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ARTICLE

Organic and organometallic derivatives of pentaphenylbenzene, C_6Ph_5X: correlation of peripheral phenyl ring orientations with the steric bulk of “X”

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Abstract: A series of C_6Ph_5X compounds, including X = H, Br, CO_2H, CO_2R, C≡CPh, *cis*-BrC=C(Br)Ph, 2-bornenyl, and ferrocenyl, have been characterized by use of X-ray crystallography. Also, the first organometallic complexes of pentaphenylbenzene have been prepared by reaction with chromium hexacarbonyl to yield (η^6-C_6Ph_5H)$Cr(CO)_3$ complexes in which the metal tripod is attached either to an *ortho* peripheral ring or to the central ring. Crystalline pentaphenylbenzoic acid exists as a hydrogen-bonded dimer; however, the steric bulk of the substituents does not allow the carboxylic acid moieties to be linked directly but instead via two bridging methanol molecules. In the solid state, the orientation of the peripheral rings in bulky C_6Ph_5X systems is very sensitive to the size of the “X” substituents, such that the twist angle of the *para* ring responds inversely with increasing bulk of “X”, which drives the *ortho* rings farther out of the plane of the central ring. The relevance of these observations to correlated motion in molecular propellers, and ultimately to molecular machines, is discussed.

Key words: polyarylbenzenes, substituent orientations, rotational barriers, correlated rotations, arene chromium complexes.

Résumé : À l’aide de la cristallographie aux rayons X, on a caractérisé une série de composés de formule C_6Ph_5X, où X = H, Br, CO_2H, CO_2R, C≡CPh, *cis*-BrC=C(Br)Ph, 2-bornényl et ferrocényl. En outre, on a préparé les premiers complexes organométalliques du pentaphényl-benzène en le faisant réagir avec de l’hexacarbonyle de chrome pour obtenir les complexes (η^6-C_6Ph_5H)$Cr(CO)_3$ dans lesquels le tripode métallique est attaché à un noyau périphérique en *ortho* ou au noyau central. L’acide pentaphénylbenzoïque existe à l’état de dimère formé par liaisons hydrogènes; toutefois, l’encombrement stérique des substituants ne permet pas la liaison directe des groupements carboxyliques qui sont plutôt reliés par un pont constitué de deux molécules de méthanol. À l’état solide, l’orientation des noyaux périphériques dans les volumineux systèmes C_6Ph_5X est très sensible à la taille des substituants « X », de sorte que l’angle de torsion du noyau en *para* répond inversement à l’encombrement croissant de « X » qui repousse de plus en plus les noyaux en *ortho* hors du plan du noyau central. Une discussion de l’intérêt de ces observations en ce qui concerne le mouvement corrélé dans les hélices moléculaires, et en bout de ligne les machines moléculaires, est offerte. [Traduit par la Rédaction]

Mots-clés : polyarylbenzènes, orientation des substituants, barrières de rotation, rotations corrélées, complexes aréniques du chrome.

Introduction

Polyarylbenzene derivatives have been intensively studied in recent years because of their applications in conducting polymers,[1] UV organic lasers,[2] and nonlinear optical devices and field effect transistors.[3] Their use as organic light-emitting diodes arises from the marked nonplanar character of systems containing one or more C_6Ph_5 moieties, which prevent aggregation by minimizing π–π stacking, thus enhancing fluorescence.[4,5] Some polyphenylbenzene derivatives have exhibited biological activity, behaving as immune suppressants, antioxidants, antithrombosis agents, and anticoagulants.[6] Very recently, a number of their thermodynamic properties, e.g., enthalpy and entropy of sublimation, have been rationalized in terms of the torsional freedom of the peripheral phenyl substituents in the gas phase.[7] Additionally, Pascal and Müllen have each reported a fascinating series of polyaryl systems that adopt picturesque structures and exhibit almost unprecedented steric strain.[8]

Although pentaaryl-phenyl, C_6Ar_5, substituents have been incorporated into a wide range of molecules, the chemistry of pentaphenylbenzene itself has been surprisingly little investigated. Until very recently, its known reactivity was limited to electrophilic substitutions at the *para* positions of the peripheral phenyls,[9] with the goal of generating networks possessing multiple specific hydrogen bond interactions,[10] dehydrogenation to form a planar “graphite-type” system,[11] the design of bulky phosphine ligands for use in palladium coupling processes,[12] and Birch reduction to 2,3,5,6-tetraphenyl-1,1′-bicyclohexylidene.[13] Many other functionalized C_6Ph_5X molecules, examples of which are depicted in Scheme 1, have been prepared by Diels–Alder addition reactions of appropriate alkynes with tetraphenylcyclopentadienone (tetracyclone) (**1**). These include a benzo[2,1,3] thiadiazole with important organic light-emitting diode properties,[4] a platinum coordination complex based on a terpyridine,[14] and variously substituted hexaarylbenzenes.[8]

We here report the syntheses and X-ray crystallographic characterization of a series of C_6Ph_5X systems and also several organometallic derivatives incorporating chromium or cobalt carbonyls. In particular, we note the influence of the X group on the orientations of the peripheral phenyls relative to the central ring.

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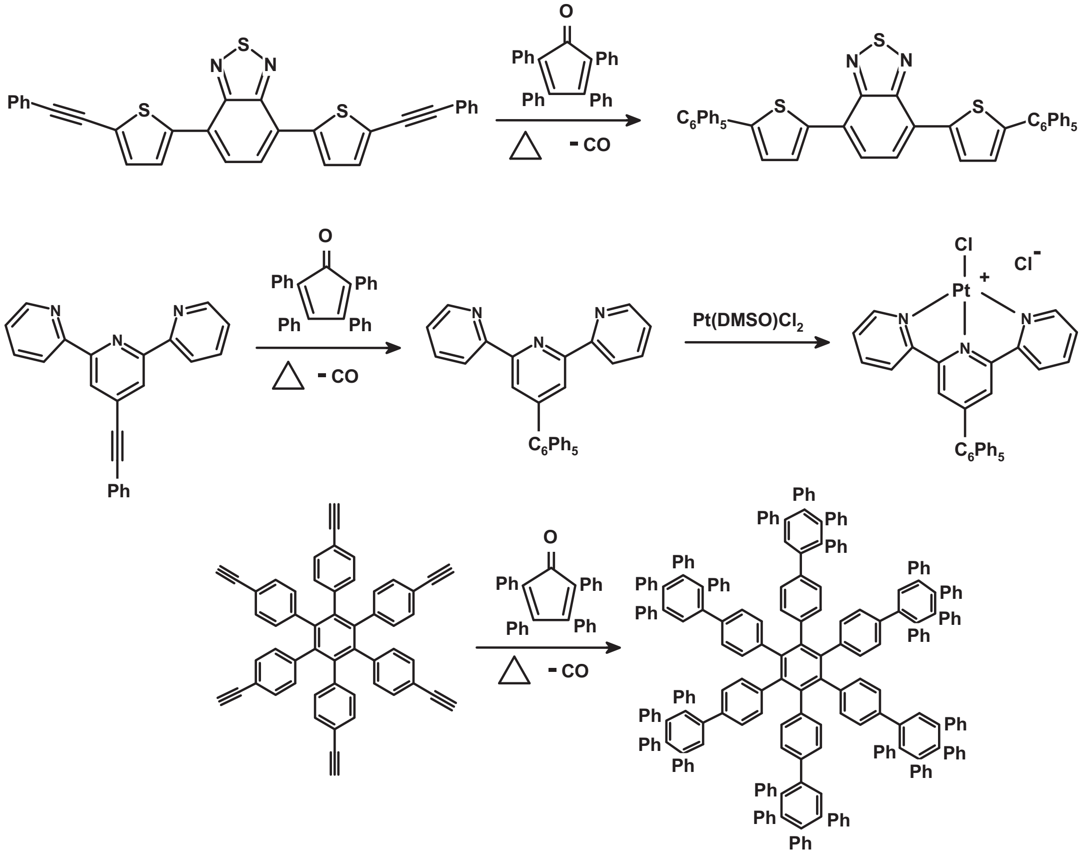
Scheme 1. A selection of C_6Ph_5X molecular systems.



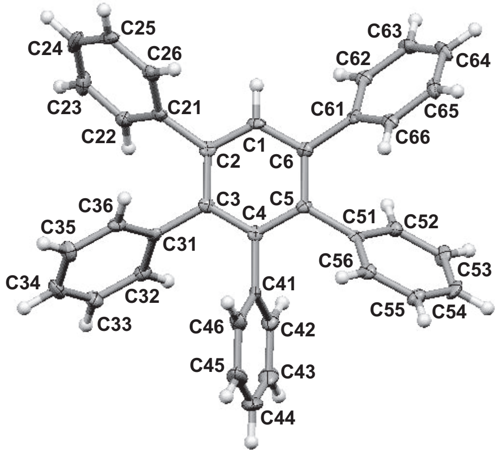
Results and discussion

Structures of organic C_6Ph_5X systems

Pentaphenylbenzene (**2**) is readily obtainable by Diels–Alder addition of phenylacetylene to tetracyclone with subsequent cheletropic loss of carbon monoxide.[15] It has also been prepared by treatment of 7-borabicyclo[2.2.1]heptadiene with methyl-lithium and then aqueous hydrolysis of the intermediate anion.[16] 1-Phenylethynyl-2,3,4,5,6-pentaphenylbenzene (**3**) was originally synthesized by Dilthey et al. in 1935[17] by heating together tetracyclone and 1,4-diphenyl-1,3-butadiyne at 250 °C under a nitrogen atmosphere; the loss of carbon monoxide from the Diels–Alder adduct yields Ph-C≡C-C_6Ph_5 (**3**) directly. A second, albeit sterically very demanding, [4+2] cycloaddition furnishes decaphenylbiphenyl, Ph_5C_6-C_6Ph_5 (**4**), as reported by Ogliaruso and Becker in 1965;[18] the acute steric crowding was confirmed by Pascal and co-workers only in 1988 as part of a comprehensive X-ray crystallographic study of highly congested polycyclic aromatic hydrocarbons.[19]

Surprisingly, perhaps, the X-ray crystal structure of pentaphenylbenzene (**2**) appears not to have been previously reported and is shown in Fig. 1. It reveals that the central ring has been slightly distorted whereby the C–C–C angles within the central ring are 118.2° at C2, 123.3° at C1, and 118.7° at C6, whereas the angles at the other three carbons are almost 120°, as expected. The bond distances C1–C2 and C1–C6 average 1.387 Å, whereas the other four ring bonds are slightly longer, average 1.409 Å. The flattening at C1 presumably minimizes steric repulsions between the phenyl rings. Unlike solid-state hexaphenylbenzene, which adopts a propeller-type geometry with a peripheral phenyl average twist angle of ~75°,[20] or ~79°,[21] relative to the central ring, the phenyl substituents in **2** exhibit a quite different pattern. The phenyls positioned *ortho* and *meta* to the central ring hydrogen relax to dihedral angles of 57° ± 1°, whereas the *para* phenyl lies at an angle of 73° to the central ring (Table 1).

Fig. 1. Molecular structure of pentaphenylbenzene (**2**). (For ease of comparison, all C_6Ph_5X molecules are numbered here such that C1 is the C-X carbon).



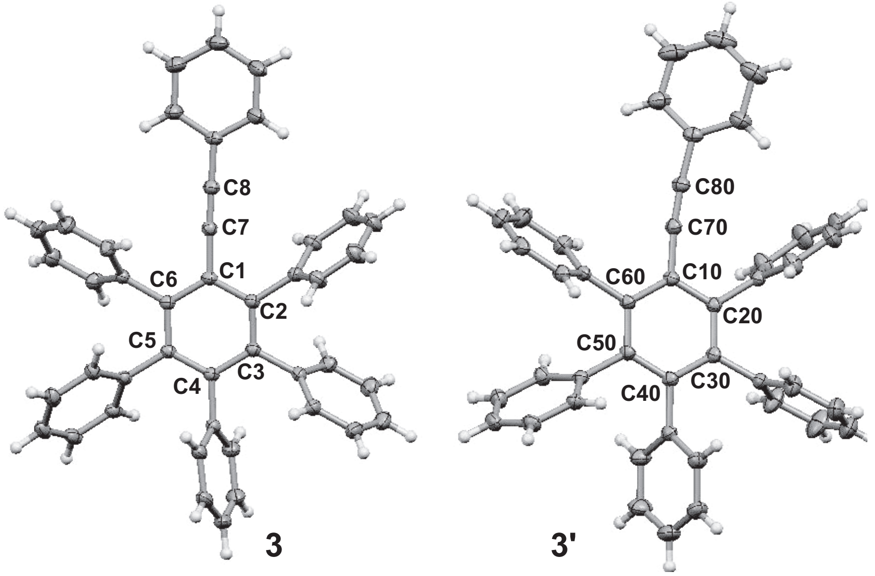
The peripheral phenyl twist angles in **2** may be compared with those found in the X-ray crystal structure of 1-phenylethynyl-2,3,4,5,6-pentaphenylbenzene (Fig. 2), which revealed the presence of two independent, and geometrically unique, molecules in the asymmetric unit. In the approximately C_2-symmetric structure **3**, the central and alkyne-linked rings are essentially coplanar (at 3.4°), and the phenyl rotors attached to the central arene

Table 1. Peripheral substituent dihedral angles (°) in pentaphenylbenzene derivatives.

C_6Ph_5X	*ipso*	*ortho*	*meta*	*para*	*meta*	*ortho*
C_6Ph_5H (**2**)		55.8	58.0	73.0	58.0	57.0
$C_6Ph_5C{\equiv}CPh$						
Linear alkyne (**3**)		67.8	60.6	69.9	56.2	60.8
Curved alkyne (**3′**)		–83.3	84.9	61.5	66.3	62.7
C_6Ph_5-C_6Ph_5 (**4**)	86.5	65.1	72.3	76.5	70.2	57.0
	–86.5	–75.4	84.5	64.0	56.5	56.8
C_6Ph_5-$C_2B_{10}H_{11}$ (**5**)		78.4	82.6	65.9	69.0	–80.1
C_6Ph_5Br (**6**)		71.9	63.3	71.5	69.6	83.0
		–76.8	68.3	65.2	77.4	79.3
$C_6Ph_5(C_5H_4)Fe(C_5H_5)$ (**7**)	50.9	64.2	69.8	81.2	89.3	–59.5
C_6Ph_5-2-bornenyl (**9**)	87	77	65	66	79	–83
$C_6Ph_5CBr{=}CBrPh$ (**11**)	69.4	73.9	70.4	69.5	75.0	66.4
	72.6	72.6	77.5	69.9	58.3	62.2
$C_6Ph_5CO_2H{\cdot}CH_3OH$ (**13**)	71.8	67.3	59.6	52.0	60.4	71.1
$[(\eta^6\text{-}C_6H_5)\text{-}C_6Ph_4H]Cr(CO)_3$ (**25**)		61.6[a]	63.3	63.5	70.7	50.9
$(\eta^6\text{-}C_6Ph_5H)Cr(CO)_3$ (**26**)		48.2	64.8	53.9	64.2	56.1
C_6Ph_6[21a]	89.6	–75.5	88.0	82.2	65.1	76.5
C_6Ph_6[21b]	83.3	–67.2	76.8	87.3	77.8	89.7
$(\eta^6\text{-}C_6Ph_6)Co(PhC{\equiv}CPh)$ (**21**)[37]	70.5	69.9	66.9	69.7	63.1	65.5
$(\eta^6\text{-}C_6Ph_6)Mo(\eta^5\text{-}C_5H_5)$ (**22**)[38]	64.9	68.4	59.4	67.6	55.5	63.5
$(p\text{-}C_6Ph_5\text{-}C_6H_4)_4C$ (**19**)[34]	64.0	63.5	66.1	63.9	63.2	64.9

[a] Chromium-complexed ring.

Fig. 2. X-ray crystal structures of 1-phenylethynyl-2,3,4,5,6-pentaphenylbenzene (**3** and **3′**).



consecutively adopt dihedral angles of 68°, 61°, 70°, 56°, and 61° from C2 to C6. In the other solid-state conformer **3′**, the alkyne phenyl is oriented 24° relative to the central plane, which is surrounded by a "picket fence" of phenyl groups in a nonpropeller arrangement marked by individual torsional angles of –83°, 85°, 61°, 66°, and 63° from C20 to C60. These structural features are most likely coupled to the bending deformation of the acetylenic unit, which is characterized by bond angles of 173.2° and 175.6° at C70 and C80, respectively. There is clearly a correlation between the alkyne curvature and twist of the terminal phenyl group with the orientations of the adjacent phenyl rings found in the solid state. Comparing the structures of **3** and **3′**, the orientations of the rings *ortho*, *meta*, and *para* to the alkyne substituent differ by +29°, +25°, and –9°, respectively, reflecting the progressive transmission of nonbonded repulsions.

As noted by Patton, Dirks, and Gust,[22] the steric interaction between "X" and the adjacent phenyl rings in C_6Ph_5X is mainly a "side-by-side" contact such as is observed between 1,3-axial groups in cyclohexane rather than the "end-to-end" interplay in biaryls. If "X" is less sterically demanding than a phenyl substituent, it is reasonable to assume that the aryl groups *ortho* and *meta* to "X" will experience less steric hindrance to rotation than will an aryl group in the *para* position, which in turn will tend to adopt a larger twist angle. Such is clearly the case in **3**, where "X" is a needle-like phenylalkynyl moiety. In contrast, when "X" is particularly bulky, as in Pascal's 1-(*o*-carboran-9-yl)-2,3,4,5,6-pentaphenylbenzene, $C_2B_{10}H_{11}$-C_6Ph_5 (**5**) (Fig. 3), the two *ortho* phenyls are rotated through ~80° in opposite directions and the spherical carboranyl cluster (molecular diameter 5.62 Å) is nestled between them. Moreover, the C1–B linkage is unusually long.[23]

Likewise, Fig. 4 depicts the structure of 1-bromo-2,3,4,5,6-pentaphenylbenzene (**6**) in which the *ortho* phenyls are twisted through ~77° in opposite directions. Once again, as in pentaphenylbenzene, the angles within the central ring of **6** are distorted with internal angles at C2, C1, and C6 of 117.6°, 123.4°, and 118.1°, respectively, while the angles at C3, C4, and C5 are each 120°.

Fig. 3. (*a*) Molecular structure of 1-(*o*-carboran-9-yl)-2,3,4,5,6-pentaphenylbenzene, $C_2B_{10}H_{11}$-C_6Ph_5 (**5**); (*b*) spacefill view of **5**. (Data taken from reference 23.)

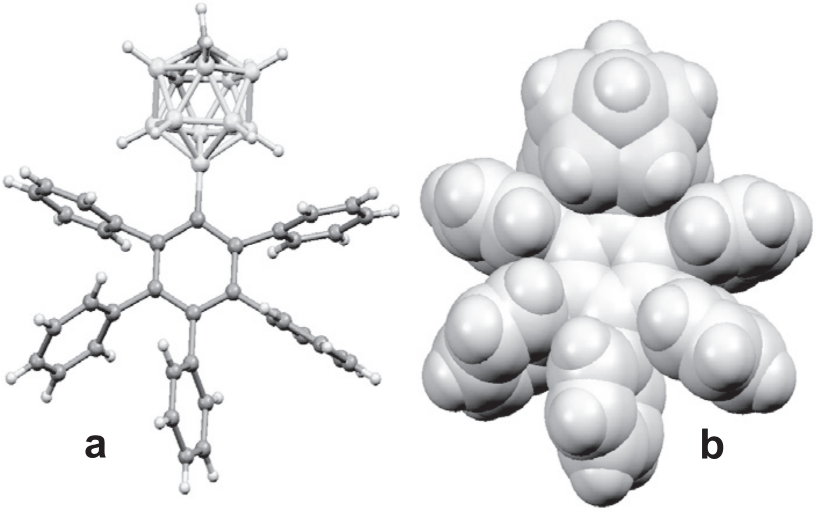
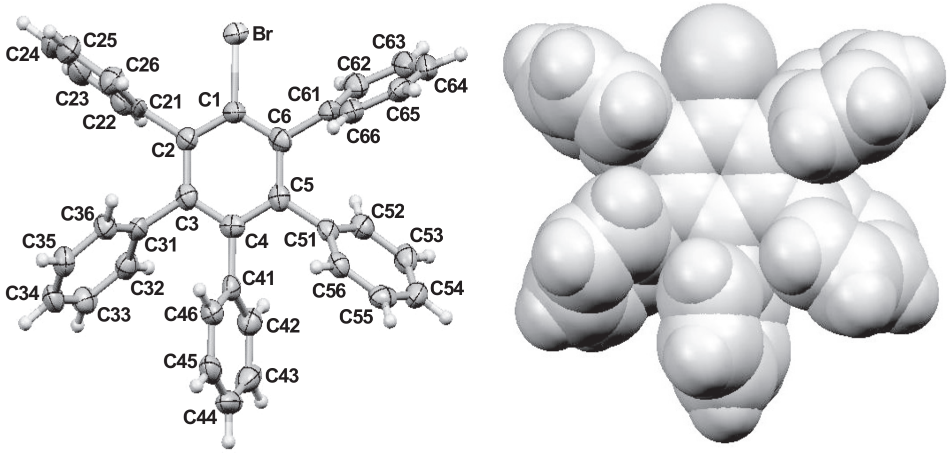


Fig. 4. Molecular structure and spacefill view of 1-bromo-2,3,4,5,6-pentaphenylbenzene (**6**).



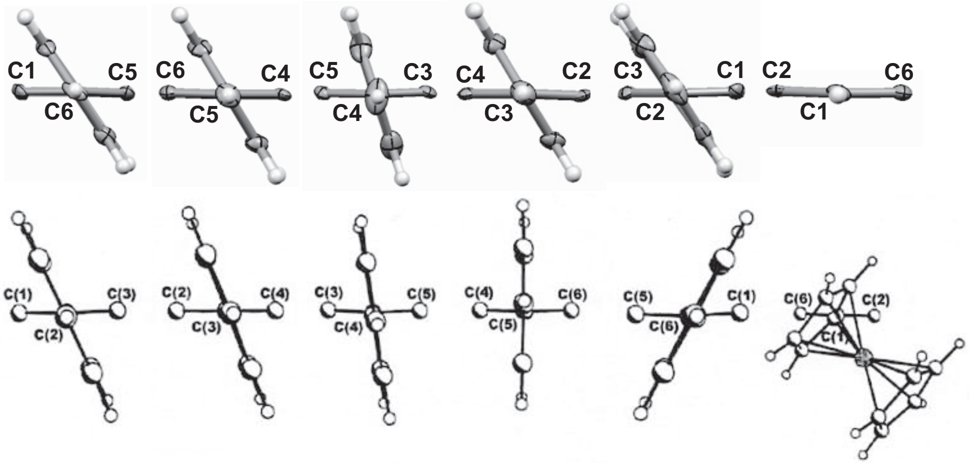
A more extreme example from our earlier work[24] is provided by 1-ferrocenyl-2,3,4,5,6-pentaphenylbenzene (**7**) whereby these deformations are enhanced; in this case, the substituents do not adopt a propeller conformation and the peripheral rings exhibit an incremental progression of twist angles relative to the central ring of 51° (Fc group), 64°, 70°, 81°, 89°, and 120° from C1 to C6, respectively. Figure 5 depicts a comparison of the peripheral ring orientations in C_6Ph_5H (**2**) and C_6Ph_5Fc (**7**).

As shown in Scheme 2, the project was then extended to include a bulky chiral substituent by addition of lithium phenylacetylide to 1*R*-(+)-camphor, which furnished 2-*endo*-phenylethynyl-2-*exo*-hydroxybornane (**8**). The propensity of reagents to approach the ketonic carbon from the less-hindered α-face (opposite to the dimethyl bridge) is well established,[25] and this was confirmed X-ray crystallographically for **8**, whose molecular structure appears as Fig. 6*a*. 2-*Endo*-phenylethynyl-2-*exo*-hydroxybornane crystallizes as two independent, yet closely related, molecules that appear as (O–H···O) hydrogen-bonded dimers in the asymmetric unit of the $P2_1$ space group. As featured in Fig. 6*b*, atom O2A in molecule 1 acts as an hydrogen bond donor to O2B in molecule 2, yielding values of 2.05 Å (H···A), 2.872(6) Å (D···A), and 165.9° (D–H···A).

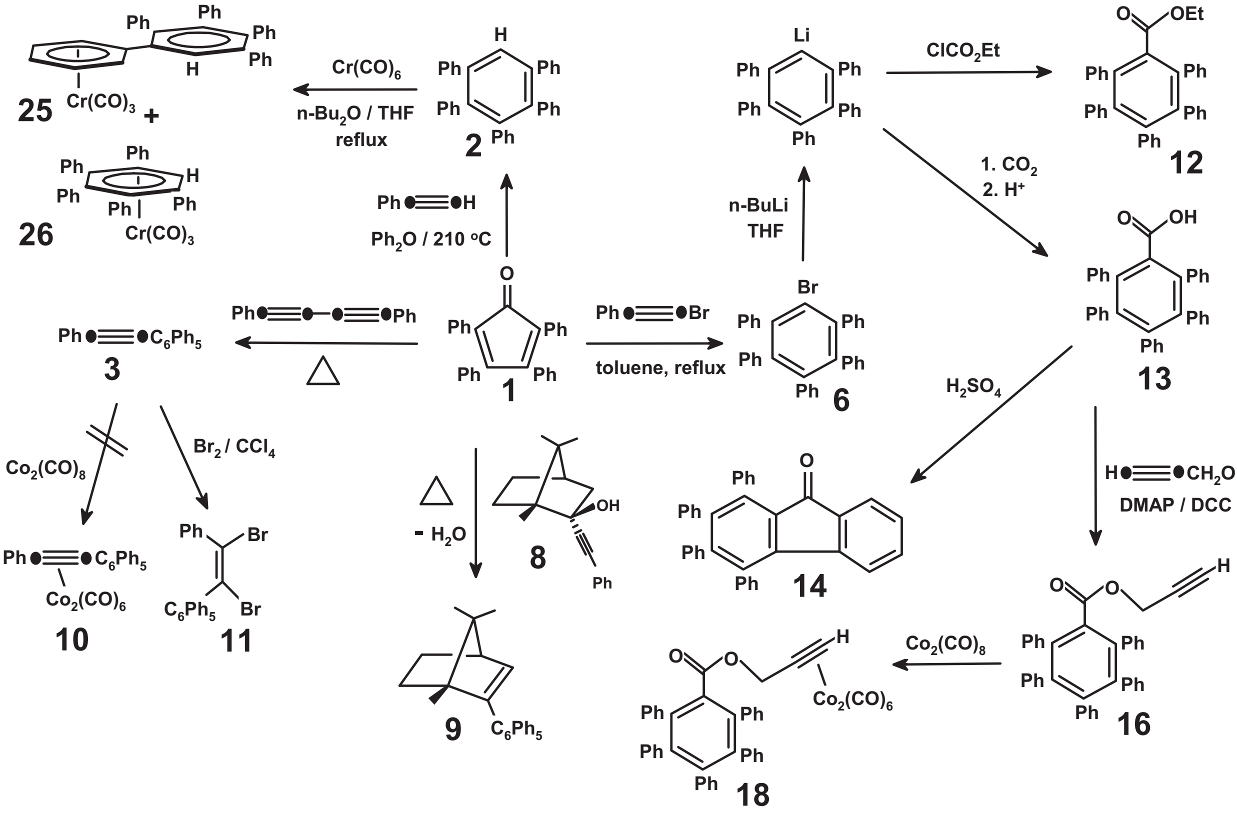
Subsequent reaction of the isoborneol **8** with tetracyclone at 200 °C proceeded with elimination of water to give 1-(2-bornenyl)-2,3,4,5,6-pentaphenylbenzene (**9**) whose X-ray crystal structure is shown in Fig. 7. Despite numerous attempts to obtain better quality crystals, the carbons in **9** could not be refined anisotropically, and so we prefer not to quote more precise geometric parameters. Nevertheless, the general features are evident and, as listed in Table 1, the C_6Ph_5-bornenyl system **9** adopts a nonpropeller arrangement of peripheral phenyls. Analogous to the carboranyl- and bromo-C_6Ph_5 systems **5** and **6**, the *ortho* phenyls in **9** are rotated by ~85° in opposite directions, thus exhibiting the most heightened conformational response to the presence of the "X" substituent in molecules of the C_6Ph_5X type surveyed thus far.

With the goal of combining organometallic fragments with bulky pentaarylphenyl units, 1-phenylethynyl-2,3,4,5,6-pentaphenyl benzene **3** was treated with dicobalt octacarbonyl, the standard route to alkyne-dicobalt tetrahedral clusters such as (**10**), but to no avail. This is presumably attributable to the potentially severe steric crowding that would be developed upon cluster formation, especially since the alkyne moiety in such systems is no longer linear but instead adopts R–C≡C–R angles of ~135°–140°. It is relevant to note that when Pascal[26] attempted the thermal reaction of **3** with $(C_5H_5)Co(CO)_2$ as a route to sterically crowded tetraarylcyclobutadiene complexes,[27] the major product was 1,2,3,4-tetraphenylfluorene, along with

Fig. 5. Views along successive peripheral ring – central ring bond axes in pentaphenylbenzene (**2**) (upper) and ferrocenylpentaphenylbenzene (**7**) (lower).



Scheme 2. Syntheses of organic and organometallic derivatives of pentaphenylbenzene.



other minor products, apparently arising via initial activation by cobalt complexation with subsequent *ortho*-metallation.

As a dienophile, **3** is not so sterically shrouded that it resists both single and double Diels–Alder reactions, so one could envisage halogenation of the C≡C bond as an extension of its reactivity. Mass spectrometric and NMR analysis of the products of reaction of **3** with bromine in CCl_4 indicated the formation of two dibromo adducts in a 1:4 ratio. Electrophilic bromine addition to aryl-substituted substrates proceeds via a vinyl cation intermediate that permits both *syn* and *anti* products, with the proportion of the latter increased in the presence of excess bromide ion and bulky substituents.[28] In 1999, Espenson et al. provided definitive solid-state evidence for the exclusive formation of the *trans* isomer of dibromostilbene from the methyltrioxorhenium-catalyzed stoichiometric reaction of bromide, hydrogen peroxide, and diphenylacetylene.[29] Subsequently, Barnes and Chudek[30] reported the X-ray crystal structure of *cis*-1,2-dibromostilbene–diphenylacetylene (2:1). Although details of its original preparation (ca. 1965) were unknown, it was conjectured that spontaneous and partial debromination of the less stable *cis* isomer had occurred over the sample's 30 year span of storage in the dark.

In the present case, the major product of the bromination of **3** was identified X-ray crystallographically as the *cis* isomer (**11**) (Fig. 8) in which the two independent molecules adopt similar propeller conformations. In the upper dynamic limit, the ^{13}C NMR spectrum of **11** should exhibit 22 signals in the aromatic region, of which eight correspond to aromatic non-hydrogen-bearing sp^2 carbons (four *ipso*

Fig. 6. (*a*) Molecular structure of 2-*endo*-phenylethynyl-2-*exo*-hydroxybornane (**8**) showing the disordered phenyl substituent in the solid state; (*b*) intermolecular hydrogen bonding between hydroxyl substituents to form dimeric units of **8**.

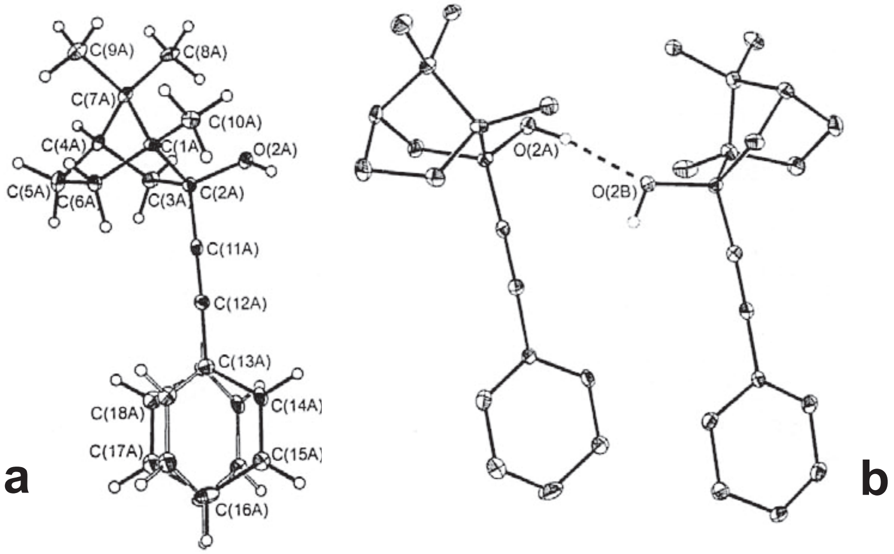


Fig. 7. Molecular structure of 1-(2-bornenyl)-2,3,4,5,6-pentaphenyl benzene (**9**).

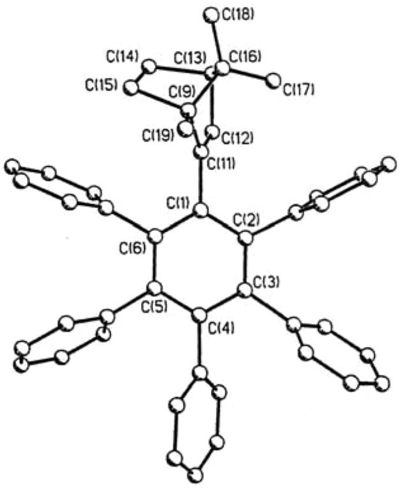
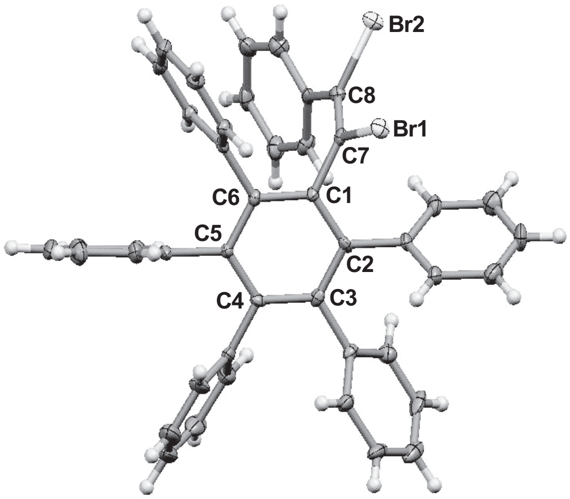


Fig. 8. Molecular structure of 1-(1′,2′-*Z*-dibromo-2′-phenyl)vinyl-2,3,4,5,6-pentaphenylbenzene (**11**).



phenyls and four in the central ring, each set of intensities 1:2:2:1), 12 CH carbons (four *ortho* (2:4:4:2), four *meta* (2:4:4:2), and 4 *para* (1:2:2:1)), and finally the two vinyl carbons. Since this number of resonances (and relative intensities) is exceeded at ambient temperature in the 125 MHz ^{13}C regime, some form of conformational rigidity is suggested. We note that, whether the angular rotation of the vinyl group is unrestricted (generating time-averaged molecular symmetry C_{2v}), or even limited to a "windshield wiper" motion (time-averaged C_s), it will not break the symmetry of the molecule unless rotation of one or more of the phenyl rings is inhibited.

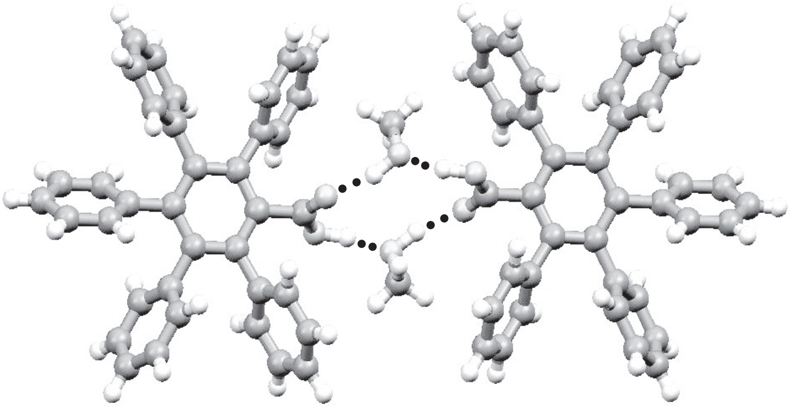
In our hands, attempted direct lithiation of pentaphenylbenzene gave very poor results. However, noting that iodo-pentaarylbenzenes can be lithiated and subsequently functionalized,[31] we chose to prepare 1-bromo–2,3,4,5,6-pentaphenylbenzene **6** from 1-bromo-2-phenylacetylene[32] and tetracyclone **1**. Treatment of **6** with *n*-butyllithium and then with ethyl chloroformate, or carbon dioxide and acidic workup, led to ethyl 2,3,4,5,6-pentaphenylbenzoate (**12**) or 2,3,4,5,6-pentaphenylbenzoic acid (**13**) in yields of 52% and 68%, respectively, based on pentaphenylbenzene recovered.

As illustrated in Fig. 9, pentaphenylbenzoic acid crystallized as a hydrogen-bonded dimer. Although carboxylic acids are generally directly connected via their CO_2H linkages, the steric bulk of the C_6Ph_5 fragment militates against such a situation. Instead, the hydrogen bonding motif in **13** comprises two carboxylic acid molecules bridged by two molecules of methanol; the carbonyl group interacts with the methanol hydrogen ($C{=}O{\cdots}HOCH_3$ = 1.703 Å), while the hydroxyl moiety is hydrogen bonded to the oxygen of the second methanol ($C({=}O)O{-}H{\cdots}O(H)CH_3$ = 1.513 Å).

The attempted acid-catalyzed esterification of **13** with propargyl alcohol, using dilute sulfuric acid, led not to the ester but instead proceeded with ring closure to form 1,2,3,4-tetraphenylfluorenone (**14**) that was identified unequivocally by X-ray crystallography. One can readily envisage (Scheme 3) initial generation of the sterically protected acylium ion (**15**), analogous to the known behaviour of other 2,6-disubstituted benzoic acids or esters bearing bulky substituents.[33]

As shown in Fig. 10, the fluorenone skeleton is planar and, to minimize steric repulsions, the four phenyl substituents are twisted out of the central plane by an average of 73°. Moreover, the C–C bonds in the substituted ring were slightly longer (average 1.402 versus 1.390 Å) than in the other benzo ring.

Fig. 9. Hydrogen-bonding pattern in the dimer $[C_6Ph_5CO_2H{\cdot}CH_3OH]_2$ (**13**).



Scheme 3. Reaction of $C_6Ph_5CO_2H$ with acid and formation of its propargyl ester.

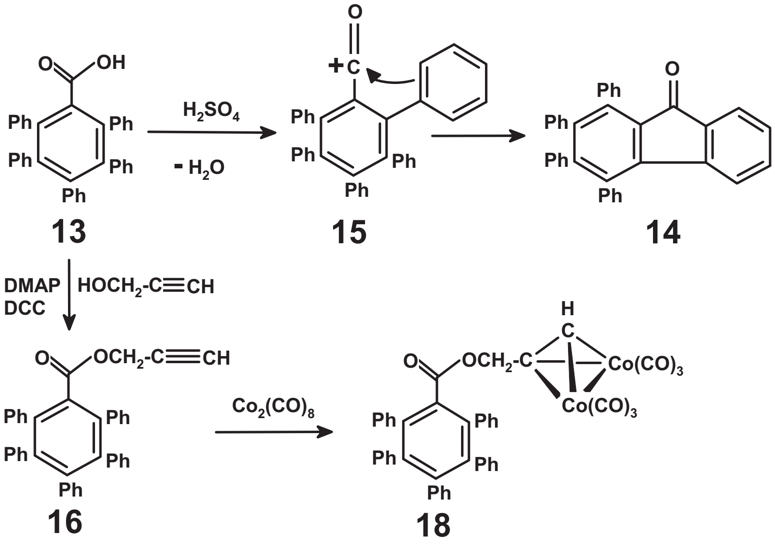
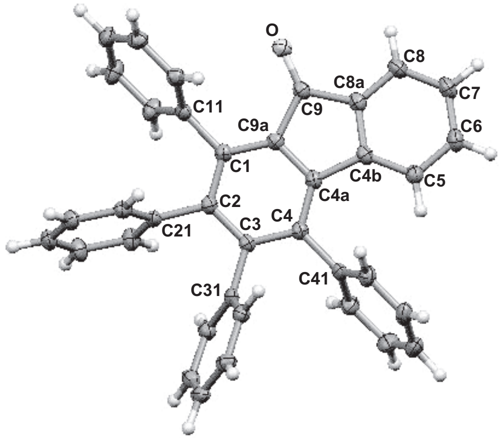


Fig. 10. Molecular structure of 1,2,3,4-tetraphenylfluorenone (**14**).

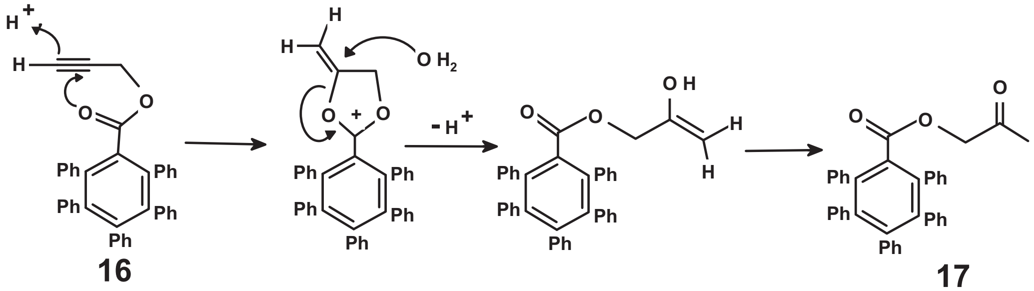


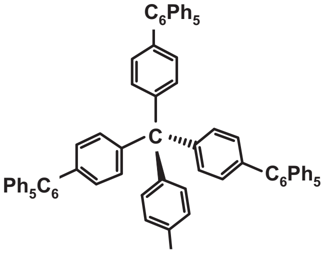
In contrast, the corresponding base-catalyzed esterification furnished the desired propargyl 2,3,4,5,6-pentaphenylbenzoate (**16**) and also a Meyer–Schuster rearrangement type product identified spectroscopically as 2-oxopropyl 2,3,4,5,6-pentaphenylbenzoate (**17**). It is likely that **17** arose during the acidic workup, and a possible mechanism involving a cyclic intermediate is depicted in Scheme 4. The lengthening of the side chain in **16** removes the steric problems associated with the directly attached alkyne in 1-phenylethynyl-2,3,4,5,6-pentaphenylbenzene **3** and allows ready formation of the tetrahedral dicobalt cluster $(C_6Ph_5\text{-}CO_2\text{-}CH_2\text{-}C{\equiv}CH)Co_2(CO)_6$ (**18**).

Correlation of *ortho* and *para* phenyl twist angles

An early X-ray study on the hexaphenylbenzene-anisole clathrate indicated a propeller-type (D_{6d}) structure with peripheral phenyl twist angles of ~75°.[20] However, more recent reports by Spek (21a) and by Munakata (21b) revealed that in hexaphenylbenzene itself, the dihedral angles ranged from 65° to 89° (average 79.5°). In the symmetrical polyaryl system 4,4′,4″,4‴-tetrakis(pentaphenylphenyl)tetraphenylmethane, $(p\text{-}C_6Ph_5\text{-}C_6H_4)_4C$ (**19**), which effectively contains four hexaphenylbenzene units, the peripheral phenyls adopt an almost ideal propeller conformation with somewhat smaller twist angles of 64° ± 2°. This was rationalized by regarding the C_6Ph_5 fragments as rigid groups with only a few degrees of rotational freedom such that the molecule maintains its tetrahedral symmetry. The packing is a distorted body-centered cubic lattice typical for the crystallization of solid spheres.[34] In contrast, in cases of severe steric encumbrance such as 3,3′,5,5′-tetrakis(pentaphenylphenyl)biphenyl (**20**), the phenyl orientations range from 26° to 89°.[34] However, the average of these 24 dihedral angles is 66°, again showing how the molecules adjust their conformations to find the minimum energy structure.

Scheme 4. Mechanistic proposal for the acid-mediated conversion of **16** into **17**.





19

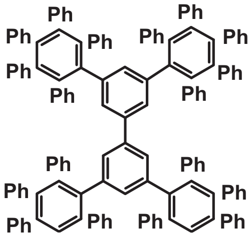


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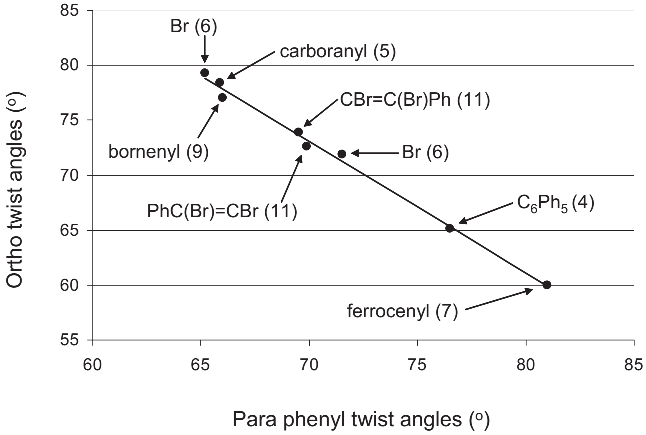
Fig. 11. Correlation of peripheral *ortho* and *para* phenyl twist angles in bulky C_6Ph_5X compounds.



Returning to the C_6Ph_5X system, solid-state structural data (Table 1) reveal that, in those cases where the bulky "X" groups most severely distort the propeller conformation, increasing the volume of "X" drives the *ortho* phenyls farther out of the plane of the central ring, and this effect is transmitted via the *meta* to the *para* ring. As shown in Fig. 11, for bulky "X" substituents, there is a clear correlation of the twist angle of the *ortho* phenyl ring with that of its *para* counterpart whereby the *ortho* twist angle can range from 80° to 60° and vice versa for the *para* phenyl.

Chromium tricarbonyl complexes of pentaphenylbenzene

We are unaware of any organometallic complexes of pentaphenylbenzene, but several derivatives of hexaphenylbenzene appear in the literature. Since the standard route to $[(\eta^6\text{-arene})RuX_2]_2$ systems involves Birch reduction of the arene to the corresponding cyclohexadiene and subsequent reaction with $RuCl_3$,[35] hexaphenylbenzene was treated with sodium in ethanol but, surprisingly, this afforded all-*cis*-1,2,3,4,5,6-hexaphenylcyclohexane.[13] There is a report of a sandwich complex $[(C_6Ph_6)Ru(C_5H_5)][BF_4]$ in which the metal is thought to be bonded to the central ring, but no X-ray crystallographic data are available.[36] Other organometallic complexes of hexaphenylbenzene include $(\eta^6\text{-}C_6Ph_6)Co(\eta^2\text{-}C_2Ph_2)$ (**21**),[37] $(\eta^6\text{-}C_6Ph_6)Mo(\eta^5\text{-}C_5H_5)$ (**22**),[38] $(\eta^6\text{-}C_6Ph_6)V(CO)_3$ (**23**),[39] and $(C_6Ph_6)Ag_2(ClO_4)_2$ (**24**).[40] The cobalt and molybdenum complexes have been crystallographically characterized as being centrally bonded; in the silver complex **24**, the metals bridge pairs of adjacent peripheral rings via η^1 and η^2 linkages, but the identification of the vanadium system **23** rests only on spectroscopic and microanalytical data. In $(\eta^6\text{-}C_6Ph_6)Co(\eta^2\text{-}C_2Ph_2)$ **21**, the peripheral phenyls form an almost ideal propeller with twist angles of 67° ± 3.5°; presumably the presence of the alkyne-cobalt moiety forces the hexaphenylbenzene structure into a rather flatter propeller. This effect is amplified somewhat in $(\eta^6\text{-}C_6Ph_6)Mo(\eta^5\text{-}C_5H_5)$ **22** whereby the dihedral angles range from 55.5° to 68.4° (average 63.2°). Finally, an attempt to coordinate a tricarbonylchromium unit to the central ring of hexaphenylbenzene led instead to $(\eta^6\text{-}C_6Ph_5\text{-}C_6H_5)Cr(CO)_3$ in which the metal was bonded to a peripheral ring; the barrier to rotation of the $(\eta^6\text{-}C_6H_5)Cr(CO)_3$ fragment relative to the central ring was found to be 12.2 kcal mol^{-1}.[41]

The reaction of pentaphenylbenzene **2** with chromium hexacarbonyl in refluxing *n*-dibutyl ether yielded, after chromatographic separation, two yellow products (**25** and **26**), each with infrared absorptions at 1970 and 1897 cm^{-1}, typical of $(\eta^6\text{-arene})Cr(CO)_3$ complexes. The ^1H NMR spectrum of **25**, the first material to elute, exhibited signals at 5.30 and 5.18 ppm, clearly indicating complexation to a peripheral phenyl ring,[42] and a singlet at 7.66 ppm, typical of the unique ring proton in pentaphenylbenzene. In contrast, in the second product **26**, the lack of ^1H NMR resonances in the region 5–6 ppm clearly suggested that the metal was bonded to the central ring. These structures were confirmed X-ray crystallographically, as illustrated in Figs. 12 and 13.

In **25**, the tricarbonylchromium moiety is sited on an *ortho* phenyl ring and is oriented towards the open space adjacent to the central ring hydrogen, thus avoiding contact with the adjacent *meta* phenyl substituent. The twist angles of the peripheral phenyls (average 62°) are listed in Table 1, and the greatest deviation (70.7°) from coplanarity with the central ring is exhibited by the phenyl substituent at C5 i.e., the group sited *para* relative to the most bulky substituent (the metal-complexed ring).

The second fraction to elute was the centrally coordinated complex **26**; it was also characterized X-ray crystallographically and, similar to the situation in **2**, **5**, and **25**, the central ring was again flattened with internal angles C5–C6–C1, C6–C1–C2, and C1–C2–C3 of 118.8°, 122.5°, and 119.3°, respectively. The peripheral phenyl twist angles in **26** range from 48° to 65° (average 58°), and the C–C bonds in the central ring are somewhat longer (average 1.423 Å) than in pentaphenylbenzene itself (1.387 Å); they are also longer than those in the *ortho* phenyl bearing the chromium tricarbonyl in **25** (1.405 Å). As shown in Fig. 14, in the solid state, $(\eta^6\text{-}C_6Ph_6)Cr(CO)_3$ **26** adopts the piano-stool geometry whereby the three carbonyls are positioned between the phenyl rings, so as to minimize repulsions. Interestingly,

Fig. 12. Molecular structure of $[(\eta^6\text{-}C_6H_5)\text{-}C_6Ph_4H]Cr(CO)_3$ (**25**).

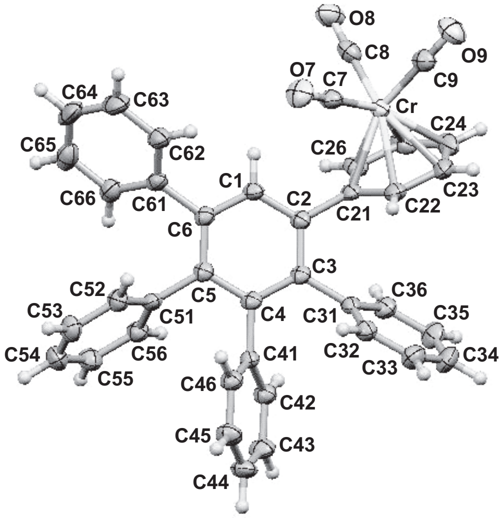
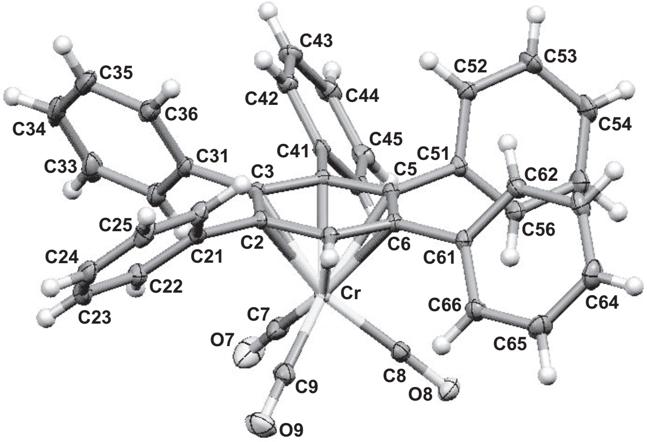


Fig. 13. Molecular structure of $(\eta^6\text{-}C_6Ph_5H)Cr(CO)_3$ (**26**).

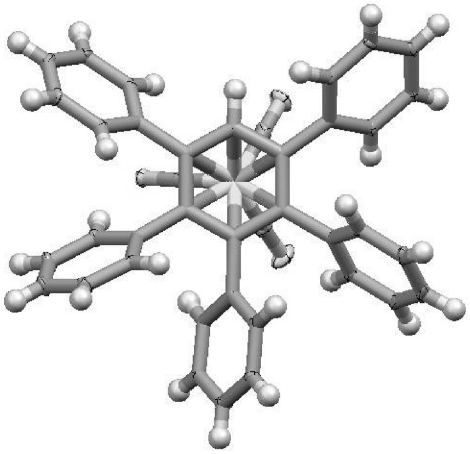


the average chromium-to-ring-carbon distances are identical for both complexes (2.220 Å).

Phenyl orientations and nano-machinery

Molecular architectures comprised of contiguous groups attached to a planar central framework continue to attract the attention of stereochemists. Molecules of the type $C_nR_n^{x\pm}$ (n = 3–7) endowed with a propeller form (R = aryl) or gear-meshed ground states (R = alkyl) present torsional circuits that may be greatly influenced by the nonbonded repulsions of voluminous substituents. One may view this particular series in terms of the reciprocal relationship between n and the angle ω subtended by adjacent moieties at the centre of the internal ring ($\omega = 360°/n = 120°, 90°, 72°, 60°$, and $51.4°$, respectively). Although increasing the ring size lengthens the radial distance of the external groups from the centre of the molecule, this is more than compensated for by the diminishing value of ω. As a result of cyclic expansion, the peripheral rotors are successively placed in a more crowded locale. This steric design has been explored in terms of correlated rotations,[43] a prospect that has gained more relevance with the intense current interest in nano-machinery.[44] Towards the construction of gears and brakes, several studies have shed light on the structural attributes and dynamic behaviour of the peripheral substituents in multi-n-rotor molecular propellers, either as hexaarylbenzenes C_6Ar_6,[45] or as metal complexes of the type $(\eta^n\text{-}C_nAr_n)ML_x$, where n is 4,[27,46] 5,[47] or 6.[35–41]

Fig. 14. Bird's eye view of $(\eta^6\text{-}C_6Ph_5H)Cr(CO)_3$ (**26**) showing the staggered orientation of the $Cr(CO)_3$ tripod relative to the peripheral phenyl substituents.



In the 1970s, in a series of now classic publications, Gust et al. established that isomerization in C_6Ar_6 systems occurs via a mechanism wherein an individual peripheral ring rotates in an uncorrelated fashion by approximately π radians.[45] Rotational barriers of 33 or 38 kcal mol^{-1}, respectively, are engendered by the incorporation of *ortho* methoxy or methyl substituents; these barriers fall to 17 kcal mol^{-1} for *meta* substituents. Increasing the ring size, as in heptaphenyltropylium, $[C_7Ph_7]^+$, might have been expected to enhance the barrier to phenyl rotation but, in fact, the system adopts a shallow boat conformation so as to minimize such interactions.[48]

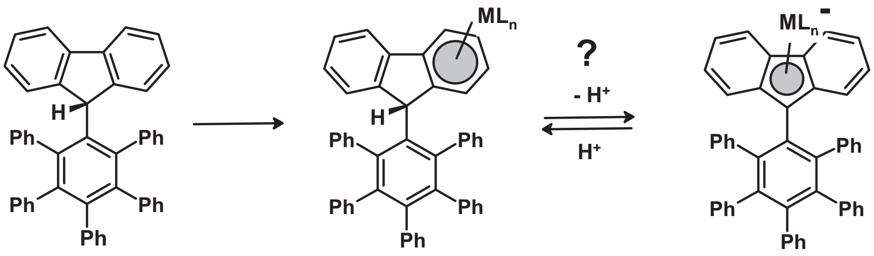
As is evident from the X-ray crystallographic data presented above (Table 1; Fig. 11), rotating rings also detect the nonbonding repulsions from remote sites around the circumference of the central benzene ring. Such buttressing effects were evinced by the free energies of activation for pentaphenylbenzene derivatives, C_6Ph_5X, bearing substituents of varying size; these range from 15.5 (X = H, **1**) to 18.7 kcal mol^{-1} (X = CMe_3).[49] In all of the C_6Ph_6 and C_6Ph_5X systems reported to date, the $\Delta G^{\neq}$ values have been ascribed to diastereomeric interconversions, since enantiomerization necessarily involves rotation of all substituted rings and is therefore energetically more demanding.

Our original idea was to construct a molecular brake that would block peripheral phenyl rotation by means of a base-promoted η^6- to η^5-haptotropic shift[50] of an organometallic unit across a fluorenyl framework (Scheme 5), thus moving the bulky $M(CO)_3$ fragment closer to the C_6Ph_5 moiety.

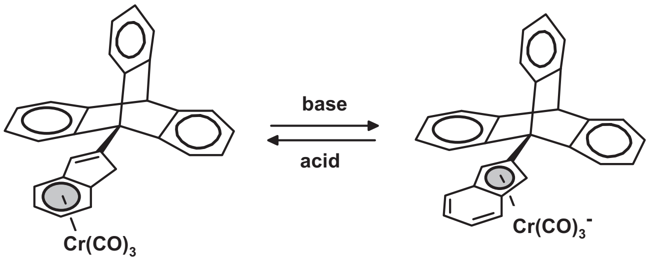
In the event, the attempted synthetic route to the desired 9-fluorenyl-pentaphenylbenzene, by Diels–Alder addition of 9-phenylethynylfluorene[51] to tetracyclone **1**, led instead to a diindenotetracene by a complex rearrangement mechanism that has been fully elucidated elsewhere.[52] The successful construction of an organometallic molecular brake that utilized a haptotropic shift process was finally achieved by incorporation of a triptycene paddlewheel rather than a pentaphenyl group (Scheme 6).[53] Migration of the metal tricarbonyl moiety from the six-membered to the five-membered ring of the indenyl fragment severely hinders rotation of the paddlewheel.[54,55]

Finally, we note that, as emphasized by Mislow[56] and by Biali,[57] transmission of cooperative torsional motion along chains of suitably meshed N-chemical gears is governed by the parity rule for gear trains, which dictates correlated disrotation of the terminal gears when N is even and conrotatory interactions when N is odd. Thus, in arranging an odd number of gears in a cyclic array, dy-

Scheme 5. Potentially reversible haptotropic shift of an organometallic moiety to block peripheral phenyl rotations.



Scheme 6. An organometallic molecular brake mediated by an η^6- to η^5-haptotropic shift.



namic gearing is disallowed and immobilization of the rotors can be expected. This is precisely the situation in pentaphenylbenzenes, C_6Ph_5X, and so introduction of a voluminous "X" group, in conjunction with suitably substituted phenyl rings, may be expected to lead to restricted peripheral ring rotation.

Conclusions

We here report the syntheses and structures of a series of pentaphenylbenzenes, C_6Ph_5X, bearing substituents encompassing a wide range of steric demand. When the "X" substituent is very bulky, there is a clear transmission of nonbonded interactions as indicated by the orientations of the *ortho* and *para* phenyls relative to the central ring plane. Moreover, in contrast with the hexaphenylbenzene case, the X-ray crystal structure of **20** showed unequivocally that a tricarbonylchromium fragment can be attached to the central ring of pentaphenylbenzene, thus making available a bulky organometallic fragment for incorporation into potentially bioactive or fluorescent molecules while expanding our repertoire of prototypes for potentially tunable, sterically controlled molecular-scale propellers and gears.

Experimental

All reactions were carried out under a nitrogen atmosphere unless otherwise stated. Merck silica gel 60 (230–240 mesh) was used for flash chromatography. ^1H and ^{13}C NMR spectra were acquired on a Bruker AC-200, Bruker Avance DRX-500, or Varian INOVA 400, 500, or 600 MHz spectrometer at 30 °C, unless otherwise stated. Assignments were based on standard ^1H–^1H and ^1H–^{13}C two-dimensional techniques and NOE measurements. Low- and high-resolution mass spectra were acquired on VG ZAB-E or ZAB-R instruments, respectively. Melting points were determined on a Gallenkamp instrument in air and are uncorrected. Elemental analyses were carried out by the Microanalytical Laboratory at the University College Dublin or by Guelph Chemical Laboratories (Guelph, Ontario). Pentaphenylbenzene (**2**), 1-phenylethynyl–2,3,4,5,6-pentaphenylbenzene (**3**), 1-bromo-2-phenylethyne, and 2-(phenylethynyl)-*iso*borneol (**8**) were prepared as described previously.[15,17,32,58]

Preparation of 1-bromo-2,3,4,5,6-pentaphenylbenzene (6)

Tetraphenylcyclopentadienone (22.0 g, 63.13 mmol) and 1-bromo-2-phenylacetylene (16.63 g, 91.87 mmol) were heated at reflux in toluene (250 mL) for 20 h. After removal of the toluene in vacuo and addition of cyclohexane (30 mL), the solution was filtered and the white solid washed with cyclohexane until the filtrate was colourless. The residue was dried to yield bromopentaphenylbenzene **6** (25.77 g, 47.95 mmol, 76%), mp 289–290 °C (lit. 281–282 °C[17]). ^1H NMR (500 MHz, $CDCl_3$) δ: 7.21 (4H, m, H_{23}, H_{25}, H_{63}, H_{65}), 7.19 (4H, m, H_{22}, H_{26}, H_{62}, H_{66}), 7.15 (2H, m, H_{24}, H_{64}), 6.88 (2H, m, H_{34}, H_{54}), 6.86 (4H, m, H_{33}, H_{35}, H_{53}, H_{55}), 6.83 (4H, m, H_{32}, H_{36}, H_{52}, H_{56}), 6.83 (2H, m, H_{43}, H_{45}), 6.80 (2H, m, H_{42}, H_{46}), 6.80 (1H, m, H_{44}). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 142.1 (C_{31}, C_{51}), 142.0 (C_2, C_6), 141.7 (C_{21}, C_{61}), 140.7 (C_{41}), 140.1 (C_3, C_5), 139.8 (C_4), 131.2 (C_{42}, C_{46}), 131.0 (C_{33}, C_{35}, C_{53}, C_{55}), 130.6 (C_{22}, C_{26}, C_{62}, C_{66}), 127.5 (C_{23}, C_{25}, C_{63}, C_{65}), 126.8 (C_{34}, C_{54}), 126.8 (C_{32}, C_{36}, C_{52}, C_{56}), 126.7 (C_{24}, C_{64}), 125.8 (C_{43}, C_{45}), 125.6 (C_{44}) 125.3 (C_1). IR (solid, KBr): 3477, 3415, 3077, 3054, 3023, 1598, 1494, 1440, 1382, 1276, 1074, 1027, 773, 696 cm^{-1}. Elemental analysis calcd. (%) for $C_{36}H_{25}Br$: C 80.45, H 4.69, Br 14.87; found: C 80.58, H 4.83, Br 14.75. A sample of **6** suitable for an X-ray diffraction study was obtained by recrystallization from dichloromethane/hexane.

Preparation of 1-(2-bornenyl)-2,3,4,5,6-pentaphenylbenzene (9)

2-(Phenylethynyl)-*iso*borneol **8** (0.666 g, 2.62 mmol) and tetracyclone (0.600 g, 1.56 mmol) were combined neat in an open flask and flame heated (>200 °C). After approximately 40 min. the molten mixture appeared to have changed from magenta to dark brown in colour, and diphenyl ether (10 mL) was added to the melt. To effect precipitation, hexanes (20 mL) were added dropwise to the cooled reaction mixture. The product was filtered under suction, reprecipitated in ethanol until the red colour of unreacted tetracyclone had disappeared, and then dried in vacuo to give 1-(2-bornenyl)-2,3,4,5,6-pentaphenylbenzene **9** as an off-white solid (0.157 g, 0.26 mmol, 17%). ^1H NMR (200 MHz, $CDCl_3$) δ: 6.59–7.09 (25H, m), 5.91 (1H, m, H_3), 2.15 (2H, m), 1.51 (2H, m), 1.09 (1H, m), 0.75 (3H, s, Me), 0.40 (3H, s, Me), 0.2 (3H, s, Me). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 140.9, 136.5 (*ipso*), 131.7, 131.4, 130.6, 126.7, 126.4, 125.9, 124.8 (*ortho*, *meta*, *para*, and C=C), 29.7, 25.3, 20.3, 17.7, 13.7, 12.8 (bornene ring system). LRMS (DEI), *m/z* (%), 592 (100) $[M]^+$, 564 (45) $[M - C_2H_4]^+$, 549 (25) $[M - C_3H_7]^+$. LRMS (DCI) *m/z* (%): 592 (100) $[M]^+$, 564 (30) $[M - C_2H_4]^+$, 469 (10) $[C_7Ph_5]^+$. HRMS: *m/z* calcd. for $C_{46}H_{40}$: 592.3101 $[M]^+$; found: 592.3130. Anal. calcd. for $C_{46}H_{40}$ (%): C 93.20, H 6.80; found: C 92.98, H 6.94. The growth of appropriately sized crystals of **9** suitable for an X-ray diffraction study proved to be difficult, although data were eventually collected on a sample extracted from an NMR tube (deuterated chloroform) stored in refrigeration.

Preparation of 1-(1′,2′-*Z*-dibromo-2′-phenyl)vinyl-2,3,4,5,6-pentaphenylbenzene (11)

To 1-phenylethynyl-2,3,4,5,6-pentaphenylbenzene **3** (0.279 g, 0.50 mmol) dissolved in CCl_4 (10 mL) were added two to three drops (large excess) of bromine, and the solution was stirred vigorously at room temperature for 5 days. Following solvent removal, the isolated solid was washed successively with CCl_4 and acetone and then dried in vacuo. Recrystallization from CCl_4/acetone yielded **11** as a yellow solid (358 mg, 0.49 mmol, 98%). ^{1}H NMR (200 MHz, $CDCl_3$). The presence of two components was verified when a sample dissolved in 90:10 acetonitrile–water was injected into a 4.6 × 150 mm HPLC analytical column. ^{1}H NMR (500 MHz, CD_2Cl_2)* δ: 7.29–7.26 (2H, m), 7.25–7.14 (8H, m), 7.09 (2H, m), 6.93–6.90 (4H, m), 6.86–6.82 (8H, m), 6.77–6.75 (4H, m), 6.51–6.49 (2H, m). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 143.4 (1C), 142.3 (2C), 140.8 (1C), 140.6 (2C), 140.5 (2C), 139.7 (1C), 138.6 (1C), 137.3 (1C) (*ipso* and central ring), 132.0, 131.8, 131.4, 131.1, 130.7, 130.7, 129.1, 129.0, 128.7, 128.6, 127.5, 127.4, 127.2, 127.1, 126.9, 126.4, 126.0 (*ortho*, *meta*, *para*, and C=C)*. LRMS (DEI) *m*/*z* (%): 716 (10) [M]$^+$, 637 (5) [M – Br]$^+$, 558 (100) [M – 2Br]$^+$, 481 (25) [M – 2Br – Ph]$^+$, 404 (20) [M – 2Br – 2Ph]$^+$. LRMS (DCI) *m*/*z* (%): 716 (15) [M]$^+$, 637 (5) [M – Br]$^+$, 558 (100) [M – 2Br]$^+$, 481 (30) [M – 2Br – Ph]$^+$ (peaks quoted correspond to the lower mass (^{79}Br); isotopic distribution is evident. HRMS: *m*/*z* calcd. for $C_{44}H_{30}Br_{2:}$ 716.0714 [M]$^+$; found: 716.0616. (*Resonances corresponding to a second isomer (~18%) were also observed in the ^{1}H NMR spectrum.) Anal. calcd. for $C_{44}H_{30}Br_2$ (%): C 73.55, H 4.21, Br 22.24; found: C 73.80, H 4.35, Br 22.07. X-ray quality crystals of the *cis* isomer, presumably the major product, were isolated from the CH_2Cl_2/hexanes supernatant.

Preparation of ethyl 2,3,4,5,6-pentaphenylbenzoate (12)

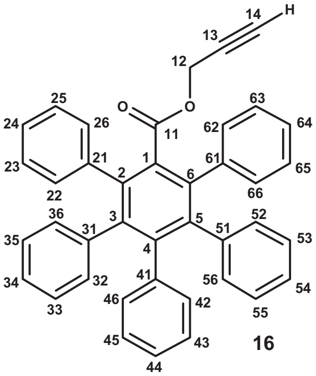
To bromopentaphenylbenzene **6** (1.00 g, 1.86 mmol) in dry THF (20 mL) at –78 °C was added BuLi (1.30 mL of a 1.6 mol L^{-1} solution in hexane, 2.08 mmol). The solution was stirred for 20 min, warmed slowly to room temperature, and ethyl chloroformate (0.22 mL, 2.30 mmol) was added. The solution was heated at reflux for 20 h, cooled to room temperature, quenched with H_2O, and the product extracted with ethyl acetate. After being washed with water and brine and dried over $MgSO_4$, the residue was chromatographed on silica, using ethyl acetate (20%) in pentane as eluent, to give two fractions. The first was pentaphenylbenzene (621 mg, 1.35 mmol); the second was a white solid identified as ethyl pentaphenylbenzoate **12** (141 mg, 0.27 mmol, 14%), mp 318–319 °C, 52% based on recovered pentaphenylbenzene. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.16 (4H, dd, *J* = 8 Hz, *J* = 2 Hz, H_{22}, H_{26}, H_{52}, H_{56}), 7.12 (4H, m, H_{23}, H_{25}, H_{63}, H_{65}), 7.11 (2H, m, H_{24}, H_{64}), 6.88 (4H, m, H_{33}, H_{35}, H_{53}, H_{55}), 6.87 (2H, m, H_{34}, H_{54}), 6.85 (1H, m, H_{44}), 6.84 (2H, m, H_{43}, H_{45}), 6.80 (4H, dd, *J* = 7 Hz, *J* = 2 Hz, H_{32}, H_{36}, H_{52}, H_{56}), 6.76 (2H, dd, *J* = 7 Hz, *J* = 2 Hz, H_{42}, H_{46}), 3.67 (2H, q, *J* = 7 Hz, H_{12}), 0.72 (3H, t, *J* = 7 Hz, H_{13}). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 169.1 (C_{11}), 142.4 (C_4), 140.6 (C_3, C_5), 140.0 (C_{41}), 139.5 (C_{31}, C_{51}), 139.3 (C_{21}, C_{61}), 138.0 (C_2, C_6), 135.0 (C_1), 131.4 (C_{32}, C_{36}, C_{52}, C_{56}), 131.2 (C_{42}, C_{46}), 130.2 (C_{22}, C_{26}, C_{62}, C_{66}), 127.4 (C_{23}, C_{25}, C_{63}, C_{65}), 126.9 (C_{33}, C_{35}, C_{53}, C_{55}), 126.8 (C_{43}, C_{45}), 126.7 (C_{24}, C_{64}), 125.7 (C_{34}, C_{54}), 125.6 (C_{44}), 60.8 (C_{12}), 13.6 (C_{13}). IR (solid, KBr): 3449, 3056, 3025, 2925, 2850, 1730 (CO), 1600, 1495, 1441, 1326, 1227, 1158, 1070, 908, 788 cm^{-1}. Anal. calcd. for $C_{39}H_{30}O_2\cdot(EtOAc)_{0.25}$ (%): C 86.92, H 5.85; found: C 86.88, H 5.84.

Preparation of 2,3,4,5,6-pentaphenylbenzoic acid (13)

To bromopentaphenylbenzene **6** (13.0 g, 24.19 mmol) in dry THF (250 mL) under nitrogen at –78 °C was added BuLi (17.0 mL of a 1.6 mol L^{-1} solution, 27.20 mmol). The solution was stirred for 20 min, warmed to room temperature, and lumps of dry ice (excess) were added. The solution was then stirred until it reached room temperature, quenched with dilute HCl, and the product extracted using ethyl acetate. The organic layer was washed with water and brine, dried over $MgSO_4$ to give a white solid, and chromatographed on silica using dichloromethane as eluent to obtain recovered pentaphenylbenzene (1.86 g, 4.06 mmol). The eluent was then changed to ethyl acetate to yield pentaphenylbenzoic acid **13** as a white solid (6.90 g, 13.73 mmol, 57%), mp 352–353 °C (lit. 342 °C[17]), 68% based on recovered pentaphenylbenzene. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 12.40 (1H, s, OH), 7.16 (4H, dd, *J* = 7 Hz, *J* = 2 Hz, H_{22}, H_{26}, H_{62}, H_{66}), 7.11 (4H, t, *J* = 7 Hz, H_{23}, H_{25}, H_{63}, H_{65}), 7.07 (2H, m, H_{24}, H_{64}), 6.88 (4H, m, H_{32}, H_{36}, H_{52}, H_{56}), 6.87 (2H, m, H_{34}, H_{54}), 6.86 (4H, m, H_{33}, H_{35}, H_{53}, H_{55}), 6.85 (2H, m, H_{43}, H_{45}), 6.82 (2H, m, H_{42}, H_{46}), 6.80 (1H, m, H_{44}). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.3 (C_{11}), 141.1(C_{41}), 140.1 (C_{31}, C_{51}), 139.6 (C_4), 139.2 (C_3, C_5), 138.8 (C_{21}, C_{61}), 136.4 (C_2, C_6), 135.8 (C_1), 130.8 (C_{32}, C_{36}, C_{52}, C_{56}), 130.7 (C_{42}, C_{46}), 130.2 (C_{22}, C_{26}, C_{62}, C_{66}), 127.0 (C_{23}, C_{25}, C_{63}, C_{65}), 126.6 (C_{33}, C_{35}, C_{53}, C_{55}), 126.5 (C_{43}, C_{45}), 126.4 (C_{24}, C_{26}), 125.6 (C_{34}, C_{54}), 125.5 (C_{44}). IR (solid, KBr): 3484, 3403, 1701 (CO), 1637, 1494, 1403, 1324, 1261, 1074, 1027, 700 cm^{-1}. A sample of **13** suitable for an X-ray diffraction study was obtained by recrystallization from dichloromethane/methanol/hexane.

Preparation of 1,2,3,4-tetraphenylfluorenone (14)

To pentaphenylbenzoic acid **13** (500 mg, 0.99 mmol) and propargyl alcohol (0.08 mL, 1.37 mmol) in toluene (20 mL) was added concentrated H_2SO_4 (2 mL) and the mixture heated at reflux for 3 h. After removal of the toluene, the resulting yellow solid was dissolved in dichloromethane, washed with $NaHCO_3$, water, and brine, dried over $MgSO_4$, and concentrated to give a yellow solid. Chromatography on silica using a gradient of ethyl acetate (5% → 10% → 50%) in pentane yielded 1,2,3,4-tetraphenylfluorenone **14** as a yellow solid (470 mg, 0.97 mmol, 98%), mp 303–304 °C (lit. 298 °C[59,60]). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.55 (1H, d, *J* = 7 Hz, H_8), 7.28 (2H, m, H_{43}, H_{45}), 7.26 (1H, t, *J* = 7.5 Hz, H_{44}), 7.22 (2H, m, H_{42}, H_{46}), 7.20 (2H, m, H_{23}, H_{25}), 7.19 (1H, m, H_{24}), 7.16 (1H, t, *J* = 7 Hz, H_7), 7.13 (2H, dd, *J* = 7 Hz, *J* = 1.5 Hz, H_{22}, H_{26}), 7.10 (1H, dt, *J* = 7.5 Hz, *J* = 1.5 Hz, H_6), 6.88 (4H, m, H_{13}, H_{15}, H_{32}, H_{36}), 6.87 (1H, m, H_{34}), 6.86 (1H, m, H_{14}), 6.84 (2H, t, *J* = 6.5 Hz, H_{33}, H_{35}), 6.79 (2H, d, *J* = 6.5 Hz, H_{12}, H_{16}), 6.13 (1H, d, *J* = 7.5 Hz, H_5). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 193.0 (C_9), 147.8 (C_{31}), 143.7 (C_{4b}), 142.9 (C_1), 141.7 (C_{4a}), 140.6 (C_2), 139.1 (C_3), 138.7 (C_{11}), 138.6 (C_{41}), 136.9 (C_{21}) 136.9 (C_4), 135.2 (C_{8a}), 134.2 (C_6), 131.2 (C_{12}, C_{16}), 130.7 (C_{33}, C_{35}), 130.1 (C_{9a}), 130.0 (C_{42}, C_{46}), 129.9 (C_{22}, C_{26}), 128.7 (C_7), 128.4 (C_{43}, C_{45}), 127.5 (C_{44}), 127.3 (C_{23}, C_{25}), 127.0 (C_{24}), 126.9 (C_{13}, C_{15}), 126.9 (C_{32}, C_{36}), 126.1 (C_{34}), 125.9 (C_{14}), 123.8 (C_8), 123.3 (C_5). IR (solid, KBr): 3423, 3241, 3056, 2919, 2850, 1708 (CO), 1602, 1440, 1205, 1087, 954, 698 cm^{-1}. A sample of **14** suitable for an X-ray diffraction study was obtained by recrystallization from dichloromethane.



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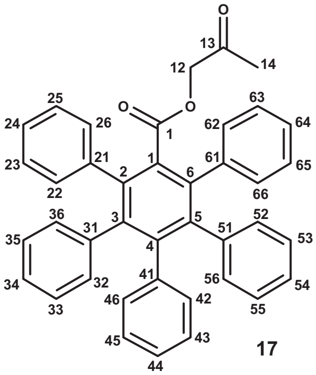

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Table 2. Crystallographic data for **2**, **3**, **6**, and **8**.

	2	**3**	**6**	**8**
Formula	$C_{36}H_{26}$	$C_{44}H_{30}$	$C_{36}H_{25}Br$	$C_{18}H_{22}O$
M	458.57	558.68	537.47	234.36
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P2_1$ (#4)
a (Å)	10.158(3)	11.0833(3)	11.409(2)	7.476(2)
b (Å)	12.101(3)	13.3548(3)	12.085(2)	11.482(4)
c (Å)	13.017(4)	21.94640(10)	19.780(4)	17.239(6)
α (°)	63.241(5)	103.1890(10)	83.909(3)	90
β (°)	68.374(5)	94.800(2)	77.544(4)	90.340(5)
γ (°)	65.662(5)	93.643(2)	79.535(4)	90
V (Å^3)	1268.3(6)	3140.17(11)	2612.2(8)	1479.8(8)
Z	2	4	4	4
$\rho_{\text{calcd.}}$ (g cm^{-3})	1.201	1.182	1.367	1.142
T (K)	100(2)	299(2)	100(2)	100(2)
μ (mm^{-1})	0.068	0.067	1.587	0.068
F(000)	484	1176	1104	552
θ range for data collection	1.80 to 23.36	1.57 to 22.50	1.06 to 24.00	1.77 to 25.35
Index ranges	$-11 \le h \le 11$	$-11 \le h \le 11$	$-13 \le h \le 13$	$-9 \le h \le 8$
	$-13 \le k \le 13$	$-14 \le k \le 14$	$-13 \le k \le 13$	$-13 \le k \le 13$
	$-14 \le l \le 14$	$-23 \le l \le 23$	$-22 \le l \le 22$	$-20 \le l \le 18$
Reflections measured	8342	17565	37592	9727
Reflections used	3656	8192	8199	4555
R_{int}	0.0482	0.0291	0.0391	0.0324
Data/restraints/parameters	3656/97/325	8192/0/794	8199/0/667	4555/1/335
Final R values ($I > 2\theta(I)$)				
R_1	0.1039	0.0447	0.0353	0.0814
wR_2	0.2711	0.1041	0.0900	0.2744
R values (all data)				
R_1	0.1171	0.0779	0.0433	0.0838
wR_2	0.2817	0.1218	0.0947	0.2763
Goodness-of-fit on F^2	1.081	1.008	1.044	1.195

Table 3. Crystallographic data for **11**, **13**, **14**, **25**, and **26**.

	11	**13**	**14**	**25**	**26**
Formula	$C_{44}H_{30}Br_2$	$C_{37}H_{26}O_2{\cdot}CH_3OH$	$(C_{37}H_{24}O)_4{\cdot}CH_2Cl_2$	$C_{39}H_{26}O_3Cr{\cdot}(C_6H_6)_3$	$C_{39}H_{26}O_3Cr$
M	718.50	534.62	2023.17	828.92	594.60
Crystal system	Triclinic	Monoclinic	Tetragonal	Triclinic	Monoclinic
Space group	$P\bar{1}$ (#2)	$P2_1/c$ (#14)	$I4_1/a$ (#88)	$P\bar{1}$ (#2)	$P2_1/c$ (#14)
a (Å)	11.5433(5)	11.676(2)	24.7661(10)	10.2723(8)	12.7827(10)
b (Å)	16.1621(8)	5.7835(10)	24.7661(10)	14.4582(12)	18.5716(14)
c (Å)	21.5017(10)	42.903(7)	16.7547(13)	15.9124(13)	13.5031(10)
α (°)	73.733(2)	90	90	72.443(2)	90
β (°)	87.728(2)	95.696(3)	90	80.507(2)	115.214(1)
γ (°)	71.871(2)	90	90	76.123(2)	90
V (Å^3)	3654.7(3)	2882.9(9)	10276.7(10)	2176.5(3)	2900.2(4)
Z	4	4	4	2	4
$\rho_{\text{calcd.}}$ (g cm^{-3})	1.306	1.232	1.308	1.265	1.362
T (K)	299(2)	100(2)	100(2)	100(2)	100(2)
μ (mm^{-1})	2.246	0.077	0.127	0.309	0.433
F(000)	1456	1128	4232	868	1232
θ range	1.38 to 22.50	1.75 to 26.00	1.47 to 26.39	2.05 to 26.00	1.76 to 30.56
Index ranges	$-12 \le h \le 11$	$-14 \le h \le 14$	$-30 \le h \le 29$	$-12 \le h \le 12$	$-18 \le h \le 18$
	$-17 \le k \le 17$	$-7 \le k \le 7$	$-30 \le k \le 30$	$-17 \le k \le 17$	$-26 \le k \le 26$
	$-13 \le l \le 23$	$-52 \le l \le 52$	$-20 \le l \le 11$	$-19 \le l \le 19$	$-19 \le l \le 19$
Reflections measured	18159	23131	31492	18860	32157
Reflections used	9565	5644	5263	8519	8772
R_{int}	0.0886	0.0301	0.0257	0.0226	0.0360
Data/restraints/parameters	9565/0/830	5654/0/479	5263/0/466	8519/0/550	8772/0/492
Final R values ($I > 2\theta(I)$)					
R_1	0.0600	0.0536	0.0413	0.0430	0.0473
wR_2	0.1314	0.1327	0.1039	0.1115	0.1279
R values (all data)					
R_1	0.1443	0.0599	0.0487	0.0489	0.0566
wR_2	0.1520	0.1370	0.1091	0.1166	0.1335
Goodness-of-fit on F^2	0.849	1.092	1.026	1.035	1.051

Preparation of propargyl 2,3,4,5,6-pentaphenylbenzoate (16)

To pentaphenylbenzoic acid **13** (600 mg, 1.19 mmol) and propargyl alcohol (0.27 mL, 4.64 mmol) in dry toluene (50 mL) under nitrogen was added dimethylaminopyridine (40 mg, 0.33 mmol) and dicyclohexylcarbimide (300 mg, 1.45 mmol), and the solution was heated at reflux for 20 h. Upon cooling to room temperature, the solution was acidified using diluted HCl and extracted with ethyl acetate, the organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated to give a white solid. Chromatography on silica using first a gradient of dichloromethane in pentane and subsequently ethyl acetate yielded three fractions. The first fraction was identified as 2-oxopropyl pentaphenylbenzoate **17** (30 mg, 0.054 mmol, 5%), mp 266–267 °C, resulting from the hydrolysis of the desired ester **16**. ^1H NMR (500 MHz, $CDCl_3$) δ: 7.16 (4H, m, H_{22}, H_{26}, H_{62}, H_{66}), 7.13 (4H, m, H_{23}, H_{25}, H_{63}, H_{65}), 7.13 (2H, m, H_{24}, H_{64}), 6.87 (4H, m, H_{33}, H_{35}, H_{53}, H_{55}), 6.84 (2H, m, H_{34}, H_{54}), 6.84 (1H, m, H_{44}) 6.82 (4H, m, H_{32}, H_{36}, H_{52}, H_{56}), 6.77 (2H, m, H_{43}, H_{45}), 6.75 (2H, m, H_{42}, H_{46}), 3.98 (2H, s, H_{12}), 1.70 (1H, s, H_{14}). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 203.2 (C_{13}), 168.4 (C_{11}), 142.9 (C_4), 140.8 (C_3, C_5), 139.8 (C_{41}), 139.3 (C_{31}, C_{51}), 139.0 (C_{21}, C_{61}), 138.3 (C_2, C_6), 133.8 (C_1), 131.3 (C_{32}, C_{36}, C_{52}, C_{56}), 131.1 (C_{42}, C_{46}), 130.2 (C_{22}, C_{26}, C_{62}, C_{66}), 127.6 (C_{23}, C_{25}, C_{63}, C_{65}), 127.0 (C_{24}, C_{64}), 126.9 (C_{33}, C_{35}, C_{53}, C_{55}), 126.8 (C_{34}, C_{54}), 125.8 (C_{43}, C_{45}), 125.7 (C_{44}), 68.9 (C_{12}), 26.3 (C_{14}). IR (solid, KBr): 3555, 3485, 3413, 3055, 3028, 2924, 1734 (CO), 1617, 1441, 1217, 1154, 1072, 698 cm^{-1}. Anal. calcd. for $C_{40}H_{30}O_3 \cdot 0.5(H_2O)$ (%): C 84.63, H 5.50; found: C 84.99, H 5.56. The second fraction to elute was identified as propargyl pentaphenylbenzoate **16** (185 mg, 0.34 mmol, 29%), mp 310–311 °C, 82% based on acid reacted. ^1H NMR (500 MHz, $CDCl_3$) δ: 7.18 (4H, dd, *J* = 8 Hz, *J* = 2 Hz, H_{22}, H_{26}, H_{62}, H_{66}), 7.14 (4H, m, H_{23}, H_{25}, H_{63}, H_{65}), 7.12 (2H, m, H_{24}, H_{64}), 6.91 (4H, m, H_{33}, H_{35}, H_{53}, H_{55}), 6.90 (2H, m, H_{34}, H_{54}), 6.86 (2H, t, *J* = 7 Hz, H_{43}, H_{45}), 6.86 (1H, m, H_{44}), 6.83 (4H, dd, *J* = 7.5 Hz, *J* = 2 Hz, H_{32}, H_{36}, H_{52}, H_{56}), 6.78 (2H, dd, *J* = 7.5 Hz, *J* = 2 Hz, H_{42}, H_{46}), 4.17 (2H, d, *J* = 2.5 Hz, H_{12}), 2.25 (1H, t, *J* = 2.5 Hz, H_{14}). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.2 (C_{11}), 142.8 (C_4), 140.7 (C_3, C_5), 139.9 (C_{41}), 139.4 (C_{31}, C_{51}), 139.1 (C_{21}, C_{61}), 138.3 (C_2, C_6), 134.1 (C_1), 131.4 (C_{32}, C_{36}, C_{52}, C_{56}), 131.2 (C_{42}, C_{46}), 130.2 (C_{22}, C_{26}, C_{62}, C_{66}), 127.5 (C_{23}, C_{25}, C_{63}, C_{65}), 126.9 (C_{24}, C_{64}), 126.9 (C_{33}, C_{35}, C_{53}, C_{55}), 126.8 (C_{34}, C_{54}), 125.8 (C_{43}, C_{45}), 125.7 (C_{44}), 77.1 (C_{13}), 74.7 (C_{14}), 52.1 (C_{12}). IR (solid, KBr): 3498, 3027, 2931, 2854, 2127, 1957, 1733 (CO), 1600, 1494, 1442, 1324, 1216, 1153, 1060, 698 cm^{-1}. Anal. calcd. for $C_{40}H_{28}O_2 \cdot 0.25(Et_2O)$ (%): C 88.05, H 5.51; found: C 88.03, H 5.45. The third fraction was unreacted pentaphenylbenzoic acid (389 mg, 0.774 mmol).

Preparation of (propargyl 2,3,4,5,6-pentaphenylbenzoate) hexacarbonyldicobalt (18)

A solution of propargyl pentaphenylbenzoate **16** (385 mg, 0.712 mmol) and $Co_2(CO)_8$ (360 mg, 1.05 mmol) was stirred in dry THF (15 mL) at room temperature under nitrogen for 20 h and then filtered through celite and washed with THF until the filtrate was clear. Chromatography on silica using a gradient of dichloromethane in pentane as eluent yielded a red solid that was identified as (propargyl pentaphenylbenzoate)hexacarbonyldicobalt **18** (433 mg, 0.53 mmol, 74%), mp 242–243 °C (decomposed). ^1H NMR (500 MHz, $CDCl_3$) δ: 7.19 (4H, dd, *J* = 7.5 Hz, *J* = 1.5 Hz, H_{22}, H_{26}, H_{62}, H_{66}), 7.14 (4H, t, *J* = 7.5 Hz, H_{23}, H_{25}, H_{63}, H_{65}), 7.11 (2H, t, *J* = 7.5 Hz, H_{24}, H_{64}), 6.88 (4H, m, H_{33}, H_{35}, H_{53}, H_{55}), 6.87 (2H, m, H_{34}, H_{54}), 6.85 (2H, m, H_{43}, H_{45}), 6.84 (1H, m, H_{44}), 6.83 (4H, m, H_{32}, H_{36}, H_{52}, H_{56}), 6.80 (2H, m, H_{42}, H_{46}), 5.66 (1H, s, H_{14}), 4.68 (2H, s, H_{12}). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 199.1 (CO's), 169.2 (C_{11}), 142.6 (C_4), 140.6 (C_3, C_5), 139.9 (C_{41}), 139.5 (C_{31}, C_{51}), 139.2 (C_{21}, C_{61}), 138.1 (C_2, C_6), 134.4 (C_1), 131.4 (C_{32}, C_{36}, C_{52}, C_{56}), 131.3 (C_{42}, C_{46}), 130.4 (C_{22}, C_{26}, C_{62}, C_{66}), 127.4 (C_{23}, C_{25}, C_{63}, C_{65}), 127.0 (C_{24}, C_{64}), 126.9 (C_{33}, C_{35}, C_{53}, C_{55}), 126.8 (C_{34}, C_{54}), 125.8 (C_{43}, C_{45}), 125.7 (C_{44}), 87.6 (C_{13}), 73.1 (C_{14}), 66.6 (C_{12}). IR (solid, KBr): 3471, 3405, 3083, 3027, 2096 (Co-CO), 2057 (Co-CO), 2023 (Co-CO), 1733 (CO), 1600, 1442, 1322, 1220, 1153, 1072, 698 cm^{-1}. Anal. calcd. for $C_{46}H_{28}Co_2O_8 \cdot (H_2O)_{0.25}$ (%): C 66.47, H 3.46; found: C, 66.44, H, 3.50.

Preparation of 2-[(η⁶-phenyl)tricarbonylchromium]-3,4,5,6-tetraphenylbenzene (25) and (η⁶-pentaphenylbenzene) tricarbonylchromium (26)

To pentaphenylbenzene (1.5 g, 3.27 mmol) in *n*-butyl ether (20 mL) and dry THF (3 mL) under nitrogen was added $Cr(CO)_6$ (720 mg, 3.27 mmol) and the solution was heated at reflux for 12 h. After allowing the solution to cool to room temperature, the solvent was removed to leave a yellow solid (2.26 g) that was chromatographed on silica using a gradient of diethyl ether in pentane as eluent to yield two fractions, each of which was successfully recrystallized from dichloromethane/hexane, under nitrogen, in the absence of light. 2-[(η⁶-Phenyl)tricarbonylchromium]-3,4,5,6-tetraphenylbenzene (**25**): ^1H NMR (400 MHz, $CDCl_3$) δ: 7.75 (1H, s, H_1), 7.26–6.74 (20H, m, noncomplexed aromatic rings), 5.30 (2H, m, H_{62}, H_{66}), 5.18 ppm (3H, m, H_{63}, H_{64}, H_{65}). IR (solid, KBr): 1970, 1897 cm^{-1}. Anal. calcd. for $C_{39}H_{26}O_3Cr \cdot 3(C_6H_6)$ (%): C 82.59, H 5.35; found: C 82.88, H 5.47. (η⁶-Pentaphenylbenzene)tricarbonylchromium (**26**): ^1H NMR (400 MHz, $CDCl_3$) δ: 7.25–6.75 (25H, m, noncomplexed aromatic rings). IR (solid, KBr): 1970, 1897 cm^{-1}. Anal. calcd. for $C_{39}H_{26}O_3Cr$ (%): C 78.77, H 4.41; found: C 78.98, H 4.62.

X-ray measurements for 2, 3, 6, 8, 9, 11, 13, 14, 25, and 26 (Tables 2 and 3)

Crystal data for **2**, **6**, **13**, **14**, **25**, and **26** were collected on a D8 Bruker diffractometer equipped with a Bruker Smart Apex CCD area detector and graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Data for **3**, **8**, **9**, and **11** were acquired on a P4 Siemens diffractometer equipped with a Siemens SMART 1K CCD area detector and a rotating anode, also utilizing graphite monochromated Mo-Kα radiation. A full sphere of reciprocal space was scanned by phi-omega scans. Data processing was carried out by use of the program SAINT,[61] while the program SADABS[62] was utilized for the scaling of diffraction data and an absorption based on redundant reflections. Structures were solved by using the direct-methods procedure in the Bruker SHELX[63] program library and refined by full-matrix least-squares methods on F^2. Depending on the crystal quality, hydrogen atoms were either located in the Fourier difference map and allowed to refine freely or were added at calculated positions and refined using a riding model. For compound **9**, no significant diffraction was observed beyond 1.05 Å resolution, resulting in an incomplete refinement of the corresponding data; the phenyl rings were modelled as ideal hexagons and all atoms were treated isotropically.[64]

Supplementary material

Supplementary material is available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2013-0257. CCDC 940512 (**2**), 940513 (**26**), 940514 (**25**), 940515 (**6**), 940516 (**14**), and 940517 (**13**) contain crystallographic data for this manuscript. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk.

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(64) Crystal data for **9**: formula $C_{46}H_{40}$, $M = 592.78$; monoclinic, cell parameters: $a = 47.379(16)$ Å, $b = 11.616(4)$ Å, $c = 12.000(4)$ Å; $\alpha = 90°$, $\beta = 90.436(7)$, $\gamma = 90°$, $V = 6604(4)$ Å³, $Z = 8$, space group $C2$ (No. 5).