CO]^+$, 468 (41) $[M-5CO]^+$, 440 (30) $[M-6CO]^+$, 380 (15) $[M+H-Co-6CO]^+$, 321 (10) $[M+H-Co_2(CO)_6]^+$; MS (DCI, NH_3): *m/z* (%): 591 (52) $[M-OH]^+$, 563 (35) $[M-OH-CO]^+$, 535 (22) $[M-OH-2CO]^+$, 507 (20) $[M-OH-3CO]^+$, 479 (20) $[M-OH-4CO]^+$, 468 (21) $[M-5CO]^+$, 399 (18) $[M+NH_4-Co-6CO]^+$, 305 (54) $[M-OH-Co_2(CO)_6]^+$, 181 (70) $[C_{13}H_8OH]^+$; elemental analysis calcd (%) for $C_{26}H_{22}Co_2O_8Si$: C 51.33, H 3.64; found: C 51.64, H 3.88.

Data for 21: Dark red solid (86 mg), m.p. 120–121 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=7.84$–7.71 (m, 4H; fluorenyl), 7.53–7.36 (m, 4H; fluorenyl), 4.09 and 3.03 (s, 1H; OH), 1.58 ppm (s, 6H; $C(CH_3)_2$); ^{13}C NMR (50 MHz): $\delta=199.1$ (CO's), 150.1, 138.8, 129.4, 127.6, 124.5, 120.1 (Ar C's), 106.9 and 102.6 (C≡C), 83.5 and 73.4 (C-OH), 32.9 ppm (CH_2); MS (DEI): *m/z* (%): 522 (4) $[M-CO]^+$, 494 (3) $[M-2CO]^+$, 466 (12) $[M-3CO]^+$, 438 (11) $[M-4CO]^+$, 410 (8) $[M-5CO]^+$, 382 (48) $[M-6CO]^+$, 364 (50) $[M-H-OH-6CO]^+$, 324 (12) $[M+H-Co-6CO]^+$; MS (DCI, NH_3): *m/z* (%): 533 (35) $[M-OH]^+$, 505 (34) $[M-H-2OH]^+$, 449 (12) $[M-OH-3CO]^+$, 438 (32) $[M-4CO]^+$, 410 (16) $[M-5CO]^+$, 382 (24) $[M-6CO]^+$, 364 (16) $[M-H-OH-6CO]^+$, 247 (13) $[M-OH-Co_2(CO)_6]^+$, 230 (11) $[M-2OH-Co_2(CO)_6]^+$, 181 (100) $[C_{13}H_8OH]^+$; elemental analysis calcd (%) for $C_{24}H_{16}Co_2O_8$: C 52.39, H 2.93; found: C 52.08, H 2.90.

Syntheses of 5, 24, 26 and 27: As for **18**, treatment of 9-(trimethylsilyl)-ethynyl-9*H*-fluoren-9-ol with *n*BuLi and benzyldimethylchlorosilane furnished 9-(benzyldimethylsilyl)ethynyl-9*H*-fluoren-9-ol as a white solid, m.p. 87–88 °C, in 68% yield. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=7.74$–7.62 (m, 4H; fluorenyl), 7.44–7.39 (m, 4H; fluorenyl), 7.21–7.03 (m, 5H; Ph), 2.69 (s, 1H; OH), 2.21 (s, 2H; CH_2), 0.17 ppm (s, 6H; $Si(CH_3)_2$); ^{13}C NMR (50 MHz): $\delta=146.7$, 139.0, 138.7, 129.6, 128.4, 128.3, 128.0, 124.3, 120.1 (Ar C's), 106.2 (*C*CSi), 86.5 (C*C*Si), 74.9 (C-OH), 25.9 (CH_2), −2.3 ppm ($Si(CH_3)_2$); MS (DEI): *m/z* (%): 354 (53) $[M]^+$, 336 (20) $[M-H-OH]^+$, 263 (100) $[M-CH_2Ph]^+$. Subsequent treatment of the alkynol with an equimolar quantity of $[Co_2(CO)_8]$ in THF at room temperature for 12 h, removal of solvent and chromatographic separation with hexanes gave complex **5** in 71% isolated yield.

Treatment of **5** (1.0 g, 1.56 mmol) with 1.5 equivalents of HBF_4 (0.33 mL, 2.3 mmol) in CH_2Cl_2 at −78 °C, and subsequent chromatographic separation on a silica column, using 1:1 dichloromethane/hexanes as eluent, afforded the tricobalt cluster **24** as a dark red solid, and the propargylallene **26** in 32 and 42% yields, respectively.

Treatment of **5** (500 mg, 0.78 mmol) with an equimolar amount of HBF_4 (0.11 mL, 0.8 mmol) in THF (or in diethyl ether) afforded the peroxide **27** as a dark red solid in 63% (or 56%), respectively, after chromatographic separation on a silica column using 50:50 dichloromethane/hexanes as eluent.

Data for 5: Dark red solid, m.p. 99 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=$ 7.69–7.55 (m, 4H; fluorenyl), 7.44–6.90 (m, 9H; fluorenyl and Ph), 2.59 (s, 1H; OH), 1.90 (s, 2H; CH_2), −0.09 ppm (s, 6H; $Si(CH_3)_2$); ^{13}C NMR (50 MHz): $\delta=200.0$ (CO's), 150.4, 139.1, 138.9, 129.6, 128.3, 128.2, 127.7, 124.3, 120.2 (Ar C's), 83.3 (C-OH), 26.6 (CH_2), −1.9 ppm ($Si(CH_3)_2$); MS (DEI): *m/z* (%): 612 (1) $[M-CO]^+$, 556 (22) $[M-3CO]^+$, 528 (8) $[M-4CO]^+$, 500 (20) $[M-5CO]^+$, 472 (95) $[M-6CO]^+$, 354 (18) $[M-Co_2(CO)_6]^+$, 263 (55) $[M-CH_2Ph-Co_2(CO)_6]^+$, 181 (88) $[C_{13}H_8OH]^+$, 149 (90) $[Si(CH_3)_2CH_2Ph]^+$; MS (DCI, NH_3): *m/z* (%): 81 (100) $[C_{13}H_8OH]^+$. HRMS: *m/z* calcd for $C_{29}H_{22}O_6SiCo_2$ ($[M-CO]^+$): 611.9850; found 611.9864; elemental analysis calcd (%) for $C_{30}H_{22}Co_2O_7Si$: C 56.26, H 3.46; found: C 56.08, H 3.70.

Data for 24: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=7.69$–7.10 (m, 8H; fluorenyl), 5.15 (s, 1H; CH), 3.34 ppm (2H; CH_2); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=199.8$ (Co-CO's), 146.8, 140.7, 128.6, 126.9, 125.7, 120.1, 58.7, 50.5 ppm; elemental analysis calcd (%) for $C_{24}H_{11}Co_3O_9$: C 46.48, H 1.79; found: C 46.08, H 1.90.

Data for 26: Yellow solid, m.p. 169–170 °C; ^{1}H NMR (200 MHz, CD_2Cl_2): $\delta=7.58$–7.45 (m, 8H; Ar), 7.14–7.05 (m, 6H; Ar) 6.74–6.71 (m, 4H; Ar), 1.72 and 1.67 (s, 2H; CH_2), −0.40 and −0.43 ppm (s, 6H; $Si(CH_3)_2$); ^{13}C NMR (125.7 MHz, CD_2Cl_2): $\delta=205.6$ (allene = C =), 147.0, 140.4, 139.0, 138.8, 138.5, 138.1, 128.8, 128.2, 128.0, 127.8, 127.3, 127.0, 125.7, 124.1, 123.9, 122.4, 120.2, 110.5, 106.1, 105.7, 86.0 (*C*CSi), 54.2 (C-33), 26.1 and 25.7 (CH_2's), −2.6 and −3.1 ppm ($Si(CH_3)_2$); IR (solid): $\tilde{\nu}=$ 2168 cm^{-1} (C≡C), 1915 cm^{-1} (=C=); MS (DEI): *m/z* (%): 674 (4) $[M-H]^+$, 337 (100) $[C_{13}H_8CCSi(CH_3)_2CH_2Ph]^+$, 149 (81) $[Si(CH_3)_2CH_2Ph]^+$; MS (DCI, NH_3): *m/z* (%): 674 (10) $[M-H]^+$, 337 (100) $[C_{13}H_8CCSi(CH_3)_2CH_2Ph]^+$, 149 (47) $[Si(CH_3)_2CH_2Ph]^+$; HRMS: *m/z* calcd for $C_{48}H_{42}Si_2$ ($[M]^+$): 674.2825; found: 674.2836; elemental analysis calcd (%) for $C_{48}H_{42}Si_2$: C 85.41, H 6.27; found: C 85.29, H 6.60.

Data for 27: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=7.58$ (d, $^3J_{H\text{-}H}=7.4$ Hz, 4H; Ar), 7.42–7.08 (m, 18H; Ar), 6.85 (d, $^3J_{H\text{-}H}=7.0$ Hz, 4H; Ar), 1.71 (s, 4H; CH_2's), −0.26 ppm (s, 12H; $Si(CH_3)$'s); ^{13}C NMR (50 MHz): $\delta=199.0$ (CO's), 147.3, 139.7, 139.2, 129.5, 128.3, 128.1, 127.1, 125.1, 124.2, 120.1 (Ar C's), 26.6 (CH_2), −1.9 ppm ($Si(CH_3)_2$); MS (ESI, negative, CH_3OH): *m/z* (%): 639 (35) $[M-C_{13}H_8OC_2Co_2(CO)_6Si(CH_3)_2Ph]^-$; elemental analysis calcd (%) for $C_{60}H_{42}Co_4O_{14}Si_2$: C 56.35, H 3.31; found: C 56.57, H 2.98.

Syntheses of 6 and 28: As for **18**, treatment of 9-(trimethylsilyl)ethynyl-9*H*-fluoren-9-ol with *n*BuLi and vinyldimethylchlorosilane furnished 9-(vinyldimethylsilyl)ethynyl-9*H*-fluoren-9-ol as a yellow oil in 74% yield. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=7.68$–7.53 (m, 4H; fluorenyl), 7.36–7.29 (m, 4H; fluorenyl), 6.15–5.76 (m, 3H; $CH=CH_2$), 3.42 (s, 1H; OH), 2.08 (s, 2H; CH_2), 0.19 ppm (s, 6H; $Si(CH_3)_2$); ^{13}C NMR (50 MHz): $\delta=146.9$, 139.0 (Ar C's), 136.1 (*C*H=C), 133.0 (C=*C*H_2), 129.4, 128.3, 124.2, 119.9, (Ar C's), 106.3 (*C*CSi), 85.6 (C*C*Si), 74.7 (C-OH), 30.7 (CH_2), −1.8 ppm ($Si(CH_3)_2$); MS (DEI): *m/z* (%): 290 (97) $[M]^+$, 275 (65) $[M-CH_3]^+$; MS (DCI, NH_3): *m/z* (%): 290 (10) $[M]^+$, 273 (100) $[M-OH]^+$. Subsequent treatment of the alkynol with an equimolar quantity of $[Co_2(CO)_8]$ in THF at room temperature for 12 h, removal of solvent and chromatographic separation with hexanes gave complex **6** in 71% isolated yield.

Treatment of **6** (500 mg, 0.87 mmol) with HBF_4 (0.12 mL, 0.9 mmol) in THF (or in diethyl ether) afforded the peroxide (**28**) as a dark red solid in 60% (or 52%), respectively, after chromatographic separation on a silica column using a 50:50 dichloromethane/hexanes solution as eluent.

Data for 6: Dark red solid, m.p. 71–72 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=7.63$–7.58 (m, 4H; fluorenyl), 7.38–7.26 (m, 4H; fluorenyl), 6.06–5.70 (m, 3H; $CH=CH_2$), 2.58 (s, 1H; OH), 0.16 ppm (s, 6H; $Si(CH_3)_2$); ^{13}C NMR (50 MHz): $\delta=199.8$ (CO's), 150.3, 138.9 (Ar C's), 137.4 (*C*H=C), 132.8 (C=*C*H_2), 129.5, 127.6, 124.3, 117.4, (Ar C's), 118.2 (*C*CSi), 83.4 (C*C*Si), 78.2 (COH), −1.3 ppm ($Si(CH_3)_2$); MS (DEI): *m/z* (%): 520 (10) $[M-2CO]^+$, 492 (5) $[M-3CO]^+$, 464 (30) $[M-4CO]^+$, 436 (34) $[M-5CO]^+$, 408 (100) $[M-6CO]^+$, 290 (8) $[M-Co_2(CO)_6]^+$; MS (DCI, NH_3): *m/z* (%): 559 (100) $[M-OH]^+$, 531 (94) $[M-OH-CO]^+$, 503 (18) $[M-OH-2CO]^+$, 464 (25) $[M-4CO]^+$, 408 (32) $[M-6CO]^+$; elemental analysis calcd (%) for $C_{25}H_{18}Co_2O_7Si$: C 52.10, H 3.15; found: C 52.48, H 2.90.

Data for 28: Dark red solid, m.p. 144–145 °C, ^{1}H NMR (200 MHz, $CDCl_3$): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=7.59$ (d, $J=6.9$ Hz 4H; Ar), 7.39–7.20 (m, 12H; Ar), 5.82–5.50 (m, 6H; $CH=CH_2$), −0.09 ppm (s, 12H; $Si(CH_3)$'s); ^{13}C NMR (50 MHz): $\delta=198.8$ (CO's), 147.4, 139.7 (Ar C's), 137.6 (*C*H=C), 132.4 (C=*C*H_2), 129.3, 127.0, 125.2, 119.9 (Ar C's), −1.5 ppm ($Si(CH_3)_2$); MS (ESI, negative, CH_3OH): *m/z* (%): 559 (10) $[C_{13}H_8C_2Co_2(CO)_6Si(CH_3)_2C_3H_5]^-$, 273 (20) $[C_{13}H_8CCSi(CH_3)_2C_3H_5]^-$; elemental analysis calcd (%) for $C_{50}H_{34}Co_4O_{14}Si_2$: C 52.19, H 2.98; found: C 51.97, H 2.90.

Table 2. Crystallographic Data.

	17	**20**	**21**	**26**	**27**	**28**
empirical formula	$C_{26}H_{19}Co_2FO_6Si$	$C_{26}H_{22}Co_2O_8Si$	$C_{24}H_{16}Co_2O_8$	$C_{48}H_{42}Si_2$	$C_{60}H_{42}Co_4O_{14}Si_2$	$C_{50}H_{34}Co_4O_{14}Si_2$
M_r	592.36	608.39	550.23	675.00	1278.84	1150.67
crystal system	monoclinic	monoclinic	tetragonal	monoclinic	triclinic	orthorhombic
space group	$P2_1/n$ (#14)	$P2_1/c$ (#14)	$P42_1/c$ (#114)	$P2_1/c$ (#14)	$P\bar{1}$ (#2)	$Pbca$ (#62)
a [Å]	8.624(2)	20.445(7)	22.489(5)	13.467(6)	10.516(5)	22.17(4)
b [Å]	20.573(5)	10.233(3)	22.489(5)	16.297(7)	12.0516)	13.24(3)
c [Å]	14.556(4)	27.202(9)	9.846(3)	8.923(4)	12.382(6)	16.93(3)
α [°]	90	90	90	90	86.312(8)	90
β [°]	95.017(4)	105.938(5)	90	95.692(8)	76.860(8)	90
γ [°]	90	90	90	90	66.034(8)	90
V [Å^3]	2572.6(11)	5472(3)	4980(2)	1948.7(14)	1395.6(12)	4969(17)
Z	4	8	8	2	1	4
ρ_{calcd} [g cm^{-3}]	1.529	1.477	1.468	1.150	1.522	1.538
T [K]	173(2)	173(2)	197(2)	173(2)	173(2)	173(2)
μ [mm^{-1}]	1.382	1.302	1.376	0.123	1.278	1.426
F(000)	1200	1952	2224	716	650	2328
θ range [°]	1.72–27.00	1.04–23.75	1.28–24.99	1.97–25.00	1.69–27.50	1.84–22.50
index ranges	$-11\le h\le 11$	$-23\le h\le 21$	$-26\le h\le 26$	$-16\le h\le 15$	$-13\le h\le 12$	$-23\le h\le 23$
	$-23\le k\le 26$	$-11\le k\le 11$	$-26\le k\le 26$	$-19\le k\le 19$	$-15\le k\le 14$	$-13\le k\le 14$
	$-18\le l\le 17$	$-30\le l\le 30$	$-11\le l\le 11$	$-9\le l\le 10$	$-16\le l\le 15$	$-18\le l\le 17$
reflections measured	22551	35492	37626	14547	12858	26564
reflections used (R_{int})	5615 (0.0608)	8346 (0.1443)	4385 (0.1088)	3424(0.0522)	6305 (0.0315)	3244 (0.1512)
data/restraints/parameters	5615/0/402	8346/243/834	4385/0/372	3424/36/296	6305/0/446	3244/0/323
final R values [$I>2\sigma(I)$] R_1/wR_2	0.0389/0.0658	0.0607/0.0762	0.0394/0.0686	0.0651/0.1168	0.0323/0.0673	0.0847/0.1172
R values (all data) R_1/wR_2	0.0718/0.0712	0.1486/0.0945	0.0856/0.0835	0.1189/0.1388	0.0536/0.0759	0.1315/0.1306
goodness-of-fit on F^2	1.010	0.975	1.077	1.020	1.009	1.129
largest diff peak/hole [e Å^{-3}]	0.368/−0.278	0.425/−0.377	0.328/−0.311	0.343/−0.305	0.357/−0.313	0.383/−0.344

X-ray measurements for 17, 20, 21, 26, 27 and 28: Crystal data were collected using a P4 Bruker diffractometer, equipped with a Bruker SMART 1 K CCD area detector, using the program SMART,[40] and a rotating anode, using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda =$ 0.71073 Å), and are listed in Table 2. A full sphere of the reciprocal space was scanned by phi-omega scans. Data reduction was carried out by using the program SAINT,[41] which applied Lorentz and polarisation corrections to the three-dimensionally integrated diffraction spots. Pseudo-empirical absorption correction based on redundant reflections was performed by the program SADABS.[42] The structures were solved by using the direct-methods procedure in the Bruker SHELXTL program library,[43] and refined by full-matrix least-squares methods on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atom treatment varied from compound to compound, depending on the crystal quality. In **17**, **21** and **27**, all hydrogen atoms were located in the difference fourier map and allowed to refine freely with isotropic thermal displacement parameters. In **26** and **28** hydrogen atoms were added at calculated positions and refined using a riding model. Molecule **20** crystallised with two crystallographically unrelated molecules in the unit cell, while the remaining structures contained only one molecule in the asymmetric unit. A small slip-disorder of one of the hydrogen-bonded fluorenyl ligands in **20** containing 73% occupancy of the major fragment, required a partial restraining of these ligands to optimise the model. The hydrogen atoms attached to disordered carbon atoms in **20** were added at calculated positions and refined by using a riding model; the hydrogen attached to the disordered oxygen was set to ride on the oxygen of the major component, but all other hydrogen atoms were refined freely. The carbonyl carbon atoms of **24** could not be refined anisotropically as a result of the weak intensity of the data, and so the fluorenyl moieties were restrained to simulate isotropic behaviour to provide a better model. A partial twist-disorder of the silyl groups in **28**, modelled so that the major component consisted of 57%, did not allow for anisotropic refinement of the silicon methyls and vinyl group. As previously mentioned, the allene **26** exhibited a centrosymmetric disorder, whereby the fluorenyl ligands and the silyl substituents of the alkyne and allene in the two equally occupied molecular orientations, overlap with one another. Likewise, for molecules **27** and **28** only half of each molecule was refined, and the other half was generated by the appropriate symmetry element.

CCDC-693776 (**17**), CCDC-693777 (**20**), CCDC-693778 (**21**), CCDC-693779 (**26**), CCDC-693780 (**27**) and CCDC-693781 (**28**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[30] Crystal data for **24**: $C_{24}H_{11}Co_3O_9$, $M_r = 620.12$, monoclinic, space group $P2_1/n$ (#14), $a = 8.702(6)$, $b = 30.56(2)$, $c = 26.752(19)$ Å, $\beta = 98.679(12)°$, $V = 7032(9)$ Å^3, $Z = 12$, $\rho_{calcd} = 1.757$ g cm^{-3}, $\mu = 2.151$ mm^{-1}, $T = 173$ K, $R_1 = 0.1098$.

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