ELSEVIER

Coordination Chemistry Reviews 233–234 (2002) 75–105

COORDINATION
CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Sterically hindered organometallics: multi-*n*-rotor ($n = 5$, 6 and 7) molecular propellers and the search for correlated rotations

Stacey Brydges, Laura E. Harrington, Michael J. McGlinchey *

Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton, ON, Canada L8S 4M1

Received 19 November 2001; accepted 8 March 2002

Contents

Abstract

For the past several years, we have focused our attention on the design, syntheses and analyses of the dynamic behaviour of sterically encumbered complexes of the type $(C_nR_n)ML_x$, where R = alkyl or aryl, $n = 5$, 6 or 7, and ML_x is an organometallic fragment. As archetypes of propellers or gear-wheels, the challenge is to construct molecules in which the internal rotations are restricted, and possibly even correlated. The incorporation of appropriate probes allows the independent measurement, by variable-temperature NMR spectroscopy, of the associated rotational barriers in these chiral arrays. In recent studies, we have successfully devised five-, six- and seven-membered ring systems that include naphthyl and other bulky organic substituents, and have further shown that an organometallic addendum can be used to monitor the stereodynamics of such conformationally flexible architectures.

Keywords: Molecular propeller; Molecular gear; Transition metal; Dynamics; Fluxionality; Restricted rotation

1. Introduction

The detection and control of rotational motion about molecular bonds are themes that have permeated the chemical literature for decades. Fundamental issues,

---

* Corresponding author. Tel.: +1-905-525-9140x27318; fax: +1-905-522-2509
E-mail address: mcglinc@mcmaster.ca (M.J. McGlinchey).

0010-8545/02/$ - see front matter
PII: S0010-8545(02)00098-X

such as circumrotation around the carbon–carbon bond in ethane [1,2] or the metal–ligand coordination axis [3–6], have been advanced and even supplanted gradually by more subtle aspects of conformational isomerism and dynamic stereochemistry [7]. Aided by recent paradigm shifts, the conceptual linkages between macromechanical principles of motion and molecular-scale systems have provided fertile grounds for such innovations as molecular gears [8–10], switches [11,12], shuttles [13,14], brakes [15], turnstiles [16], and a mill [17].

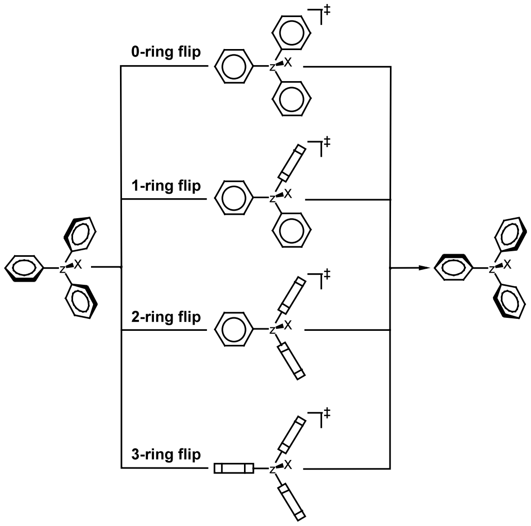
At both the macroscopic and microscopic levels, the arrest and promotion of movement are intricately tied to structure and constitution. With their attendant opportunities for coupled molecular motions [7], their suggested roles as micro-machines [18,19], and their consequent relevance to nanotechnology [20,21], *sterically crowded molecules* [22] offer a nexus between the two scales of size and dynamic function. Germane to the aforementioned topic are *molecular propellers*, a broad class of compounds comprised of two or more substituents arranged in a helical (chiral) conformation about a central core [23,24]. Such a molecular model combines topological features with internal mobility, introducing the possibility of restricted, or even correlated, rotation and complex stereoisomerization phenomena. This concept is intricately tied to the time-scale of observation, and is rendered more likely when the internal rotors (such as aryl groups) of the propeller framework are tightly intermeshed.

Whereas propellers of two- or threefold symmetry (C_2, D_2 or C_3, D_3, respectively) have been studied in considerable detail, including: diaryl-sulfoxides, -sulfones, -ethanols and -ethers [25,26]; di- and triarylboranes [27,28]; triarylcarbenium ions [29–31]; trialkoxymethanes [32]; triarylamines [33]; triarylphosphines and derivatives [34,35]; polyarylethanes and ethylenes [36,37]; and multiple propeller units [38–41], the attention dedicated to higher order systems has been less systematic and comprehensive. From a computational, design, synthetic, structural and stereodynamic perspective, molecular paddle-wheels of the type $C_nR_n^{\pm}$ (where $n = 5$–7, R = alkyl, aryl) and their organometallic derivatives are chemically rich targets of inquiry. Indeed, insight into the static and dynamic stereochemical complexities of such species may eventually corroborate the topological parameters necessary to effect hindered, and possibly even intercoupled, rotations on the laboratory time-scale, and therefore found a more direct morphological relationship to macroscopic devices. Keeping cognisance of this goal, an overview of recent developments in the area of sterically demanding persubstituted cyclopentadienyl (Cp), arene and cycloheptatrienyl C_nR_n organotransition metal architectures is presented herein, albeit not necessarily in chronological order.

2. Molecular propellers to molecular bevel gears

2.1. Static and dynamic stereochemistry

Conducted by Gust and Mislow [42,43] in the early 1970s, the extensive analyses of interconversion processes in di- and triaryl propeller structures presenting restricted conformational equilibria were pivotal to the development of modern stereochemical concepts. In the ground state, the number and symmetry of isomers can be enumerated mathematically and depend on the degenerate features of each molecule. A consideration of viable rearrangement alternatives identified the flip mechanisms, proposed by Kurland et al. [44], in which helicity reversal may be effected by ring rotation through the reference plane, with concomitant edge interchange, or through a direction perpendicular to the propeller plane (denoted as a ring flip). Among the four classes of ring flips, the *two-ring flip*, whereby only one ring passes through the reference plane, has been firmly established as the isomerization pathway of lowest energy in systems of the type Ar_3Z and Ar_3ZX (Scheme 1) [45], although the cog-wheel effect has also manifested itself in other n-ring flip routes. From this realization was borne the unifying theory of *stereochemical correspondence* [23], which identifies relationships among various groups of constitutionally dissimilar propeller molecules. For example, triarylboranes (Ar_3B) and the transition metal tris-chelates are intrinsically associated by the number and kind of both stereoisomers and respective n-ring flip or Rây-Dutt and trigonal twist (Bailar) rearrangements. Another important and general phenomenon, *residual stereoisomerism*, was first adduced for maximally labelled Ar_3Z and Ar_3ZX moieties [43,46]. On a particular time-scale, the observation of closed subsets of interconverting isomers,

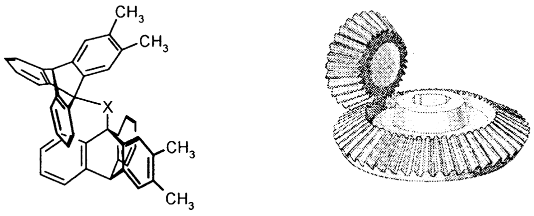


Scheme 1. Viable *ring-flip* isomerization pathways available to Ar_3Z and Ar_3ZX molecular propellers.

separated by substantial barriers, emerges as a fascinating consequence of *correlated ring rotation.* Whereas there are no restrictions on the individual torsional angles, the interdependent motion of all three rings imposes a constraint on the relationship between torsional angles, thus blocking a number of interconversion pathways among the full set of conformers.

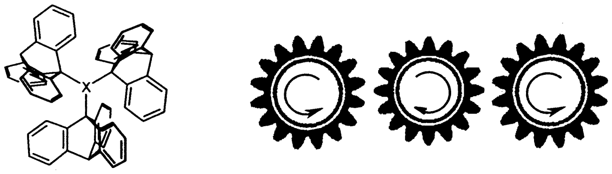
These static and dynamic stereochemical features were also considered for propeller systems in which the contiguous groups are attached to a planar central framework, as opposed to a central atom. In striking contrast, the evidence furnished by Gust and co-workers [47,48] indicated that inter-annular rotation in appropriately substituted penta- and hexaarylbenzenes and analogous molecules is *uncorrelated*, as will be expounded upon in the ensuing sections.

Meanwhile, the research groups of Mislow and Iwamura [49] contemporaneously recognized the astonishing resemblance between correlated disrotation in three-bladed molecular propellers and the coupled motions of meshed gears. Already pervading the chemical literature were examples of the *static gear effect*, the interlocking of alkyl groups or n-fold rotors in the ground state 'by virtue of cooperative non-bonded repulsions' induced under conditions of intramolecular crowding [50]. In extending the analogy to *dynamic gearing* [51], the intermeshing of a chemical rotor with a neighbouring group is manifested in the mechanical selection rules (disrotatory allowed, conrotatory disallowed) and the observation of residual stereoisomerism in a differentially labelled molecule. Although the stereochemical similarities between bevel gears and molecular propellers are apparent, Mislow cautioned that the cogwheel metaphor is flawed for the latter structures since the two-fold nature of the aryl rings precludes the obligatory tongue-and-groove interaction [18]. Ideal candidates for highly mobile (with cogwheeling rates on the order of 10^9 s^{-1}) and tightly meshed bevel gears proved to be Tp$_2$X (X = CH$_2$, etc.) systems **1** comprised of 9-triptycyl (Tp) moieties, previously shown by Oki [7] to possess exceptionally large threefold torsional barriers (Scheme 2). A unique marriage of the propeller and gear models was unveiled in the triskelion species, Tp$_3$XZ (X = Ge, Z = Cl **2**; X = C$^+$, Z = ClO$_4^-$ **3**), for which structural rigidity was induced by the odd number of securely interlocked rotors [8]. The transmission of cooperative torsional motions along macromolecular chains of suitably meshed N-chemical gears is governed by the parity rule for gear trains, which dictates correlated disrotation of the terminal gears if N is even and conrotatory interactions if N is odd [18,38]. Thus, in arranging an odd number of gears in a cyclic array, dynamic gearing is disallowed and immobilization of the rotors can be expected. The strict specificity of cogwheeling under steric control is illustrated in these molecular gear systems, particularly the 'frustrated' cogwheel-propellers, **2** and **3** (Scheme 3) [8].



1

Scheme 2. A labeled Tp$_2$X (Tp = 9-triptycyl; X = CH$_2$, O, CO, etc.) molecule **1** and its analogic resemblance to macroscopic bevel gears.



2: X = GeCl
3: X = C$^+$, Z = ClO$_4^-$

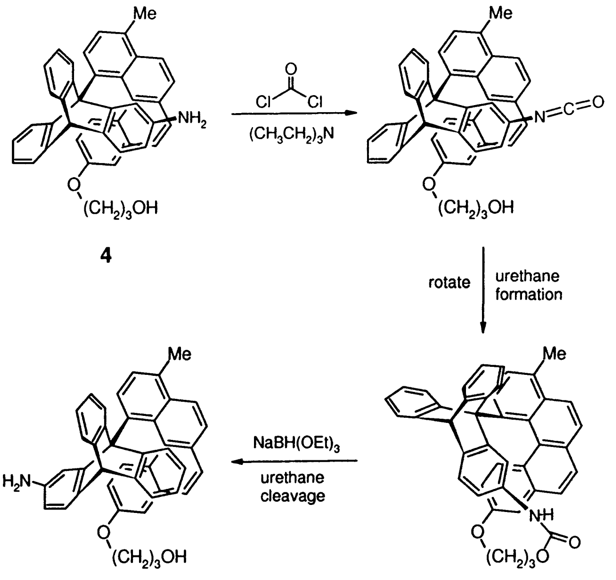
Scheme 3. Immobilization of the rotors in the tris-(9-triptycyl) propeller-gear Tp$_3$XZ (**2**, **3**) is a consequence of the parity restriction on dynamic gearing.

2.2. Macromechanical models

Since broached by Richard Feynman in his 1959 historic address, "*There is Plenty of Room at the Bottom*" [52], the notion of applying mechanical principles at the molecular level has enticed practitioners from numerous realms of chemistry to tackle the problem of constructing an artificial 'molecular machine'. By definition, a machine is a device "consisting of two or more resistant, relatively constrained parts, which, by a certain predetermined intermotion, may serve to transmit or modify force and motion so as to produce some given effect or to do some desired kind of work" [53]. In analogous molecular systems, large-amplitude movements induced by external (photochemical, chemical, electrochemical or other) stimuli lead to real translocation of selective parts of the compound, effecting *reversible* transformations that are (hopefully) detectable by some intrinsic property (electronic absorption, luminescence, NMR signals, electrochemical potentials, et cetera) [54]. "This metamorphosis of molecule to model requires a process of abstraction and selective emphasis" of non-trivial mechanical parameters, and therefore entails, according to Mislow, "a deliberate falsification of the object that the model supposedly represents" [18]. As highlighted by the earlier examples, it is important to distinguish between static or *iconic* models, and those which possess the additional feature of internal mobility (such as molecular propellers), termed *analogic* [18].

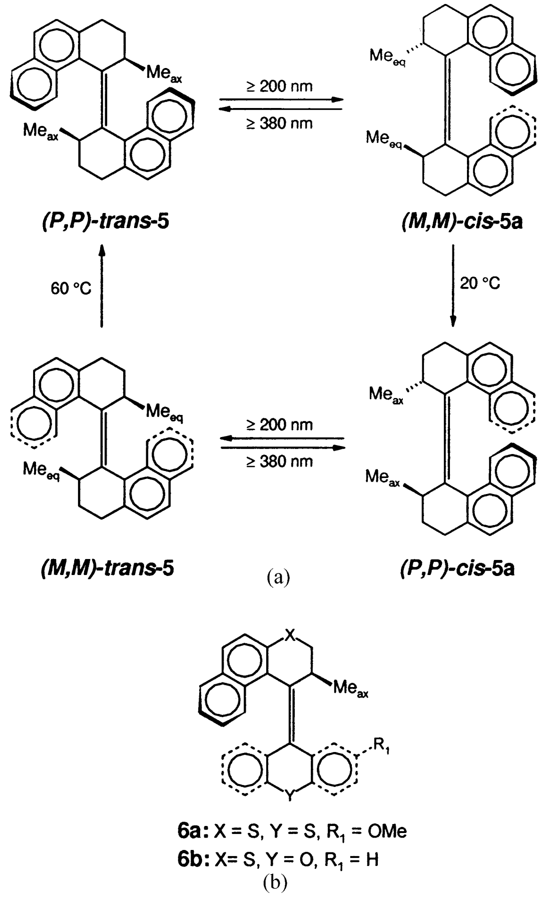
Although the design and construction of molecular devices has been routinely regarded as a curiosity-driven quest [55], several recent reports of prototypical structural units demonstrate that it is possible to devise analogic models of machines [56,57]. The motivation for such studies is derived in part from the desire: (a) to mimic, and therefore further comprehend, essential biological processes involving motion [58], such as the rotary motor adenosine triphosphatase [59–61] or the myosin-actin linear motor present in muscles [62]; and (b) to fabricate artificial systems which may perform tasks as varied as catalysis, nanoscale manipulation, information storage, processing and replication. To date, most efforts have focused on controlled submolecular motion that involves either biomolecular recognition [63] or translocation between two or more active sites [64–66]. However, two striking examples of propeller-type models have honed strategies and provided further confirmation that macromechanical features, including those that enable continuous, unidirectional motion, may be incorporated into molecular-scale assemblies.

In a modification to an earlier ratchet proposal [67,68] which would have violated the second law of thermodynamics [69], Kelly et al. [70,71] have devised a system **4** that relies on chemical energy to activate and bias a thermally induced isomerization reaction, and thereby achieve unidirectional rotation. Comprised of a three-bladed triptycene ('wheel') moiety connected via a single bond ('axle') to a curved, asymmetric [4]helicene ('brake'), controlled rotary motion by π/3 radians is effected by the introduction of an urethane tether. It is the reaction of a phosgene-activated isocyanate on triptycene and a hydroxypropyl substituent on the helicene which energetically favours this clockwise rotation ($\Delta G^{\ddagger} = 25$ kcal mol^{-1}) prior to urethane cleavage and regeneration of a low-energy rotamer (Scheme 4). By shortening the hydroxyalkyl group attached to the helicene, the urethane-linked molecule is trapped in an even higher energy conformational state, thereby accelerating the rate of rotation (cf. $t_{1/2}$ of 5 min vs. 3 h for the 2- and 3-carbon tethers, respectively) [72].



Scheme 4. Unidirectional rotary motion is chemically promoted in the chiral triptycenyl-helicene unit **4**.

In the elegant propeller system advanced by Feringa and co-workers [73], monodirectional rotation is photochemically promoted. The 2π radian revolution of a helical olefin **5** is achieved for three full cycles, each comprising four discrete steps of consecutive cis–trans photoisomerizations and irreversible, thermally induced helicity inversions (Scheme 5a). It is the molecular architecture of **5**, which features the unique combination of axial chirality about the adjoining carbon–carbon double bond and two stereogenic centres in the identical phenanthryl-derived halves, that facilitates the concerted rotary behaviour. Second generation rotor models **6**, comprising two distinct upper and lower parts, namely (2*R*)-methyl-2,3-dihydronaphthothiopyran and



Scheme 5. (a) Unidirectional rotary motion is realized in a photochemically activated and thermally driven helical alkene **5**; and (b) its second generation analogue, **6**.

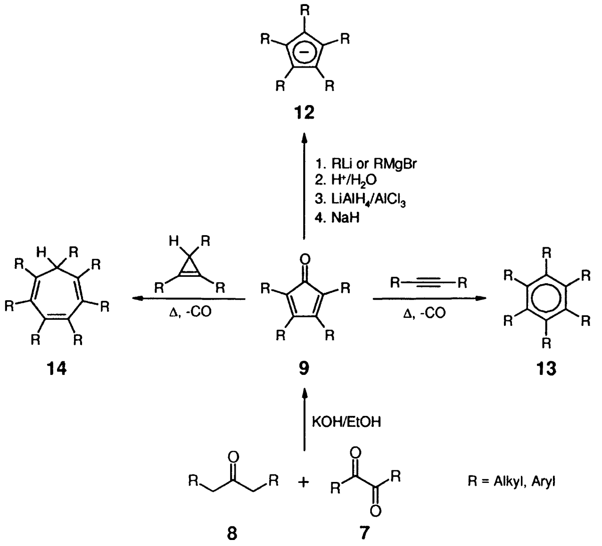
heteroatom-bridged xanthene, respectively, have provided additional structural details (Scheme 5b). Not only is a single stereogenic centre a sufficient condition for unidirectional motion, but the thermal isomerization barriers, which govern the rotation rate, may be tuned by appropriate steric modifications [74,75].

Despite their disparate structural compositions, the molecular motors of Kelly (**4**) and Ferringa (**5** and **6**) are conceptually related, both employing chirality as the fundamental basis for unidirectional motion [76]. Having restricted the internal degrees of freedom of each system, the influx of external energy activates the submolecular components to move with respect to each other in a predetermined manner. In advancing our goal of constructing an organometallic bevel gear, such critical aspects of design must be carefully considered in conjunction with past theoretical and experimental contributions (vide supra) and current exploratory research.

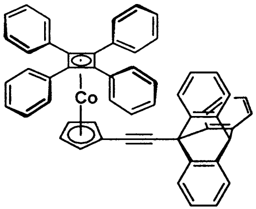
2.3. An organometallic approach

Molecules of the type C_nR_n ($n = 3$–7) endowed with a propeller form (R = aryl) or gear-meshed ground states (R = alkyl) present torsional circuits which may be greatly influenced by the non-bonded 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, to 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. Motivated by this simple geometric argument, we have logically restricted our focus to $C_5R_5^-$, C_6R_6, and $C_7R_7^+$ systems, for which the peripheral rotors are increasingly placed in a more crowded locale.

Since both the structure and its internal motions must be controlled with regard to symmetry, sterics and strain, there are numerous design complexities associated with the detailed conformational studies of such extended, aromatic arrays. The observation of stereoisomerism crucially depends on the appropriate desymmetrization, or substitution on, the basic molecular framework. Furthermore, the complementary steric interplay between the n-fold rotors and hence, the detection of interconversion processes (with barriers typically in the range of 5–25 kcal mol^{-1}) by use of variable-temperature NMR spectroscopy, is promoted by the judicious selection of organic fragments and their ligating metal moieties. Taking these factors into account, our preparative schemes concentrically feature tetrasubstituted cyclopentadienones, versatile synthons which offer avenues to the five-, six- and seven-membered ring systems, and which themselves serve as candidates for fluxional studies. As featured in Scheme 6, the condensation of a substituted diketone **7** with an appropriately 1,3-derivatized propanone (**8**) affords the desired cyclopentadienone **9**, which resists Diels–Alder dimerization because of its bulky periphery. Access to cyclopentadienes **11** (and the corresponding cyclopentadienide salts **12**) is gained via aryl- or alkyl-Grignard treatment of **9**, and subsequent reduction of the intermediate cyclopentadienols **10**. Conversely, the [4+2] cycloaddition of **9** with alkynes or cyclopropenes, followed by decarbonylation of the respective bicyclic and tricyclic systems, gives the persubstituted arenes **13** or cycloheptatrienes **14**. Organometallic transformations of **12**–**14** (Scheme 6) lead to architectures with the potential for engaged gearing interactions of the C_nR_n and ML_n components. To the best of our knowledge, the [(9-triptycylethynyl)cyclopentadienyl](tetraphenylcyclobutadiene)cobalt (**15**) reported by Richards et al. [77,78] is the only example of a C_nR_n (R = Ph, $n = 4$) ligand deliberately incorporated into a molecular gear formulation (Scheme 7). Whereas there was no spectral indication of coupled torsional motions of any of the metallocene fragments (Tp, C_4–ML_n, C_4–Ar) in **15** on the NMR time-scale (260–203 K), earlier evidence of impeded C_4–Ar rotation effected by either steric hin-



Scheme 6. A general synthetic template for C_nR_n systems, where $n = 5$, 6 and 7.



15

Scheme 7. An organometallic gearing array (**15**) comprised of a 4-toothed metallocene and a 3-toothed 9-triptycenyl moiety.

drance of the groups neighbouring a pivot bond or a ‘chiral pin’ on the C_5 ring has been cited by the research groups of Rausch et al. [79,80] and Takahashi [81], respectively. In the following sections we feature our contributions to the area of sterically encumbered, conformationally flexible organic and organometallic molecules of these types.

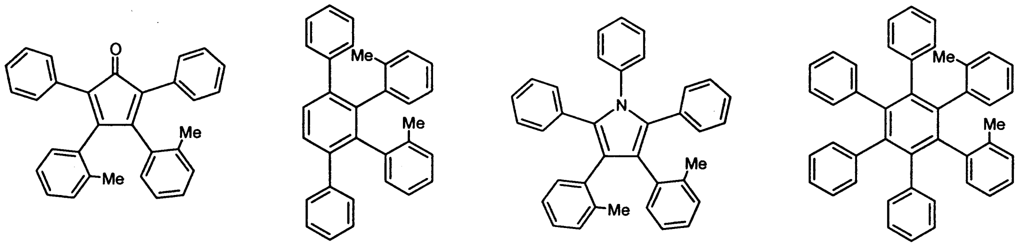
3. Persubstituted cyclopentadienyls: C_nR_n, where $n = 5$

Somewhat in contrast to the higher C_nR_n propeller analogues, polysubstituted Cp systems have been the subject of intense scrutiny. The development of Cp chemistry was first marked by the serendipitous discovery of ferrocene in 1951 [82,83], and has been subsequently expedited by its modification. Notwithstanding the much more common and frequently studied C_5H_5 and its permethylated derivative, C_5Me_5 [84], sterically demanding Cps such as the pentaphenylcyclopentadienyl ligand (C_5Ph_5 (**16**)) have been found to confer novel properties on transition metal centres, including: (i) a high kinetic stability imparted through its large volume [85,86]; (ii) a wider variety of accessible oxidation states, presumably reflecting the ability of the aryl substituents to buffer electronic changes at the metal centre [87]; and (iii) a rich and diverse chemistry, including potential applications in enantioselective synthesis [88,89] and catalysis [90,91].

3.1. Tetraarylcyclopentadienone and pentaarylcyclopentadienyl derivatives

In 1971, Hayward-Farmer and Battiste [92] provided the first evidence that central ring size influences restricted inter-annular rotation in biphenyl-like molecules. The free energies of activation for stereoisomerization of 3,4-bis(*o*-tolyl)-2,5-diphenylcyclopentadienone (**17**) and 1,2-bis(*o*-tolyl)-3,6-diphenylbenzene (**18**) by rotation of the *o*-tolyl rings were determined to be 21.8 and >25.6 kcal mol^{-1}, respectively. As quantitative models, however, these polyaryl systems presented certain shortcomings, including incommensurate substituents and Hückel $4n$ vs. $4n+2$ electron counts. To expand upon these concepts, Fagan and Gust [93] examined the analogous 6-π electron pentaarylpyrroles, which eliminate complications caused by the presence of an unpaired electron ($C_5Ph_5^{\bullet}$) or a negative charge ($C_5Ph_5^-$) and associated cation. Utilizing the stereochemical framework proposed for hexaarylbenzenes (Section 4.2) [47,48], the barriers to diastereomerization of 3,4-bis(*o*-tolyl)-2,5-diphenylpyrrole (**19**) and 1,2-bis(*o*-tolyl)tetraphenylbenzene (**20**) were found to be 19.9 and 38 kcal mol^{-1} by VT-NMR line shape analyses and classical kinetic methods, respectively. The $\Delta G^{\ddagger}$ difference of ca. 18 kcal mol^{-1} was ascribed to decreased steric interactions in the C_s-symmetric transition state of **19** relative to **20**, which are in turn a consequence of the larger angle subtended by adjacent rings. Conversely, the 2.1 kcal mol^{-1} difference in rotational barriers for **17** and **19** was argued not only on the premise of disparate steric influences of the carbonyl and phenyl groups, but variations in bond lengths, bond angles, and central ring deformability of the five-membered ring systems (Scheme 8).

Notwithstanding energy barrier magnitudes, the aforementioned studies failed to address any stereochemical variations between the constitutionally distinct C_5Ar_4O and C_5Ar_5 ligands. Whereas a small phenyl group oscillation about the planes orthogonal to the C_5 ring of the neutral pentaphenylcyclopentadienyl radical was deduced from EPR spectroscopy in 1964 [94], the conformational features of tetraarylcyclopentadienones remained relatively ambiguous until 1981. By analogy with C_6Ar_6 propellers, Willem et al. [95] proposed a static, C_{2v} symmetric tetraphenylcyclopentadienone (tetracyclone) skeleton in which the four aryl groups are orthogonal to the central C_5-ring, at least on the NMR time-scale. A variable-temperature NMR analysis of the maximally labelled tetra-*o*-tolylcyclopentadienone (**21**), which exists as a mixture of 10 rotamers, revealed two coalescence regions, below and above room temperature. From a consideration of all possible rearrangement modes, the spectral data were attributed to two dynamic processes: an uncorrelated alpha-one-ring rotation in the direction of the carbonyl moiety, corresponding to



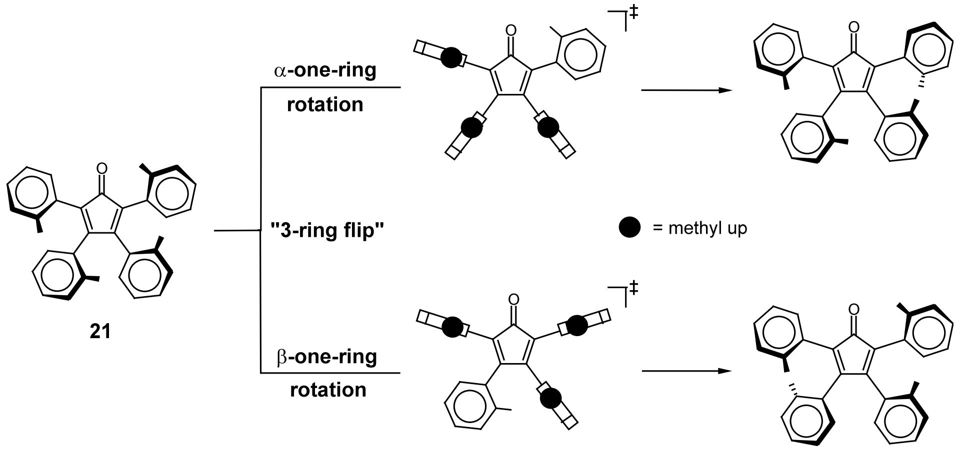
17 **18** **19** **20**

Scheme 8. Original (**17**, **18**) and ensuing (**19**, **20**) model systems for evaluating the effect of ring size on the magnitude of the energy barrier to rotation of the peripheral rings in C_5 and C_6 systems.

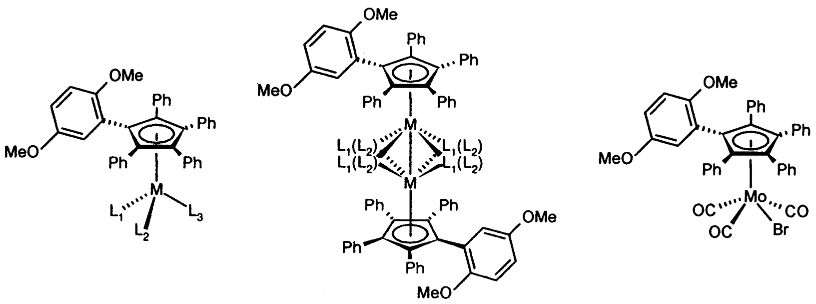
the threshold isomerization pathway, and a more sterically demanding, uncorrelated beta-one-ring rotation ($\Delta G^{\ddagger} \approx 20$ kcal mol^{-1}) (Scheme 9) [96]. As previously established by Gust and co-workers [97] for C_6Ar_5X systems, rings adjacent to an 'X' substituent can be expected to rotate much more rapidly than the other rings if 'X' is less bulky than an aryl group. In placing these results in the context of earlier studies, Willem et al. [95] proposed, perhaps prematurely, that uncorrelated, one-ring rotations are a general mechanistic phenomena for molecules containing peripheral aryl substitutents attached to a central ring.

Comparative studies of rotational dynamics in metal-ligated systems comprising tetrahapto $Ar_4C_4C{=}O$ and pentahapto Ar_4C_5OH, Ar_4C_5H and C_5Ar_5 ligands can be found scattered among the plethora of reports pertaining to the preparation, physical properties and reactivity of polyarylated Cp-based complexes, spanning both early and late transition metals. In the uncomplexed ligand C_5Ph_5 (**16**), free rotation of the peripheral aryl substituents imparts effective D_{5h} symmetry; in contrast, hindered libration imposes cyclic directionality on the ring and the effective symmetry of the enantiomeric system is reduced to D_5. This propeller conformation is also manifested in the solid state (cf. C_5Ph_5 radical with torsional angles of ca. 50°) [98], and represents a compromise between stabilizing orbital overlap and destabilizing steric interactions. Furthermore, the preferential labelling of one face of the Cp ring with an organometallic fragment (ML_n) lowers the maximum symmetry to C_{5v} and in principle, allows for the detection of restricted phenyl rotation since the edges of each arene ring are differentiable by their proximal and distal positioning relative to the metal. The addition of a second stereogenic element, via a chiral metal auxiliary, renders inequivalent the Cp ring carbons in the event of steric inhibition of the tripodal rotation about the fivefold axis. The resulting molecular asymmetry may manifest itself in both the solution and the solid state; if $C_5{-}ML_n$ and phenyl rotation are incidentally slowed on the NMR time-scale, the degeneracy of all 30 phenyl ring carbons in *each* diastereomer is removed. Commensurate activation barriers for the two fluxional processes–rotation about both the Cp plane-metal vector and the Cp-substituent bond–would substantiate the cooperative, gearing interaction of the π-ligated ML_n moiety with the C_5Ph_5 pentacycle. As highlighted earlier, the detection of correlated behaviour in the chiral aryl array alone would require the incorporation of appropriate NMR probes on adjacent phenyl substituents. In the absence of arene edge labels, it is more challenging to measure the barrier to peripheral ring rotation since, even on a high field spectrometer, there is considerable overlap of ^1H and ^{13}C resonances, rendering spectral simulation a non-trivial task. Of course, the substitution of a peripheral phenyl ring to give Ar_4C_5OH, Ar_4C_5H and $Ar_4C_5R^*$ (R^* = menthyl, neomenthyl [89], for example) has static and dynamic stereochemical consequences which must be considered in distinction to the preceding logic.

As solid state evidence for the stereochemical non-rigidity of the C_5Ar_5 moiety, Colbran et al. [99] cite the occurrence of both the proximal and distal orientations of the 2,5-dimethoxyphenyl substituent (R) in X-ray crystallographic structures of $[M(C_5Ph_4R)L_1L_2L_3]$ complexes (M = Mo, L_1,L_2 = O, L_3 = OMe **22**; M = Ru, L_1,L_2 = CO, L_3 = Br **23** [99]) and respective dimers, $\{[M(C_5Ph_4R)L_1L_2]_2\}$ (M = Mo, L_1 = μ-CO, L_2 = μ-Br **24**; M = Mo, $L_1 = L_2$ = Br **25**) [100] (Scheme 10). Additionally, the splitting of the solution C–O stretching absorptions in the solid state IR spectra of several chiral complexes, including $[Fe(\eta^5\text{-}C_5Ph_5)(CO)(PMe_3)Br]$ (**26**) [101] and $[Os(\eta^5\text{-}C_5Ph_5)(CO)(L)Br]$, where L = PMe_2Ph (**27**), $P(OEt)_3$ (**28**) and $P(OCH_2)_3CCH_3$ (**29**) [102], has been rationalized on the basis of diastereoisomerism arising from the propeller helicity.



Scheme 9. The two rearrangement modes adduced for tetraarylcyclopentadienones involve a combination of alpha-ring (low energy) and beta-ring (higher energy) rotations.



22: M = Mo; $L_1 = L_2$ = O; L_3 = OR
(R = Me, Et, ^{i}Pr, ^{t}Bu)
23: M = Ru; $L_1 = L_2$ = CO; L_3 = Br
38: M = Mo; $L_1 = L_2$ = O; L_3 = Br

24: L_1 = CO; L_2 = Br
25: $L_1 = L_2$ = Br

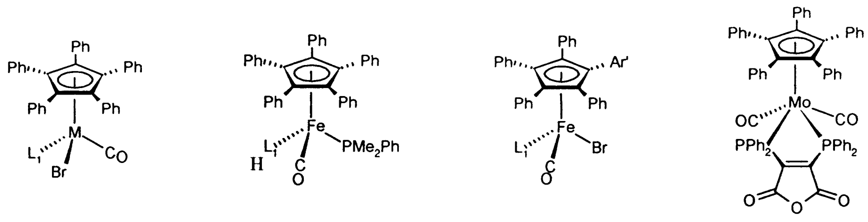
39

Scheme 10. Pentaarylcyclopentadienylmetal systems containing the 2,5-dimethoxyphenyl substituent.

In agreement with the presence of two diastereomers in the solid, and hindered rotation of both the tripod and the phenyl groups, the solid state ^{13}C-NMR spectrum of **26** displayed a 1:1:2:1:1:1:1:2 peak pattern corresponding to 10 distinct Cp ring carbon atoms [101]. Finally, the reduced molecular motion resulting from restricted libration of the phenyl groups has been suggested as an explanation for the extreme insolubility of decaphenylmetallocenes, $(C_5Ph_5)_2M$ (M = Fe **30** [103], Ni **31** [104], W^+ **32** [105], Ge **33**, Sn **34**, Pb **35** [106]).

Accounts of the dynamic behaviour of pentaarylcyclopentadienyl metal complexes in solution reveal that, in general, the aryl substituents rotate freely about their bonds to the central C_5-plane at ambient temperature. One exception provided by Adams et al. [88] is $Ru(C_5Ph_5)(CO)(PPh_3)Br$ (**36**), which exists as a mixture of diastereomers on the NMR time-scale, as evidenced by two $^{31}P\{^1H\}$-NMR signals. Unfortunately, the instability of **36** in solution at elevated temperatures, in the absence of an excess of triphenylphosphine, precluded attempts to acquire activation parameters by use of VT-NMR spectroscopy. In replacing the triphenylphosphine ligand with the less bulky $P(OMe)_3$ or $P(OPh)_3$, the intramolecular steric interactions, and hence rotational barriers, associated with the polyaryl array were significantly reduced. Similarly, the room temperature ^{1}H-NMR spectrum of $Fe(\eta^5\text{-}(o\text{-tolyl})C_5Ph_4)(CO)_2Br$ (**37**) exhibited two resonances for the methyl groups in the ratio of 7:4, consistent with the presence of proximal and distal rotamers [107]. While no VT-NMR data were provided by Field, Masters and colleagues, this example established that substituents of at least the size of a methyl moiety can be accommodated at the aryl ortho position of these half sandwich compounds (Scheme 11).

The rotational barrier for the 2,5-dimethoxyphenyl substituent (R) in $[Mo(C_5Ph_4R)O_2(Br)]$ (**38**), was calculated to be 16.4 ± 0.2 kcal mol^{-1} [87]. In progressing from the static (300 K) to dynamic (370 K) limit, the four ^{1}H-NMR signals attributable to the methoxy group gradually coalesced to two resonances, while concomitant changes were also observed in the phenyl spectral region. Whereas the underlying exchange phenomenon could be attributed to either hindered rotation of the labelled aryl ring or of the metal tripod, Colbran and coworkers [87] argued the former fluxional mechanism on the premise that $\Delta G^{\ddagger}$ values in related C_5Ph_5 and C_5Ph_4H systems are much lower for the latter process. Interestingly, this interconversion of proximal and distal rotamers is mentioned but not quantified in earlier reports of $[Ru(C_5Ph_4R)(CO)_2(Br)]$ (**23**) [99], $[Mo(C_5Ph_4R)(CO)_3(Br)]$ (**39**) [100], and analogues. In



26: M = Fe; L_1 = PMe_3
27: M = Os; L_1 = PMe_2Ph
28: M = Os; L_1 = $P(OEt)_3$
29: M = Os; L_1 = $P(OCH_2)_3CCH_3$
36: M = Ru; L_1 = PPh_3

45: L_1 = COEt
46: L_2 = COMe

37: Ar' = o-tolyl; L_1 =CO
47: Ar' = m-xylyl; L_1 =PMe_3

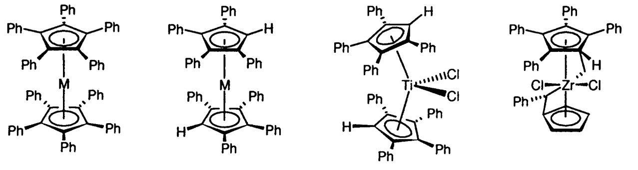
44

Scheme 11. A selection of pentaarylcyclopentadienyl half-sandwich complexes.

the dimers $[Mo(C_5Ph_4R)(\mu\text{-}CO)(\mu\text{-}Br)]_2$ (**24**) and $[Mo(C_5Ph_4R)(\mu\text{-}Br)_2]_2$ (**25**) [100], the dimethoxyphenyl groups remained static but the phenyl substituents exhibited restricted rotation over the 500 MHz ^{1}H-NMR experimental temperature range. Once again, however, $\Delta G^\ddagger$ estimates for these systems were not provided by the researchers [100].

There was no evidence (293–178 K) for hindered rotation about the two $Cp\text{–}ML_n$ bonds in the linear and bent bis(tetraphenylcyclopentadienyl) complexes $Fe(C_5Ph_4H)_2$ (**40**) [108] and $[Ti(C_5Ph_4H)_2Cl_2]$ (**41**) [109], respectively. Analysis of the temperature dependence of the 500 MHz ^{1}H-NMR spectra of **40** yielded a barrier of 9 ± 1 kcal mol^{-1} for (beta) phenyl ring rotation, with alpha and beta substituents adopting coplanar and perpendicular conformations, respectively, relative to the central C_5 ring. A concomitant high frequency shift of the Cp proton was attributed to the deshielding from ring currents of the adjacent coplanar aryl rings [108]. Within experimental error of the free energy of activation determined for **40**, the dynamic ^{1}H-NMR studies of **41** gave a commensurate value ($\Delta G^\ddagger = 9.8 \pm 0.2$ kcal mol^{-1}) for the restricted libration of the phenyl rings [109]. Whereas the low temperature limiting spectrum of $Ru(C_5Ph_4H)_2$ (**42**) could not be accessed before the solvent freezing point, allowing only for a $\Delta G^\ddagger$ extrapolation of ca. 9 kcal mol^{-1} [110], the paramagnetic nature of the other octaphenylmetallocenes with M = V, Cr, Co and Ni did not lend themselves to NMR studies. In the ^{1}H VT-NMR spectra (293–183 K) of the related ansa-metallocene complex, rac-$[1\text{-}(\eta^5\text{-}Cp)\text{-}1\text{-}Ph\text{-}(\eta^5\text{-}C_5Ph_4)Et]ZrCl_2$ (**43**), the slowed rotation of the beta phenyl substituents (273 K) was detected in advance of the sterically less hindered alpha phenyl groups (253 K) [111] (Scheme 12).

In 1989, Tyler et al. [112] approximated the barrier to $Cp\text{–}ML_n$ rotation as 9.1 kcal mol^{-1} from the dynamic ESR spectrum of $Mo(\eta^5\text{-}C_5Ph_5)(CO)_2L_2$, where L_2 = (2,3-bis(diphenylphosphino)maleic anhydride) (**44**). The large, negative activation entropy ($\Delta S^\ddagger = -22.9 \pm 0.3$ cal K^{-1} mol^{-1}) was noted as additional justification of free Cp rotation, since this process necessitates cooperative 'gearing' of the phenyl substituents on the Cp periphery and phosphorus ligand and a corresponding transition state structure which is highly organized. The second observation of steric inhibition of the tripodal rotation in a persubstituted Cp half-sandwich complex was reported by Brégaint et al. [101] in 1992. The ^{13}C VT-NMR data for $[(\eta^5\text{-}C_5Ph_5)Fe(CO)(PMe_2Ph)(C(O)Et)]$ (**45**), from 293 to 163 K (the lowest accessible temperature owing to poor solubility), revealed a decoalescence phenomenon whereby the single resonance of the C_5 ring split into four distinct signals in the ratio of 1:2:1:1. To date, the only solution state NMR-derived free activation energy of $C_5Ar_5\text{–}ML_n$ rotation has been adduced by Li et al. of our laboratory, in collaboration with our colleagues in France [113]. Evaluation of the temperature-dependent ^{13}C-NMR spectral changes (293–173 K) associated with the Cp ring nuclei of $[(C_5Ph_5)Fe(CO)(PMe_2Ph)(C(O)Me)]$ (**46**) yielded an E_a value of 8.7 ± 0.3 kcal mol^{-1}. A second, non-coupled fluxional process ($E_a = 11.7 \pm 0.3$ kcal mol^{-1}) was measured from the splitting of the diastereotopic phosphorus-coupled methyl resonances (from two ^{13}C signals at room temperature to four at 173 K), and ascribed to either slowed libration of the peripheral phenyls or the phosphine ligand. We recognized the possibility that the dimethylphenylphosphine ligand may not serve as an innocent probe for chirality inversion in the C_5Ph_5 moiety if it introduces an additional source of asymmetry. Unfortunately, attempts to clarify the steric contributions of these moieties via the VT-NMR study of $(C_5Ph_4\text{–}m\text{-}C_6H_3\text{–}Me_2)Fe(CO)(PMe_3)(Br)$ (**47**), incorporating an m-xylyl substituent and a small, symmetrical phosphine were unsuccessful, either because the PMe_3 does not gate the phenyl rotations or because the methyl ^{13}C chemical shift differences are too small to be observed in solution. In hindsight, the inability to detect exchange between distal and proximal rotamers could likely have been circumvented by ortho, as opposed to meta, aryl labelling of the C_5Ar_5 ligand.



30: M = Fe
31: M = Ni
32: M = W⁺
33: M = Ge
34: M = Sn
35: M = Pb

40: M = Fe
42: M = Ru

41

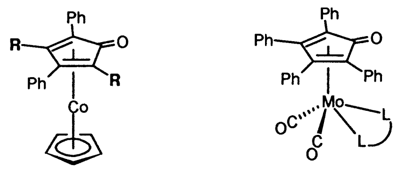
43

Scheme 12. C_5Ph_5 and C_5Ph_5H linear and bent metallocene derivatives.

In all cases of hindered Cp–substituent bond rotations featured above, an uncorrelated, stepwise or one-ring interconversion, as opposed to a correlated, synchronous rotational mechanism has been postulated. Moreover, slowed libration about the $Cp\text{–}ML_n$ bond is clearly effected by the interannular repulsion of the bulky ring substituents in metallocenes, or a ring-substituent metal–ligand steric interaction in half-sandwich complexes. Despite the numerous accounts of metal-ligated cyclopentadienones generated either indirectly by metal carbonyl-promoted alkyne oligomerizations [114–116] or less frequently via direct metallation methods [117], few investigations have considered the stereochemical features of such systems. The exclusive formation of $[(\eta^5\text{-}(C_5Ph_5)Co(\eta^4\text{-}(C_4\text{–}2,4\text{-}Mes_2\text{–}3,5\text{-}Ph_2C{=}O)]$ (**48**) and the corresponding cyclobutadiene complex (refer to Section 2.3) from the reaction of

$CpCo(CO)_2$ and mesitylphenylacetylene was noted in a 1979 report by Rausch et al. [79]. At ambient temperatures, the ^{1}H-NMR spectrum of **48** exhibited six methyl resonances in the aliphatic region, consistent with impeded rotation about the mesityl–cyclopentadienone bonds in both the alpha and beta positions. Although it would have been particularly instructive to compare activation parameters for the alpha- and beta-ring rotations (cf. tetra-*o*-cyclopentadienone (**21**)), even in the presence of a metal moiety, no dynamic NMR studies were conducted. In 1993, Adams et al. [118] reported the synthesis and variable-temperature ^{31}P-NMR of complexes $[Mo(CO)_2(L{-}L)(\eta^4\text{-}(C_4Ph_4C{=}O))]$ $(L{-}L = Ph_2PCH_2PPh_2$ (**49a**) or $Ph_2PCH_2CH_2PPh_2$ (**49b**)). Whereas the low-temperature limiting spectrum of **49a** could not be accessed, transformation of the dppe ^{31}P AB pattern to a singlet over the temperature range of 193–308 K allowed for an activation energy (E_a) of 11.6 kcal mol^{-1} to be estimated for **49b** (Scheme 13). Recently, Gupta, Rampersad and Stradiotto from our research group [117] provided only the second and third examples of enhanced conformational rigidity in $(C_4Ar_4C{=}O)ML_n$ complexes resulting in cyclopentadienone–ML_n rotational barriers measurable by dynamic NMR spectroscopy.

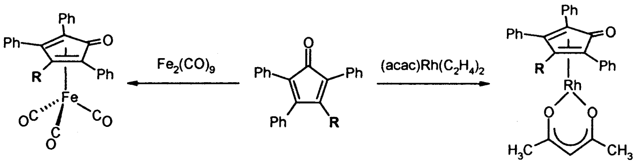
The separate treatment of tetracyclone (**50**) and its organometallic analogue, 3-ferrocenyl-2,4,5-triphenylcyclopentadienone (**51**) with $Fe_2(CO)_9$ afforded η^4-$(C_4Ph_4C{=}O)Fe(CO)_3$ (**52**) and the novel complex, η^4-$(C_4Ph_3FcC{=}O)Fe(CO)_3$ (**53**), respectively (Scheme 14) [117]. Whereas in the X-ray crystal structure of **52** the peripheral aryl rings adopt the conventional propeller conformation with average interplanar angles of ca. 49°, the orientations of the aryl blades in **53** are markedly influenced by the nearly coplanar C_5H_4 ring of the *exo* ferrocenyl moiety. These solid-state structural incongruities are also apparent in the solution behaviour of both complexes. In accordance with earlier studies by Kruczynski and Takats [119], a low barrier to tripodal rotation in **52** precluded the observation of this dynamic process in the experimental limit (167 K) of the ^{13}C-NMR regime. In contrast, the ^{1}H- and ^{13}C VT-NMR (173–300 K) spectral patterns of the ferrocenyl derivative **53** indicated an unequal isomeric distribution of 80:20, possibly corresponding to Fc *exo* and *endo* positions; an activation barrier of 12.5 ± 0.5 kcal mol^{-1} was extracted from the decoalescence data (177 K) of the ^{13}CO resonance of the major rotamer.



48: R = mesityl

49a: L-L = $Ph_2PCH_2PPh_2$
49b: L-L = $Ph_2PCH_2CH_2PPh_2$

Scheme 13. η^4-Tetraarylcyclopentadienone cobalt and molybdenum complexes that exhibit hindered Cp–Ar and Cp–ML_n rotation on the NMR time-scale, respectively.



52: R = Ph
53: R = Fc

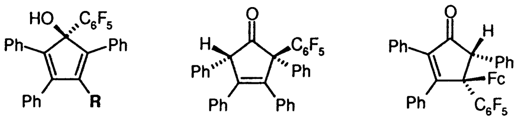
50: R = Ph
51: R = Fc

54: R = Ph
55: R = Fc

Scheme 14. Organometallic derivatives of tetraarylcyclopentadienones **50** and **51**.

Similarly, η^4-$(C_4Ph_4C{=}O)Rh(acac)$ (**54**) and η^4-$(C_4Ph_3FcC{=}O)Rh(acac)$ (**55**) were synthesized by gentle reflux of the appropriate ligand **50** or **51** with $(acac)Rh(C_2H_4)_2$ [117]. X-ray crystallographic studies revealed that **54** adopts a head-to-tail dimeric arrangement with the individual dienones possessing a cup-shaped, as opposed to a helical, arrangement of phenyl rings about their periphery. In solution, the Rh-acetylacetonate moiety was presumed to straddle the molecular mirror plane, thereby preventing the detection of restricted rotation about the Cp–ML_n axis. On the other hand, the monomeric form of **55** was enforced by the presence of the bulky ferrocenyl substituent, which again disturbs the propeller conformation and appropriately desymmetrizes the system. At low temperature the methyl groups of the acac ligand were rendered magnetically non-equivalent, yielding a rotational barrier of 12.5 ± 0.5 kcal mol^{-1} for the Rh-acac moiety. Apparently, there is little distinction between the steric interplay of the $Fe(CO)_3$ and Rh(acac) fragments with the peripheral substituents of **51**, owing perhaps to the comparable metal–diene carbon distances in **53** (2.061(2)–2.136(3) Å) and **55** (2.098(5)–2.165(6) Å).

In our endeavour to systematically and collectively quantify the fluxional properties of $(C_5Ar_5)ML_n$ derivatives, we have aimed to develop methods of incorporating ^{19}F-NMR probes, which have larger chemical shift dispersions than do ^{1}H or ^{13}C nuclei. As highlighted earlier in Scheme 6, the derivatization of an already sterically demanding C_5 system such as tetracyclone **50** via treatment with aryl Grignard reagents offers synthetic access to C_5Ar_5 pentacycles and their organometallic complexes. As a first entry point to fluorinated analogues, we [120] have examined the syntheses, structures and dynamic behaviour of pentafluorophenyl-containing Cp systems. The reaction of pentafluorophenyllithium with cyclopentadienones **50** and **51** yielded, in both cases, the cyclopentadienols **56** and **57** as a result of 1,2 additions, and the cyclopentenones **58** and **59**, as the products of 1,6 and 1,4 additions,



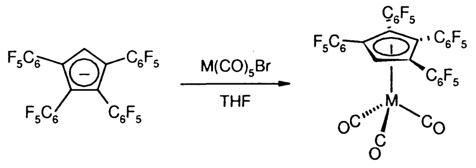
56: R = Ph
57: R = Fc
58
59

Scheme 15. Products from the reaction of pentafluorophenyllithium with **50** and **51**.

respectively (Scheme 15). X-ray crystallographic characterization of **56**, **58** and **59** clarified the regiochemistry of these adducts and the non-bonded environments of the pentafluorophenyl moiety. The observation of five different resonances in the room temperature ^{19}F-NMR spectra of **56**, **57** and **59** further corroborated the conformational rigidity induced by the steric crowding about the C_6F_5 rings. However, the barriers to pentafluorophenyl ring rotation could not be evaluated directly from line-broadening measurements because the expansive chemical shifts of both the ortho and meta fluorines prevented the observation of complete peak coalescence. Rather, the approximate $\Delta G^{\ddagger}$ values of 20 ± 1, 21 ± 1, and 19 ± 1 kcal mol^{-1}, respectively, were obtained by simulation of the variable temperature 282 MHz ^{19}F-NMR spectra. Ultimately, the demonstration of restricted rotation of C_6F_5 groups in synthetically feasible peraryl-substituted organic platforms, such as the cyclopentadienols **56** and **57**, offers promise for the design of gated organometallic complexes.

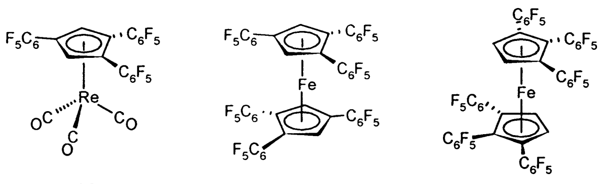
Relevant to both our interest in ancillary perfluoroaryl groups and the C_5Ar_4H metallocene derivatives **40**–**43**, a 2001 report by Deck and co-workers [121] outlines the synthesis and characterization of piano stool complexes derived from the tetrakis(pentafluorophenyl)cyclopentadienyl ligand **60**. The diene was isolated from the reaction of sodium cyclopentadienide with excess hexafluorobenzene and sodium hydride in refluxing diglyme, and readily converted to $[(C_6F_5)_4C_5H]Na$ **60(Na)** upon treatment with sodium hydride in THF. Whereas attempts to generate the octaarylated Fe(II) and Co(II) metallocenes by use of standard methods failed, the $[(C_6F_5)_4C_5H]M(CO)_3$ (M = Mn **61**; M = Re **62**) complexes were prepared in moderate yields from **60(Na)** and the corresponding metal carbonyls, $M(CO)_5Br$ (Scheme 16). In the solid state, the molecular structures of **60**, **61** and **62** display a helical arrangement of the C_6F_5 groups, as evinced from single crystal X-ray diffraction data. Dynamic ^{19}F-NMR studies (173–298 K) of **61** and **62** revealed that the beta C_6F_5 moieties are in slow exo(distal)–endo(proximal) exchange at all temperatures, while rotation of the alpha rings is not frozen out until 198 K. Accompanying Eyring analyses generated the same activation parameters ($\Delta G^{\ddagger} = 8.0 \pm 0.2$ kcal mol^{-1}) for both complexes. Moreover, there was no evidence for hindered libration about the Cp–$M(CO)_3$ axes within the experimental limits. Earlier fluxional analyses of a homologous series of mono-, bis- and tris(pentafluorophenyl)cyclopentadienyl complexes (Scheme 17) established that 'isolated' C_6F_5 rings undergo rapid rotation on the NMR timescale, whereas vicinal C_6F_5 groups in $[1,2,4\text{-}(C_6F_5)_3C_5H_2]Re(CO)_3$ (**63**) display temperature-dependent rotational behaviour, with an associated E_a of 9 ± 1 kcal mol^{-1} ($\Delta G^{\ddagger} \approx 8.4$ kcal mol^{-1}). In the related metallocene, $[1,2,4\text{-}(C_6F_5)_3C_5H_2]_2Fe$ (**64**), both Cp–C_6F_5 and Cp–Fe rotational processes can be monitored by use of ^{19}F VT-NMR, yielding an activation energy of 11 ± 2 kcal mol^{-1} ($\Delta G^{\ddagger} \approx 11.4$ kcal mol^{-1}) for the latter racemization. In the case of three contiguous aryl moieties in $[1,2,3\text{-}(C_6F_5)_3C_5H_2]_2Fe$ (**65**), the rotational barrier (E_a) for the 'outer' C_6F_5 rings was calculated to be 10 ± 1 kcal mol^{-1} ($\Delta G^{\ddagger} \approx 9.2$ kcal mol^{-1}), whereas the central ring is conformationally locked. The buttressing effects engendered by the anisotropic steric profile of C_6F_5 groups are significantly different than for a phenyl substituent, as evidenced by the fast exo–endo edge exchange of the beta rings in $Fe(C_5Ph_4H)_2$ (**40**) at ambient temperature [108]. As a rationale for the stereochemical behaviour of perfluoroarylated metallocenes, Deck invoked a qualitative model of transannular Cp–Fe steric interactions coupled (synchronized) with torsional Cp–C_6F_5 strain [122].

In yet another pertinent article by Thépot and Lapinte in 2001 [123], the preparation and characterization of several bromopentaarylcyclopentadienes of the formula $C_5Ar_4Ar'Br$ (**68**) (Ar = C_6H_5 or 3,5-$C_6H_3Me_2$ and Ar′ = C_6H_5, 3-C_6H_5X, 3,5-$C_6H_3X_2$, 2,4-$C_6H_3X_2$, 2,4,6-$C_6H_2X_3$ where X = methyl; 3-C_6H_5X, 3,5-$C_6H_3X_2$, 2,6-$C_6H_3X_2$ where X = fluorine) have been detailed. Treatment of the tetraarylcyclopentadienones **66** with the



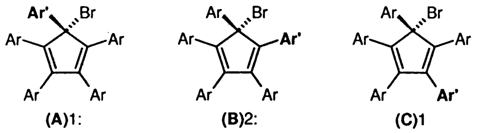
60
61: M = Mn
62: M = Re

Scheme 16. The synthesis of transition metal half-sandwich complexes comprising the tetrakis(pentafluorophenyl)cyclopentadienyl ligand, **60**.



63
64
65

Scheme 17. Various metallocene and piano-stool derivatives (**63**–**65**) of tris(pentafluorophenyl)cyclopentadienyl ligands.



68

Scheme 18. Conversion of methyl- and fluorine-containing pentaarylcyclopentadienols **67** to bromopentaarylcyclopentadienes **68** gives a regio-isomeric distribution of products when Ar and Ar′ groups are different.

corresponding lithium-aryl (Ar′Li) reagents in THF allowed for the systematic introduction of the fifth aryl moiety. Conversion of the tetraarylcyclopentadienols **67** into their bromo derivatives **68** was achieved by reaction with $SOBr_2$–pyridine, and resulted in three different positional isomers (1:2:1) when the Ar′ and Ar groups were different, but only a single, sterically moderated beta-product **68C** in the di-*ortho*-substituted Ar′ cases (Scheme 18). It is anticipated that the bromopentaarylcyclopentadienes will allow facile access to iron piano stool complexes via a formal oxidative addition of pentacarbonyliron(0) and subsequent ligand exchange. Certainly, the differential labelling at ortho and meta arene sites in Ar′ and the steric bulk of the 3,5-dimethylphenyl groups should allow for rational quantification of the activation parameters associated with rotational processes in these diversely substituted metal–Cp arrays.

3.2. *Pentaalkylcyclopentadienyl derivatives*

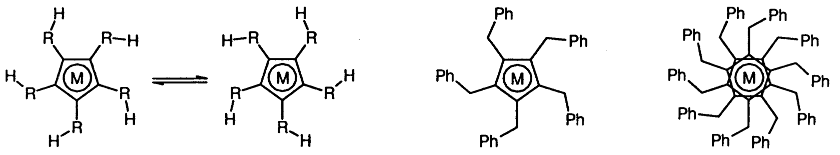
The study of rotational dynamics in peralkylated Cp π-complexes has emulated the corresponding analyses of C_6 homologs (refer to Section 4.1) and since reviewed earlier by Janiak and Schumann [85], will only be considered briefly here. The barriers ($\Delta G^{\ddagger}$) to enantiomerization in the penta(isopropyl)- and penta(neopentyl)cobalticinium salts, $[C_5(^{i}Pr)_5]CoCp^+$ (**69**) (17.1 ± 0.2 kcal mol^{-1}) and $[C_5(CEt_2H)_5]CoCp^+$ (**70**) (19.4 ± 0.2 kcal mol^{-1}), respectively, were reported in 1990 by Gloaguen and Astruc [124]. Coalescence temperatures of 338 and 373 K were extracted from the variable-temperature ^{1}H- and ^{13}C-NMR spectra of **69** and **70**, which displayed features consistent with metallocenic chirality arising from hindered Cp–R rotation at room temperature. The methyl protons are rendered diastereotopic by the pentacycle helicity and sense the clockwise–counterclockwise exchange of alkyl groups, which occurs via a stepwise, uncorrelated mechanism deemed prevalent for gear-meshed systems [50]. In the related half-sandwich complex $[C_5(^{i}Pr)_5]Mo(CO)_3CH_3$ (**71**), the activation energy for this interconversion process was estimated to be 13 ± 1 kcal mol^{-1}, with an associated ^{1}H VT-NMR coalescence temperature of 288 K [125]. A further decrease in rotational barrier was noted in the silicon analogue, $[C_5(SiMe_2H)_5]Mn(CO)_3$ (**72**), which yielded an approximate $\Delta G^{\ddagger}$ value of 9.5 kcal mol^{-1} [126]. A combination of differing steric and electronic requirements in these sym-metallocenes and piano stool complexes undoubtedly accounts for these trends in isomerization barriers. In the absence of solid state structural data for **69** and **71**, one might speculate that the Cp–M distance is significantly decreased in **69** (cf. **71**) given its electronically deficient metal centre, while **71** and **72** might be expected to possess unequal ML_n cone angles and Cp–R ($R = C$ or Si) bond lengths. Similar steric predictions are realized in the fluxional behaviour of pentabenzyl–Cp based bent metallocenes, $[C_5(CH_2Ph)_5]_2M$ ($M = Ge$ **73** [127], Sn **74**, Pb **75** [128]) and half-sandwich complexes $(PhCH_2)_5C_5M$ ($M = Tl$ **76**, In **77** [129], $Co(CO)_2$ **78** [130], $Mn(CO)_3$ **79** [131]), which exhibit both free Cp–ML_n and Cp–CH_2Ph rotation at ambient temperature, in contrast to the stereorigid, linear decabenzylferrocene **80**, and its derivatives [131–134]. In the absence of computational or VT-NMR spectroscopic data, it has been argued that the deca-*anti*-benzyl arrangement, which is found crystallographically, also persists in the solution state of **80** because of severe transannular repulsions [132] (Scheme 19).

4. Persubstituted arenes: C_nR_n, where $n = 6$

With their sterically diverse, radially functionalized hexagonal cores, C_6R_6 scaffolds have adopted key roles in various fields of research. From a synthetic vantage, persubstituted benzenes are products of two of the most intensely studied, useful transformations: namely, the metal (for example Co(0) [135–137]) or non-metal (for example Si_2Cl_6 [138,139]) catalysed trimerization of alkynes, and the [4+2] Diels–Alder cycloaddition of cyclopentadienones and ethynyl moieties [140,141]. Conferred with novel optical and electronic properties, these highly alkylated and arylated 6-π electron centres have been exploited as: (a) synthons for polyaromatic hydrocarbons or graphite building blocks [142–144], complex, highly branched dendrimers [145–147], and nanosize homogeneous catalysts [148,149]; (b) polymeric side chains [150]; (c) room-temperature discotic nematic liquid crystals [151]; (d) hosts in self-assembled supramolecular networks [152,153]; (e) ligands in organometallic complexes; (f) subjects of theoretical studies [154]; and (g) candidates for stereochemical analyses (vide infra).

4.1. *Hexaalkylbenzenes*

In the molecular ground state and under the appropriate conditions of intramolecular crowding, the arrangement of neighbouring alkyl groups around the



69: M = CoCp$^+$; R = CMe$_2$
70: M = CoCp$^+$; R = CEt$_2$
71: M = Mo(CO)$_3$CH$_3$; R = CMe$_2$
72: M = Mn(CO)$_3$; R = SiMe$_2$

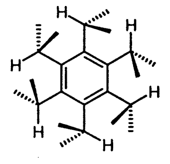
73: M = Ge[C$_5$(CH$_2$Ph)$_5$]
74: M = Sn[C$_5$(CH$_2$Ph)$_5$]
75: M = Pb[C$_5$(CH$_2$Ph)$_5$]
76: M = Tl
77: M = In
78: M = Co(CO)$_2$
79: M = Mn(CO)$_3$

80: M = Fe

Scheme 19. A selection of chiral peralkyl-cyclopentadienyl metal π-complexes.

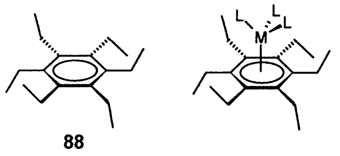
arene periphery can be compared to a system of meshed gears, as delineated by Mislow [18]. The static and dynamic stereochemistry of several persubstituted arenes (C_6R_6) have been reported, including R = isopropyl **81** [155–158]; dimethylsilyl **82** [159]; bis(1-bromoethyl), tetraisopropyl **83** [160]; dichloromethyl **84** [161]; bis(bromochloromethyl), tetraisopropyl **85** [162]; and dimethylamino **86** [163]. Among these, hexaisopropylbenzene (**81**) has served as a spectacular example of the precise interlocking of contiguous groups via bisected conformations to generate a helical C_{6h} structure (Scheme 20). While **81** resists metal complexation, its symmetry was reduced by selective deuteration, and the barrier to homomerization (attendant rotation of isopropyl substituents by π radians) estimated to have a lower limit of 22 kcal mol^{-1} by VT-NMR methods (298–398 K). Empirical force field (EFF) calculations corroborated that the threshold mechanism for stereoisomerization in prototype **81** and its derivatives is a stepwise, uncorrelated rotation (or inversion, in the case of **86**) of individual side chains. This dynamic circuit follows the pattern observed or calculated for tetraisopropylethylene [164] and other statically geared systems (vide infra) [50], and corresponds, with the exception of **86**, to slippage of one gear at a time in the mechanical counterpart [18]. However, in an extension of the parity rule for gear trains, all hexaalkylbenzenes are *in principle* capable of correlated disrotation, even if these conformational interconversions are associated with high-energy regions of the potential energy surface (PES) [18]. Only if the threefold alkyl rotors possess deep grooves is gear slippage suppressed, as has been exemplified by hexamethylbenzene **87**, which engages in correlated, internal rotations, but only at very low temperatures [165].

Hexamethylbenzene is the parent representative of a subclass of hexaalkylbenenes (also including R = ethyl **88**; cyclopropyl **89** [166]; trimethylsilylmethyl **90** [167]; bromomethyl **91** [168]; neopentyl **92** [22,169]; benzyl **93** [170] and others) in which the alkyl groups adopt antiparallel conformations, so as to impart approximate D_{3d} or S_6 symmetry to the molecule. For almost two decades, the static and dynamic stereochemistry of hexaethylbenzene (HEB, **88**) and its organometallic derivatives fostered a vigorous debate between several research groups, including that of McGlinchey [171]. In 1980, Hunter et al. [172,173] established by use of X-ray crystallography that the ethyl groups project alternately above and below the ring plane in the hydrocarbon **88**, and that ligated $Cr(CO)_3$ (**94**) and $Mo(CO)_3$ (**95**) tripods eclipse the distal ethyl groups of the D_{3d} conformer, confirming our earlier claims [174]. The barrier to site exchange of the diastereotopic ethyl groups in **94** (and **95**) was measured as 11.5 kcal mol^{-1} by dynamic NMR spectroscopy and attributed by EFF studies to uncorrelated side chain rotation [173]. Despite the energetic preference of the 1,3,5-distal-2,4,6-proximal isomer, this arrangement is not always found in the solid state or solution, as was first demonstrated by the hexa-distal (C_{6v}) HEB conformation and the ^{13}C-NMR spectral temperature invariance (298–189 K) of [(HEB)Cr-(CO)$_2$PPh$_3$] (**96**) [173,175]. The results of these and many subsequent studies raised questions regarding the effect of metal complexation on the barrier to topomer-



81

Scheme 20. The static gear effect is most strikingly exhibited by hexaisopropylbenzene (**81**).



88

94: ML$_3$ = Cr(CO)$_3$
95: ML$_3$ = Mo(CO)$_3$
96: ML$_3$ = Cr(CO)$_2$PPh$_3$
97: ML$_3$ = Cr(CO)$_2$CS
99: ML$_3$ = [Cr(CO)(CS)(NO)][BF$_4$]
100: ML$_3$ = [Cr(CO)$_2$(NO)][BF$_4$]

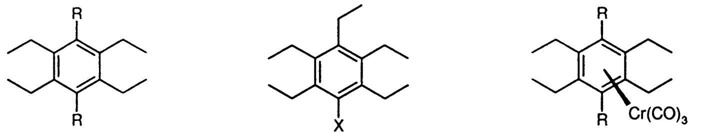
Scheme 21. The alternate 'up-down' conformational preference of hexaethylbenzene (**88**) and a selection of its transition-metal complexes for which different ethyl group arrangements may be adopted.

ization, thereby prompting the evaluation of barriers to metal tripod rotation (Scheme 21).

Steric inhibition of tripodal rotation is only detectable if the C_{3v} symmetry of **94** and its congeners is reduced, either by carbonyl ligand exchange or arene substitution (i.e. to generate C_6Et_5X). Jointly with our colleagues in France [176], we thus prepared [(HEB)Cr(CO)$_2$CS] (**97**), which closely parallels **94** in its solid state structure, and which exhibits a C_s-consistent 2:1:2:1 pattern for each of the aromatic ring carbon, methylene and methyl environments in the static ^{13}C-NMR regime. Even with comparable solid-state ^{13}C-NMR data [177], our interpretation of slowed tripodal rotation was challenged by Hunter and Mislow [178], who raised the possibility of a solution-state 1,2,3,5-distal-4,6-proximal conformer in which HEB itself possesses C_s symmetry. To validate the assertion of restricted rotation about the arene–ML$_n$ axis, it was necessary to establish that the desymmetrization source was not the altered orientation of HEB in solution. Temporarily circumventing this particular issue, Downton, Mailvaganam, and others from our laboratory [179] applied the alternate substitution scheme to the generation and combined X-ray crystallographic and NMR spectroscopic characterization of [(C_6Et_5COMe)Cr(CO)$_3$] (**98**). While the complex adopts the successive proximal-distal conformation in both phases, the 2:1 splitting pattern of the Cr(^{13}CO)$_3$ signal in the solid state and in solution at 173 K unequivocally demonstrated the cessation of tripodal rotation ($\Delta G^{\ddagger} \approx 9$ kcal mol^{-1}). Having distinguished the resonance assignments for proximal and distal ethyl environments, Mailvaganam, Frampton and co-workers [180] refocused on the analogous C_6Et_6 species. The cationic derivatives [(HEB)Cr(CO)(CS)(NO)][BF$_4$] (**99**) and [(HEB)Cr(CO)$_2$(NO)][BF$_4$] (**100**) both exhibit the 1,3,5-distal-2,4,6-proximal arrangement in the solid state. In solution, the behaviour of the former is consonant with that of the thiocarbonyl species **97**, whereas the chiral tripod in the latter complex renders inequivalent all six ethyl substituents in the unperturbed C_s symmetric HEB ligand. These observations, together with data on **97**, are rationalized in terms of two independent fluxional processes: tripodal rotation ($\Delta G^{\ddagger} \approx 9.5$ kcal mol^{-1}), and uncorrelated rotation of the ethyl groups ($\Delta G^{\ddagger} \approx 11.5$ kcal mol^{-1}; cf. **94** and **95**) [180].

To allow for independent yet concomitant evaluation of these two interconversion pathways, Kilway and Siegel [181,182] elegantly extended the aforementioned desymmetrization concepts to the design of 1,4-R$_2$-2,3,5,6-tetraethylbenzene ligands (R = 4,4-Me$_2$-3-oxypentyl **101**; OMe **102**; CH$_2$OMe **103**; neohexyl **104**) (Scheme 22). Nearly commensurate barriers to alkyl rotation in the free and Cr(CO)$_3$-complexed systems, **101(Cr)** to **104(Cr)**, were attributed to a cogwheel-like ('lock and key') complementarity of rotation between the ethyl substituents and the metal tripod [182]. This apparent dynamic correlation is not manifested in the energetic requirements of the two pathways, however; for **101** the free energies of activation for alkyl rotation (11.3 kcal mol^{-1} in **101** and 11.5 kcal mol^{-1} in **101(Cr)**) and tripodal rotation (9.5 kcal mol^{-1}) are obviously disproportionate [181], as evinced by our systems [180]. In further support of the innocuous role of the metal in the stereodynamics of **94**, Gottlieb and co-workers [183,184] have recently provided VT-NMR and computational (MM3 force field) data for a series of pentaethylated benzenes, C_6Et_5X (X = H, Br, OCOCH$_3$, C_6Et_5, et cetera) **105**–**110**, for which the diastereotopic methylene hydrogens of the ortho and meta ethyl groups serve as rotational probes (Scheme 22). A re-examination of the interconversion pathway established that in the *consecutive* (*step-wise*) rotation of contiguous alkyl groups, the third (4th-alkyl) [184], as opposed to the first (2nd-alkyl) [173], step is rate-determining. In its entirety, the hexaethylbenzene narrative is a powerful example of the need to apply rigorous symmetry and steric principles in the design of templates for stereochemical analyses.

For example, both the static-gearing effects and the stereodynamics of the pendant alkyl groups will determine the utility of hexaethylbenzene derivatives as preorganized templates for the supramolecular assembly of nanomaterials with tailored physical properties, or as building blocks for large, maximally alkylated polycyclic aromatic hydrocarbons. In 2001, Kilway and Siegel [185] broadened the scope of this area by demonstrating how cooperative conformational networks can control the proximity and direction of functional groups in surrogates of HEB (Scheme 22). Variable-temperature ^{1}H-NMR studies of 1,4-disubstituted-2,3,5,6-tetraethylbenzenes (**101**, **103**, **104**, **111**–**117**), for which the diastereotopic geminal methylene protons of the ethyl groups served as a spectroscopic probe for alkyl motion, established that in the static (solution) limit all isomers adopt the divergent C_{2h} conformation, as in the solid state. Furthermore, the free energies of activation ($\Delta G^{\ddagger}$), calculated by use of the Gutowsky-Holm approximation, were distinctly influenced by the effective steric bulk of the substituents. Taking into account the relative interaction of each position (α, β, γ) with relation to the arene carbon on which the group resides, it was found that the barrier height is directly correlated with the van der Waals radius of the α and β locales, with the exception of CH$_2$CN, which is best described by its Taft parameter. On the other hand, the γ moiety does not bias the energetics of the vicinal ethyl group rotation but instead serves as a magnetic perturbation to desymmetrize the system. Repulsive van der Waals interactions also serve as the major conformational determinant of polyethylated hydrocarbon analogues. Gottlieb and co-workers [186,187] have applied the HEB model to the



101: R = $CH_2CH_2COCMe_3$
102: R = OMe
103: R = CH_2OMe
104: R = $CH_2CH_2CMe_3$
111: R = Br
112: R = $CH_2NHCOMe$
113: R = $CH_2CH_2NO_2$
114: R = CH_2Cl
115: R = CH_2SMe
116: R = CH_2CN
117: R = CH_2NH_2

105: X = H
106: X = Br
107: X = OCOMe
108: X = OCOPh
109: X = C_6Et_5
110: X = COMe

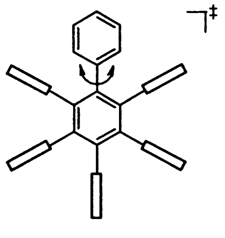
98: R_1 = Et, R_2 = COMe
101(Cr): R_1 = R_2 = $CH_2CH_2COCMe_3$
102(Cr): R_1 = R_2 = OMe
103(Cr): R_1 = R_2 = CH_2OMe
104(Cr): R_1 = R_2 = $CH_2CH_2CMe_3$

Scheme 22. Mono- and di-(1,4)-substituted analogues of hexaethylbenzene, including metal-ligated derivatives of the latter systems.

study of sp^2–sp^3 rotational barriers in persubstituted biphenylene, anthracene, and fluorene. The appropriate quantification of structural features (size, arrangement) and the identification of corresponding $\Delta G^{\ddagger}$ trends within these C_6R_6 subsets provide critical calibration points for the future design of conformationally controlled architectures.

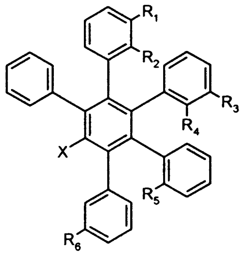
4.2. Hexaarylbenzene and derivatives

In the solid state, the nascent six-bladed propeller, hexaphenylbenzene **118**, adopts a helical conformation with interplanar angles of ca. 65(75)° [188,189] between the peripheral phenyl substituents and the central ring. Earlier gas phase electron diffraction studies revealed an essentially orthogonal form, with phenyl oscillations of ±10° [190]. Correspondingly, the fluxional nature of C_6Ar_6 molecules in solution is rationalized by an effective NMR time-averaged D_{6h} perpendicular arrangement [47]. In order to observe restricted rotation about the sp^2–sp^2 bonds joining the central and peripheral aromatic rings, proper substitution of the aryl rings is required. The pioneering stereochemical studies of C_6Ar_6 systems by Gust and Patton [47,48] established that isomerization occurs via a mechanism wherein an individual peripheral ring rotates in an uncorrelated fashion by approximately π radians (Scheme 23). Rotational barriers of ca. 33, 38 or 17 kcal mol^{-1} are engendered by the incorporation of ortho or meta (methoxy, methyl) substituents, respectively (**19**, **119**–**122**). Whereas the differing steric requirements of *ortho*-positioned groups are evidently manifested in the interconversion barriers, the influences of electronically and spatially dissimilar meta substituents are minimal, such that $\Delta G^{\ddagger}$ values of the latter species indirectly reflect the interactions of ortho hydrogens on adjacent aryl rings. Rotating rings also detect the non-bonded repulsions from remote sites around the circumference of the central C_6-ring. Such buttressing effects were evinced by the free energies of activation for pentaarylbenzene (C_6Ar_5X) derivatives **123**–**128** bearing various substituents, which ranged from 15.5 (X = H) to 18.7 (X = $C(CH_3)_3$) kcal mol^{-1} [47,97]. In all of the C_6Ar_6 and C_6Ar_5X systems reported to date (Scheme 24), the $\Delta G^{\ddagger}$ values have been ascribed to diastereomeric interconversions, since enantiomerization necessarily involves rotation of *all* substituted rings and is therefore energetically more demanding. A spectacular example is provided by the D_3-symmetric propeller 1,3,5-tris{[3,4-bis(4-methoxyphenyl)-2,5,6-triphenyl]phenyl}benzene (**129**), which yielded a barrier



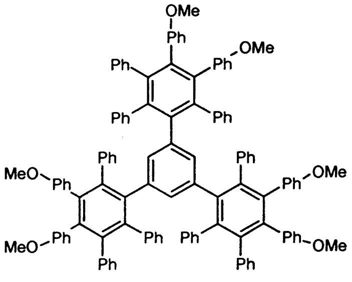
118

Scheme 23. Diastereomerization of all hexaarylbenzenes is rationalized by a mechanism involving rotation by π radians of a single peripheral aryl group, as depicted by this idealized transition state.



119: X = Ph; R_2 = OMe; R_4 = Me
120: X = Ph; R_2,R_5,R_6 = Me; R_4 = OMe
121: X = Ph; R_1 = R_3 = OMe
If R_1,R_3 = Me:
122: X = Ph
123: X = H
124: X = $CH(CH_3)_2$
125: X = CH_3
126: X = CH_2CH_3
127: X = $CH(OH)CH_3$
128: X = $C(CH_3)_3$

Scheme 24. Suitably substituted penta- and hexaarylbenzenes that have demonstrated rotational stereoisomerization on the NMR timescale if not otherwise noted R_n = H.



129

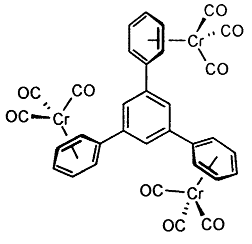
Scheme 25. The hexamethoxy derivative **129** of the D_3-symmetric propeller, 1,3,5-tris(pentaphenylphenyl)benzene.

($\Delta G^{\ddagger}_{333\ \mathrm{K}}$) of 18.9 kcal mol^{-1} for C_3–C_1 diastereomerization achieved by 180° rotation about one of the Ph_5Ph–benzene bonds (Scheme 25) [191].

These experiments have subsequently been extended to complexes of the type $(C_nAr_n)ML_x$ whereby the π-bonded organometallic fragment(s) render inequivalent the *faces* rather than the *edges* of the aryl rings. We first demonstrated the fecundity of this approach by attaching one, two and three $Cr(CO)_3$ pendant functionalities to the periphery of 1,3,5-triphenylbenzene (**130**–**133**) [192]. Whereas the X-ray crystallographic characterization of 1,3,5-tris[(η^6-C_6H_5)$Cr(CO)_3$]benzene (**133**) revealed a radially-disposed (two-up, one-down) trimetallic system of moderate congestion (Scheme 26), the VT-NMR spectra (298–183 K) provided no evidence of hindered rotation of the labelled aryl rings. Otherwise, chromium tricarbonyl complexes of arenes typically display metal-tripod rotations with barriers less than 3 kcal mol^{-1}, well below the detectable limits of NMR methods [3,171,193,194]. In order to slow the libration of either the organometallic domain or the propeller blades [195] it is therefore necessary to employ extremely bulky arenes.

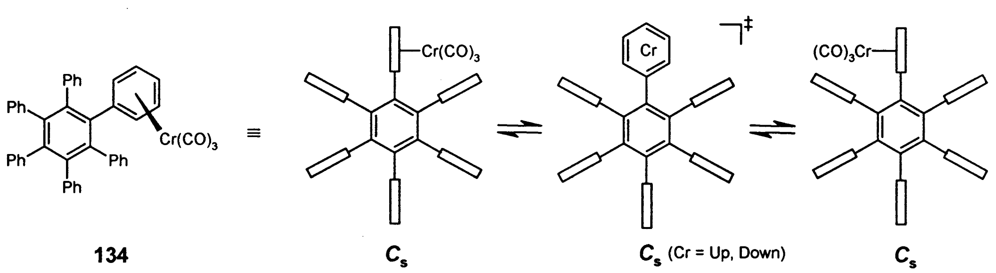
Accordingly, efforts were directed towards functionalization of the more sterically encumbered perarylated benzene **118**, for which both in-plane splaying and hydrogen interactions are negated [97]. Ligation of a tricarbonylchromium moiety to an external ring in (C_6Ph_6)$Cr(CO)_3$ (**134**) was achieved, albeit in low isolable yields, following treatment of **118** with $Cr(CO)_6$ [196]. A dynamic ^{13}C-NMR spectroscopic analysis yielded a $\Delta G^{\ddagger}$ value of 12.2 kcal mol^{-1} for the independent rotation of the metal-substituted ring relative to the central plane. Although not discernable under the experimental conditions, a concomitant isomerization process involving a low energy oscillation which inverts the handedness of the enantiomerically related chiral propellers was proposed. Thus, (C_6Ph_6)$Cr(CO)_3$ (**134**) exists in two stereoisomeric forms, namely a **d**, **l** pair each having C_1 symmetry, which may only be observed as a NMR time-averaged C_s isomer at low temperature (193 K) and as an effective C_{2v} conformation at 300 K (Scheme 27). This rationale is in agreement with the peak splitting patterns for all ortho, meta and para carbons, which indicate that the rapid libration of the metal-complexed ring in the dynamic limit equilibrates both the σ-related halves and top and bottom faces of the molecule. On lowering the temperature, signal decoalescence (i.e. 2:2:1 to 1:1:1:1:1 for para carbons of uncomplexed rings) reveals six differentiable, yet locally C_2-equivalent, peripheral ring environments arising from a rotamer in which the ligated ring is perpendicularly disposed to the central arene plane. Since the ortho and meta carbons in any particular aryl ring are magnetically equivalent in both the static and dynamic regimes, restricted rotation of the non-complexed rings is unobservable in the absence of further substitution. Interestingly, the measured activation energy for this isomerization process is ca. 5 kcal mol^{-1} less than the associated barrier in the free 1,2-bis(*m*-tolyl)-3,4,5,6-tetraphenylbenzene (**121**) [47,48]. These differences are likely a combination of ground-state destabilization through repulsive steric interactions and electronic stabilization of the transition state engendered by metal complexation.

While we are not aware of other dynamic NMR studies of metal-complexed hexaphenylbenzene (HPB), it is noteworthy that a few molecules of this type have been prepared and structurally characterized (Scheme 28). In connection with the cobalt-catalysed cyclotrimerization of alkynes, Biagini et al. [197] have described the irreversible disproportionation of $[Co(py)_6][BF_4]$ in the presence of diphenylacetylene to give (η^6-C_6Ph_6)Co(η^2-C_2Ph_2) (**135**) as one of two products. From a generalized synthetic route to sterically crowded ruthenium arene cations advanced by Crocker et al. [198], diphenylacetylene was also employed in a photochemically promoted ring expansion reaction with an η^4-cyclobutadiene complex, [CpRu(CO)(η^4-C_4Ph_4)]-$[BF_4]$, yielding [CpRu(η^6-C_6Ph_6)]$[BF_4]$ (**136**). Geiger and co-workers [199] have recently reported the corresponding molybdenum 17-electron mixed-sandwich metallocene, CpMo(η^6-C_6Ph_6) (**137**), generated from the thermolysis of CpMo(CH_2Ph)(η^2-PhC_2Ph)[P(OMe)$_3$] and diphenylacetylene. In contrast to the three aforementioned complexes, in which the metal fragments are



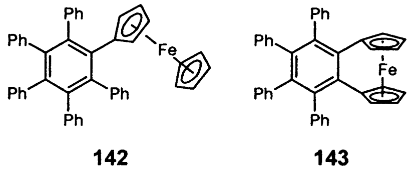
133

Scheme 26. The effectively C_{3h}-symmetric tris(tricarbonylchromium(0)) complex of 1,3,5-triphenylbenzene (**133**).



Scheme 27. The fluxional behaviour of $C_6Ph_6Cr(CO)_3$ (**134**) is rationalized in terms of the interconversion of average C_s (low T) and C_{2v} (high T) symmetric conformations, excluding the low energy oscillation of the peripheral aryl rings that interconverts enantiomers.

bound in a η^6-fashion to the central arene ring of HPB, Munakata and co-workers [200,201] have provided examples of the varied (η^1, η^2) coordination topologies of silver(I) ions around the peripheral rings of the propeller ligand, including $[Ag_4(HPB)(ClO_4)_4]$ (**138**) and $[Ag_2(HPB)(ClO_4)_2(THF)_2]$ (**139**). The collaborative efforts of Constable et al. [202] have led to the realization of yet another supramolecular utility of these six-spoked cartwheels, namely metallostars **140** comprised of hexaalkyne arms possessing multiple $\{C_2Co_2(CO)_6\}$ cluster motifs. Finally, van Koten and co-workers [148,149] have capitalized on the rigid aromatic hydrocarbon skeleton of HPB to generate multimetallic (tris)pincer compounds, such as $[C_6\{3,5\text{-}(CH_2SPh)_2\}_6C_6H_2\text{-}4\text{-}(PdCl)]$ (**141**) and analogues, with homogeneous Lewis-acid catalytic capabilities.



Scheme 29. Ferrocenyl-substituted polyarylbenzenes **142** and **143**.

In continuation of our stereochemical studies of $(C_6Ar_6)ML_n$ propeller systems with dynamic gearing potential, we have endeavoured to rationally quantify the influences of structural perturbations on the barriers to isomerization and the static geometries. Further insight may therefore be accrued by the incorporation of different sterically demanding organometallic domains. This can either be achieved by metalation procedures following the construction of the organic

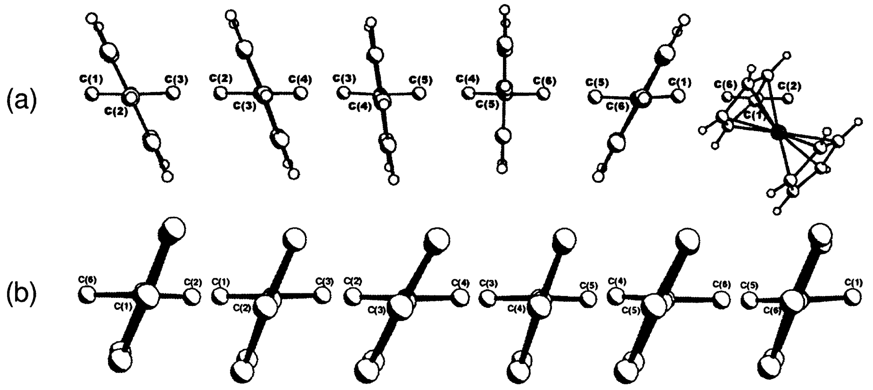
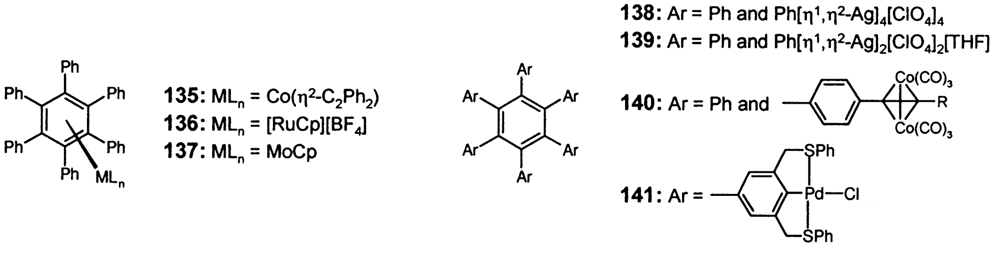
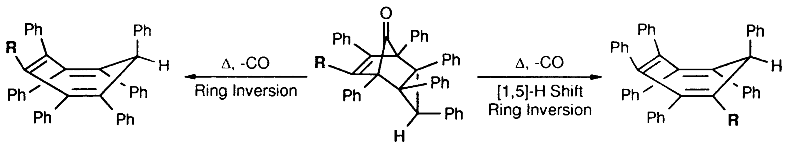


Fig. 1. Views along successive peripheral ring–central axes in: (a) C_6Ph_5Fc (**142**) (top); and (b) C_6Ph_6 (**118**) (bottom), depicting the differences in phenyl ring orientations.



Scheme 28. Hexaarylbenzenes coordinated with various early and late transition metal fragments.



146: R = Ph **147** **153:** R = Fc

Scheme 30. Isomerization processes in the cycloheptatriene derivatives **146** and **153**.

core, as in the case of **133** or **134**, or by direct linkage of the metal centres to the molecular framework. Employing the latter strategy, the preparation of ferrocenyl-substituted pentaphenylbenzene, C_6Ph_5Fc (**142**), by the Diels–Alder cycloaddition of tetraphenylcyclopentadienone (**50**) to ferrocenylphenylacetylene and subsequent decarbonylation of the intermediate bicyclic ketone, was reported by Rausch and Siegel [203] in 1978. We elected to synthesize **142**, for which no structural or dynamic data were available, via a complementary Diels–Alder approach involving diphenylacetylene and the versatile synthon 3-ferrocenyl-2,4,5-triphenylcyclopentadienone (**51**) [204] (Scheme 29).

From the solid state structure of **142** it is evident that the peripheral aryl substituents *do not* adopt a regular propeller type conformation, but instead exhibit an incremental progression of twist angles (51, 64, 70, 81, 89 and 120°, from C(1) to C(6), respectively) relative to the central ring (Fig. 1) [205]. These values are significantly different from those observed in **118**, as well as in the molecular structure of the related 1,1′-(tetraphenyl-*o*-phenylene)ferrocene (**143**), reported by Yasufuku et al. [206]. In this [2]ferrocenophane, the outer phenyl groups adopt interplanar angles of 57, 65, 62 and 66°, whereas the Cp rings are internally constrained at 91 and 95° to the central ring. It is tempting to postulate that the 'domino' phenomenon in **142** is a manifestation of the low energy oscillation process that interconverts enantiomeric forms, but one cannot dismiss the presence of symmetry artefacts or the potential influences of crystal packing forces. Probing the fluxional behaviour of **142** by VT-NMR spectroscopy (293–188 K) has revealed a substantial reduction in the barrier to rotation of the π-complexed ring from **134** to **142**; even at the lowest attainable temperature, the interconversion process previously detailed for $(C_6Ph_6)Cr(CO)_3$ is rapid on the time-scale of observation [196].

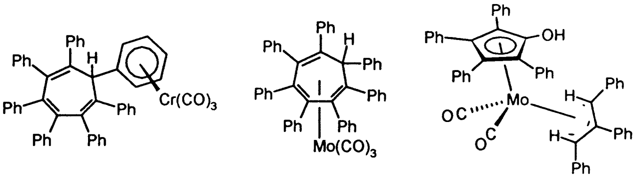
While ML_n desymmetrizes the π system by rendering the arene faces nonequivalent, the utility of this method is limited by the degree to which the presence of the metal fragment disturbs the parent compound's stereodynamics [182]. Evidently, the steric influence imparted by any moiety (organometallic or otherwise) must be reflected in both of the relevant dimensions in order to effect hindrance to rotation [205]. Using $(C_6Ph_6)Cr(CO)_3$ (**134**) and C_6Ph_5Fc (**142**) as calibration points, we continue to explore the subtleties associated with structural variability and multiple arene substitution and ligation. In the identification of possible synthetic targets, there is a plethora of conjugated dienes (substituted cyclopentadienones) and dienophiles (symmetrical or non-symmetrical alkenes, alkynes) which may be considered for the Diels–Alder cycloaddition required to generate the polyarylated benzene derivatives. Towards this end, some of our current research directives are featured in Section 6.

5. Persubstituted cycloheptatrienyls: C_nR_n, where $n = 7$

In the development and modification of sterically demanding peralkylated and perarylated $C_nR_n^{x\pm}$ ($n = 5$–7) templates and their diverse applications in organotransition metal chemistry, π-coordinated cycloheptatrienyl systems have evaded experimentalists until just recently. This is perhaps surprising, given that the parent aromatic cations, $C_7Me_7^+$ **143** and $C_7Ph_7^+$ (**144**), have been known for decades [207,208]. As one of the most stable carbenium species (pK_a value of 4.75 [209]), the tropylium cation ($C_7H_7^+$) **145** itself has been incorporated as part of host–guest architectures [210–212], intramolecular charge-transfer complexes [213,214], extended macrocyclic frameworks [215,216] and metal complexes [217–219].

5.1. Heptaarylcycloheptatriene and -enyl complexes

Heptaphenylcycloheptatriene, C_7Ph_7H (**146**), originally synthesized by Battiste in 1961 [220], was structurally characterized only in 1995 by Chao et al. of our research laboratory [221], as was its precursor, the tricyclic Diels–Alder adduct (**147**) of tetraphenylcyclo-



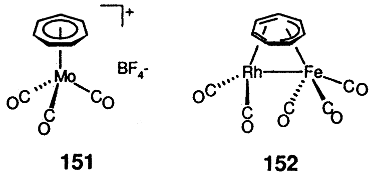
146(Cr) **149** **150**

Scheme 31. Various modes of metal coordination anticipated (ex. **149**) and realized (**146**(Cr), **150**) from the reactions of either C_7Ph_7H (**146**) with $Cr(CO)_8$ or **147** with $M(CO)_6$.

pentadienone (**50**) and 1,2,3-triphenylcyclopropene (**148**) (Scheme 30). Studies of tolyl derivatives of **146** corroborated the intermediacy of a boat isomer in which the phenyl substituent at the sp^3 position occupies the sterically hindered pseudo-equatorial site prior to a conformational ring inversion that reorients it pseudo-axially, impeding further [1,5]-suprafacial sigmatropic hydrogen shifts [221]. Despite the reduced steric interactions in the conformer **146**, the rings alpha, beta and gamma to the methine hydrogen, with solid state dihedral angles of ca. 50, 63 ± 4, and 92/87°, respectively, are sufficiently encumbered so as to engender slowed rotation in solution. An evaluation of the ^1H- and ^{13}C VT-NMR spectra yielded rotational barriers of 11.0 ± 0.5 (beta ring), ca. 9.1 (gamma ring) and ca. 9 kcal mol^{-1} (alpha ring), thereby excluding a correlated interconversion pathway. The reaction of **146** with metal carbonyls, notably $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_3(CH_3CN)_3$, furnished a definitive, stable product in the first case only (Scheme 31). As opposed to η^6-coordination to the cycloheptatriene, the metal moiety in **146(Cr)** was found to attach to the unique sp^3-based aryl ring, either directly because of steric accessibility or indirectly as a result of hydrogen migration after ligation. Unfortunately, a comparison of the fluxional properties of **146** and **146(Cr)** was not possible owing to low yields. Adopting a slightly different approach, we attempted to complex a metal tricarbonyl fragment to the open face of the tricyclic ketone **147**, in the expectation that subsequent metal-assisted cyclopropane ring opening and decarbonylation would yield the hexahapto species **149**. Instead, treatment of **147** with hexacarbonylmolybdenum(0) yielded the retro Diels–Alder product $(\eta^5\text{-}C_5Ph_4OH)Mo(CO)_2(C_3Ph_3H_2)$ (**150**), as confirmed by mass spectrometric, NMR spectroscopic and X-ray crystallographic analyses. In relation to Section 3, it was demonstrated that **150** may be directly prepared from the heating of $Mo(CO)_6$, C_3Ph_3H and tetracyclone.

In accordance with an earlier report [208], the salt $C_7Ph_7^+Br^-$ (**144(Br$^-$)**) was generated via a hydride abstraction of C_7Ph_7H (**146**) by bromine, and subsequently modified by counterion exchange [222]. The solid state characterization of the heptaphenylcycloheptatrienyl cation, $C_7Ph_7^+$ (**144**), in $[C_7Ph_7^+][CF_3CO_2^-]\cdot 2CF_3CO_2H$ represents the *first non-disordered* structure solution of a *free* tropylium cation and ended a formidable, three-decade long crystallographic quest. In the molecular structure the central C_7-ring of the 6-π electron propeller adopts a shallow boat conformation (defined by interplanar angles of 13 (ϕ) and 11° (γ)), with the peripheral phenyl groups possessing an average dihedral angle of 80° relative to the plane containing their attached central ring carbon and neighbouring ring atoms (Fig. 2). This geometry was rationalized by semi-empirical (AM1 Hamiltonian) calculations, and indicates a compromise between steric congestion and the fractional loss in aromaticity as the central ring distorts from planarity. The existence of an energetically accessible gas-phase D_{7h} minimum, only 0.2 kcal mol^{-1} above the C_1 ground-state isomer, attests to the conformational flexibility of this propeller and advances the possibility that a planar crystal form of **144** may eventually be realized. It also supports the dynamic symmetry that is observed in both the ^1H- and ^{13}C-NMR regimes (cf. $C_5Ph_5^-$ **16** and C_6Ph_6 (**118**)).

In principle, enhanced π-delocalization in $C_7Ph_7^+$ may be achieved by complexation of the perphenylated cation with selected transition metal fragments [223–227]. Whereas numerous $(C_7H_7)ML_n$ derivatives have been reported [218], including the mononuclear and dinuclear systems, $[(\eta^7\text{-}C_7H_7)Mo(CO)_3]^+[BF_4]^-$ (**151**) and μ-(1-3-η:4-7-η-C_7H_7)$Fe(CO)_3Rh(CO)_2$[Fe–Rh] (**152**), respectively (Scheme 32) [228,229], our attempts to coordinate a metal moiety to the central C_7-ring in heptaphenylcycloheptatriene and -enyl salts have thus far been thwarted. Therefore, to avoid any steric impediments that may be associated with metal binding,



Scheme 32. Two recent examples (**151**, **152**) of cycloheptatrienyl metal complexes.

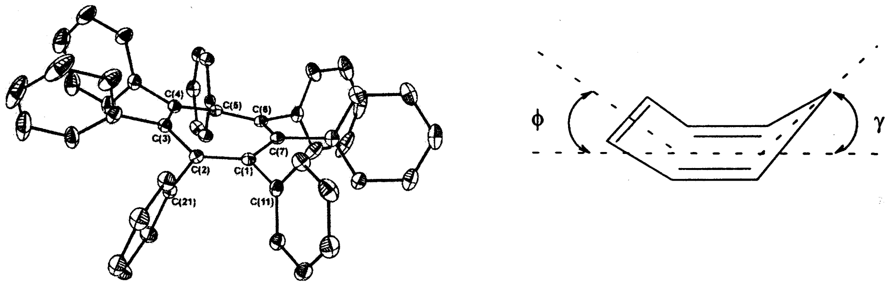


Fig. 2. Structure of heptaphenylcycloheptatrienyl cation **144** (with hydrogen atoms omitted for clarity), presenting the boat conformation of the central ring.

we elected to incorporate the organometallic fragment as part of the molecular periphery. The Diels–Alder addition of **148** to 3-ferrocenyl-2,4,5-triphenylcyclopentadienone (**51**) yielded, upon thermolysis, C_7Ph_6FcH (**153**) [205]. The characteristic puckered geometry of the central seven-membered ring and the canting of peripheral aryls are apparent from the X-ray crystal structure solution of **153**, which further reveals that the ferrocenyl substituent is positioned at C(1), adjacent to the sp^3-hybridized carbon of the CHPh unit (Scheme 30). Such an isomer, in which the Fc moiety resides in the least hindered locale (cf. **153** to **146**), must have arisen as the result of a [1,5]-hydrogen shift after decarbonylation but prior to ring inversion. In probing for the possibility of restricted rotation in **153**, definitive coalescence data could only be extracted for phenyls 7 (9.3 ± 0.5 kcal mol^{-1}) and 4 (10.1 ± 0.5 kcal mol^{-1}), although the other rings clearly experienced slowed libration within the spectral window examined. Subsequent efforts to generate the corresponding 'metal-stabilized' tropylium cation, $C_7Ph_6Fc^+$ (**154**), from the precursor **153**, unexpectedly resulted in the formation of the ferricinium complex, $[C_7Ph_6FcH]^+[SbCl_6]^-$ (**155**). While its paramagnetic nature precluded dynamic NMR studies of this complex, X-ray crystallographic characterization of **155** confirmed that the boat structure of the cycloheptatriene was maintained.

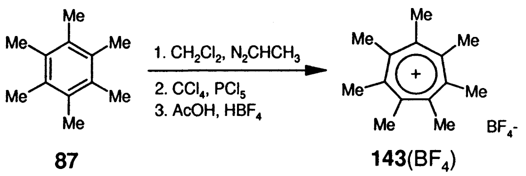
To date, attempts to desymmetrize $C_7Ph_7^+$ (**144**) by metal complexation and therefore study stereodynamic phenomena within this propeller system have not been entirely successful. To extend our quantification of rotational barriers beyond the geometry-constrained cycloheptatriene precursors, Gust's [47,48] labelling approach may be adopted. Indeed, cycloheptatrienyl derivatives bearing substituents in the ortho or meta positions of adjoining aryl rings should give rise to distinguishable stereochemical features.

5.2. *Heptaalkylcycloheptatriene and -enyl derivatives*

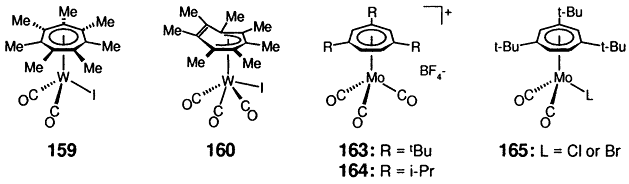
In lieu of the multistep preparation reported by Knoche in 1964 [230], an improved synthetic protocol for heptamethylcycloheptatriene **156** was introduced by Tamm et al. in 2000 [231]. The diazoethane-promoted ring expansion of hexamethylbenzene **87** afforded **156** in nearly quantitative yields (based on recovery and reuse of **87**). Hydride transfer from **156** to phosphorus pentachloride and subsequent dissolution in acetic acid/anhydride and hydrogen tetrafluoroborate furnished **143**(BF_4) (Scheme 33). The X-ray crystallographic characterization of the heptamethylcycloheptatrienyl cation **143** provides only the second solid state example of an unconstrained, persubstituted C_7R_7 platform. The static gear effect is manifested in the molecular structure of **143**, which possesses an intermeshed arrangement of methyl groups along the π-periphery of a non-planar ($\phi \approx 29$, $\gamma \approx 21°$; cf. **144** in Fig. 2) Hückel $4n+2$ system. The ground-state C_s-optimized structure ($\phi \approx 22$, $\gamma \approx 18°$) of **143** was previously estimated by Brydges and Pole of our group [222] to be almost 15 kcal mol^{-1} more stable than its planar C_{7h} conformer. The computational prediction that persubstitution of the C_7 border with n-fold rotors ($n > 2$) would induce central ring deformations is therefore validated.

Given the literature precedent for cycloheptatrienyl metal complexes of the type $[\eta^7\text{-}(C_7R_7)M(CO)_3]^+$ (**157**) or $[\eta^7\text{-}(C_7R_7)M(CO)_2X]$ (**158**) (where M = Mo, W; X = Br, I) [232,233], Tamm et al. [234] attempted analogous synthetic routes with the $C_7Me_7^+$ ligand. However, the reaction of **143**(BF_4) with *fac*-$[W(CO)_3(NEt)_3]$ in the presence of a catalytic quantity of $[Cp_2Fe][PF_6]$ and subsequent treatment of the cationic intermediate with sodium iodide did not yield $[\eta^7\text{-}(C_7Me_7)W(CO)_2I]$ (**159**), as anticipated. Instead, the stable, isolated complex was identified by spectroscopic (IR, NMR) and single crystal X-ray diffraction methods as $[\eta^5\text{-}(C_7Me_7)W(CO)_3I]$ (**160**) (Scheme 34). With its pendant double bond, the η^5-bound cycloheptatrienyl retains vestiges of its original boat conformation [231], which likely imparts unusual reactivity to **143**.

Whereas no other bonding modes have yet to be demonstrated for $(C_7Me_7)ML_n$ complexes, Tamm et al. [235] have prepared symmetrically η^7-coordinated 1,3,5-substituted cycloheptatrienyl species. Concomitant arene exchange—molybdenum tricarbonyl transfer from $[(\eta^6\text{-}p\text{-xylene})Mo(CO)_3]$ to $(1,3,5\text{-}C_7H_4R_3)BF_4$ (R = *tert*-butyl **161**; R = isopropyl **162**) produced the cationic species $[(\eta^7\text{-}1,3,5\text{-}C_7H_4R_3)Mo(CO)_3][BF_4]$ (**163**–**164**) and upon reaction with the appropriate alkali metal halide, the neutral complexes $[(\eta^7\text{-}1,3,5\text{-}C_7H_4{}^tBu_3)Mo(CO)_2X]$ (X = Cl or Br) (**165**) (Scheme



Scheme 33. Synthetic route to the hexamethylcycloheptratrienyl cation **143**, based on a ring-expansion of hexamethylbenzene (**87**).



Scheme 34. Proposed (**159**) and isolated (**160**–**165**) complexes containing the hepta- and 1,3,5-trialkylsubstituted tropylium ligands.

34). The solid state structures of both **161** and **163** reveal an effectively planar, C_s-symmetric tropylium cation, in agreement with our theoretical predictions for the related 1,3,5-trimethylcycloheptatrienyl cation [222]. Unfortunately, no experimental data pertaining to the stereodynamics of **163**–**165** were provided.

Beyond their topological interest, sterically demanding $C_7R_7^+$ molecules allow for the possibility of incorporating multimetallic fragments with markedly different spatial and electronic properties. Despite the counsel of Haywood-Farmer and Battiste in 1971 [92], there remains a paucity of information pertaining to the fluxional properties of these systems, owing in part to the belated development of their derivatization and metal coordination chemistries.

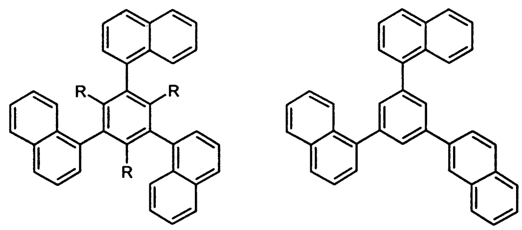
6. Current directions

6.1. Versatile synthetic templates

Systematic modification of the molecular periphery of five-, six- and seven-membered C_nR_n cyclic arrays by the introduction of 'X' pendant groups is expected to have static and dynamic conformational consequences. Our choice of 'X' is primarily dependent on appropriately asymmetric and sterically anisotropic achiral and chiral fragments which (a) possess sufficient bulk in advance of metal complexation, but have the potential to bind to metal moieties, and which (b) incorporate NMR 'signatures' for monitoring the internal fluxional processes. From among the plethora of organic residues that satisfy these conditions, we have identified the naphthalene moiety as one of several viable 'rotor' groups. Substitution at either the 1- or 2-position affords a planar, asymmetric fragment of varying steric profiles with a labelled 'phenyl edge' to distinguish multiple distal (anti) and proximal (syn) arrangements relative to the central frame. Aided by the substantial NMR chemical shift difference of the nuclei under study, we continue to probe the details of torsional motions in crowded propellers possessing rich stereochemical options.

Whereas the use of bulky naphthyl groups for the control of structure and reactivity has been established (vide infra), only a few studies have recognized the potential of these rotors in dynamic propeller and gear architectures. For instance, Lockhardt and co-workers [236,237] have designed a series of crown ethers **166** containing fluxional dinaphthyl- (Ar_2ZX_2) and phenyldinaphthyl-methane (Ar_3ZX) propeller skeletons that serve as conformational switches for the flexing of the polyether segments on the NMR time-scale. Mislow and co-workers [33] and Ito et al. [238,239] have conducted dynamic stereochemical analyses of Ar_3Z systems, providing the first demonstration of residual diastereoisomerism in the maximally labelled triarylamine, methyl-*N*-(biphenyl-2-yl)-*N*-(1-naphthyl)anthranilate (**167**) (11–12 kcal mol^{-1}; two-ring flip) and the flipping-ring-controlled enantiomerization of 1- and 2-naphthyl analogues of (tri-1-azulenyl)methyl cations (**168**) (9.8 kcal mol^{-1}; one-ring flip), respectively. Finally, Clayden and Pink [9] have devised a 'two-toothed' 1-naphthamide molecular gear that exhibits 'gated' Ar–CO and C–N rotations, while Kiefl [240] has provided ^{1}H VT-NMR evidence for correlated motions in axially chiral naphthyl ketones (Scheme 35).

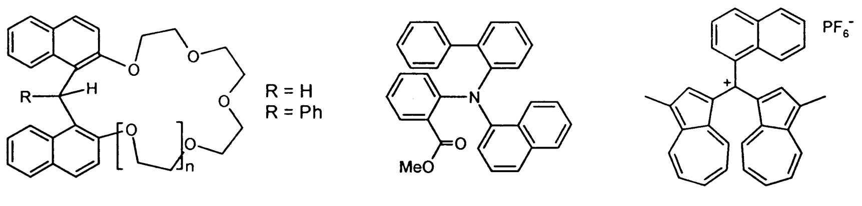
Beyond their synthetic challenges, interest in naphthyl-based C_nR_n scaffolds, particularly mono-, di- and tri-substituted benzenes, has focused on metal–ammonia reduction [241], conformeric fluorescence [242,243] and viscosity and glassy behaviour [244–246]. During early studies of factors affecting the glass transition, Magill and co-workers [244,245] claimed that 'propeller-like' 1,3,5-tris(1-naphthyl)benzene (**169**) molecules interlock in the melt, and further presumed that free rotation about the aryl-naphthyl bond does not occur. In 1996, Whitaker and McMahon [246] discounted this assertion, structurally reassigned Magill's original sample as 1,3-bis(1-naphthyl)-5-(2-naphthyl)benzene (**170**) (Scheme 36), and established rotational barriers for the 1- (12±



169: R = H
171: R = Me

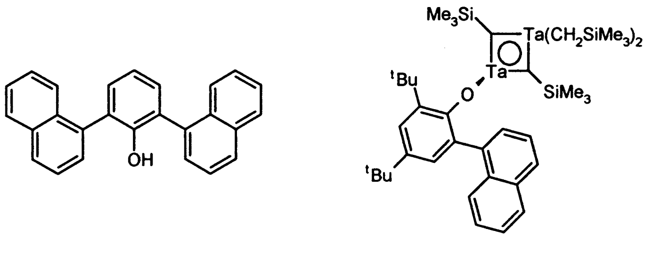
170

Scheme 36. Various tri-naphthyl-substituted benzene scaffolds.



166 **167** **168**

Scheme 35. Examples of propeller fragments incorporating naphthyl substituents.

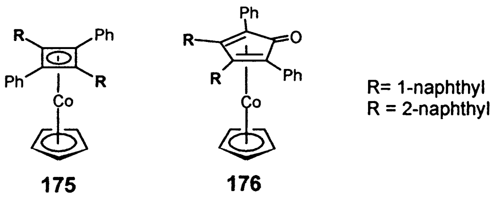


172 **173**

Scheme 37. Examples of fluxional organometallic precursors containing naphthyl moieties.

0.4 kcal mol^{-1}) and 2-naphthyl (ca. 2 kcal mol^{-1}) substituents by use of ^{13}C VT-NMR and computational methods, respectively.

With the goal of constructing a rigidly oriented, convergent tridentate metal-binding unit, Katz [247] synthesized 1,3,5-trimethyl-2,4-6-tris(1-naphthyl)benzene (**171**) and confirmed by use of dynamic NMR that isomer interconversion is sterically hindered at room temperature ($\Delta G^{\ddagger} \sim 30$ kcal mol^{-1} at 373 K). Rothwell and co-workers [248] measured the activation parameters ($\Delta G^{\ddagger} = 18 \pm 0.5$ kcal mol^{-1} at 340 K) for 2,6-bis(1-naphthyl)phenol (**172**) and estimated a higher barrier to 1-naphthyl rotation in the corresponding 2-(1-naphthyl)-4,6-di-*tert*-butylphenoxide μ-alkylidyne tantalum derivatives **173** under study. In search of chiral cyclopentadienylmetal complexes applicable to asymmetric transformations, Baker and co-workers [249] have proposed the design of chiral Cp ligands **174** asymmetrically substituted with a 1-naphthyl moiety that serves to constrain the site for metal coordination through hindered Cp–naphthyl rotation (Scheme 37).

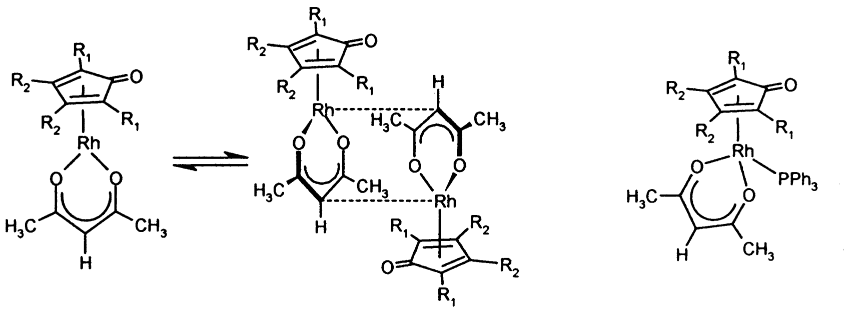


175 **176**

Scheme 38. Metal-ligated tetraaryl-cyclobutadienes **175** and -cyclopentadienones **176** bearing two 1- or 2-naphthyl substituents.

Given the relatively untapped stereochemical potential of 1- and 2-naphthyl appendages, we recently embarked on studies of organometallic derivatives of such diversely substituted cyclopentadienones. The syntheses of tetraarylcyclopentadienones bearing one to two naphthyl moieties have been detailed in the early literature [140,141,250,251], and we are aware of only one report of metal complexes comprising such ligands. In 1979, Rausch et al. [252] described the preparation and characterization of a series of (η^5-C_5H_5)Co(η^4-$C_4Ph_2R_2$) (**175**) and (η^5-C_5H_5)Co(η^4-$C_5Ph_2R_2O$) (**176**) isomers (where R = 1- or 2-naphthyl) (Scheme 38) generated in high (ca. 85%) and low (ca. 2%) isolable yields, respectively, from the reaction of an unsymmetrical acetylene and (η^5-C_5H_5)Co$(CO)_2$.

As first candidates for fluxional analyses, we earmarked the rhodium acetylacetonate derivatives (**179**–**182**) of the synthetically accessible 3,4-di(2-naphthyl)-2,5-diphenylcyclopentadienone (**177**) and 3,4-di(2-naphthyl)-2,5-di(*m*-xylyl)cyclopentadienone (**178**) (Scheme 39) [253]. As in the analogous Rh-ligated tetracyclones, **179** and **181** both crystallize as head-to-tail dimers in the solid state and undergo a rapid monomer–dimer equilibrium in solution at ambient temperature. The diastereotopic methyl groups of the acac ligand in **179** (or **181**) provide an indirect probe for hindered naphthyl rotation by use of ^{1}H- and ^{13}C VT-NMR, and upon decoalescence at 173 K (or 193 K), revealed the anticipated presence of several proximal-distal conformers (maximum of 7) with overlapping resonances. The reaction of dimeric **179** (or **181**) with triphenylphosphine afforded the monomeric species **180** (or **182**), thereby restricting the number of possible rotamers to three (distal–distal, proximal–distal, and proximal–proximal). In the ^{31}P VT-NMR regime of **180** (Fig. 3), the splitting of the ^{31}P signal was observed at 183 K, yielding a barrier to 2-naphthyl rotation of ca. 8.3 ± 0.5 kcal mol^{-1} (cf. $\Delta G^{\ddagger} = 12.5$ kcal mol^{-1} in η^4-($C_4Ph_3FcC{=}O$)Rh(acac) (**55**)). To eliminate the possibi-



179 R_1 = phenyl; R_2 = 2-naphthyl
181 R_1 = *m*-xylyl; R_2 = 2-naphthyl

180 R_1 = phenyl; R_2 = 2-naphthyl
182 R_1 = *m*-xylyl; R_2 = 2-naphthyl

Scheme 39. Rhodium complexes (**179**–**182**) of 3,4-di(2-naphthyl)-2,5-diarylcyclopentadienones.

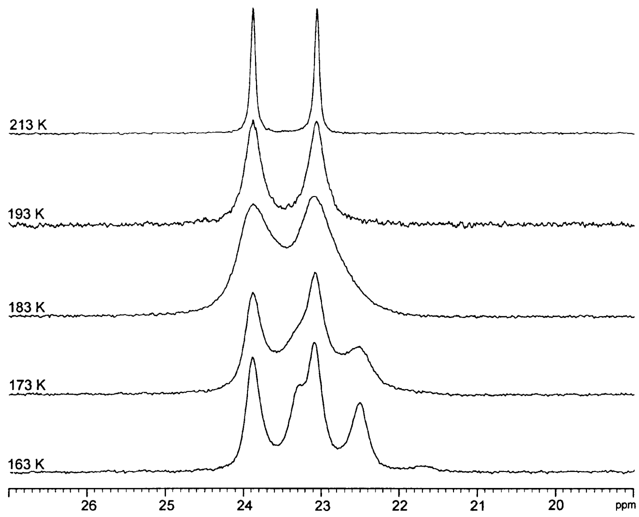
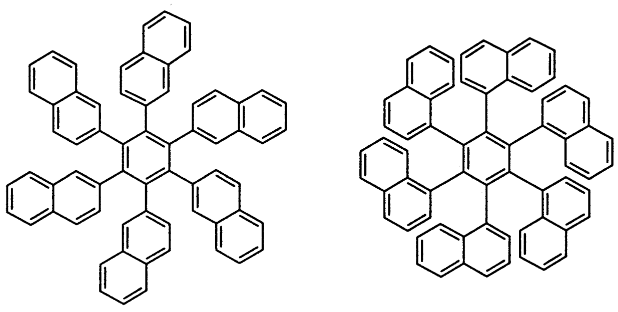


Fig. 3. ^{31}P variable temperature NMR spectra of **180** (213–163 K), demonstrating peak coalescence at 183 K as a result of restricted rotation of the naphthyl substitutents.



183 **184**

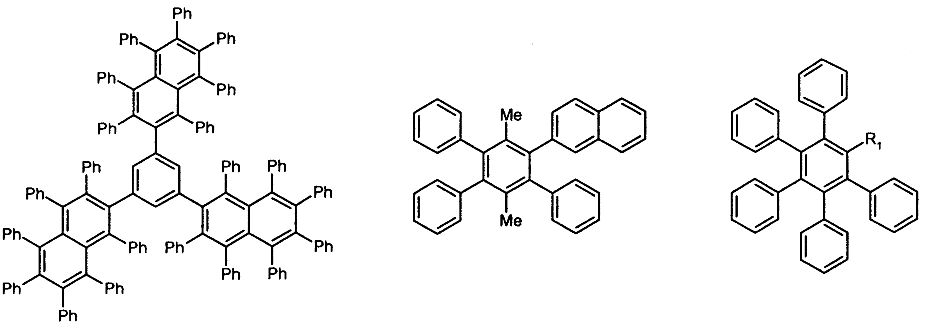
Scheme 40. Hexanaphthylbenzenes **183** and **184**, each giving rise to 128 possible stereoisomers.

lity of restricted Cp–ML$_n$ rotation as an explanation for the spectral attributes, we established the temperature-invariant (298–162 K) ^{31}P-NMR behaviour of the corresponding tetracyclone complex. As might have been predicted on the basis of comparable non-bonded repulsions of the *m*-xylyl and phenyl substituents with the 2-naphthyl moieties, the cyclopentadienone derivatives **181** and **182** demonstrate fluxional behaviour analogous to **179** and **180**.

Efforts are now directed toward the more challenging preparation of the sterically enhanced 1-naphthyl homologues and other differentially arylated systems. Such synthons are at the nucleus of C$_n$R$_n$ ($n = 5$, 6 and 7) platforms (refer to Scheme 6), including the highly sought, stereochemically complex molecular propellers **183** and **184** (Scheme 40). In the related 1,3,5-tris(heptaphenyl-2-naphthyl)benzene (**185**) described by Pascal and co-workers [191], the interconversion of the C_3 and C_1 isomers via rotation of the 2-naphthyl moiety is slow even at 413 K ($20 \leq \Delta G^{\ddagger} \geq 26$ kcal mol^{-1}). To the best of our knowledge, the 1988 report by Bhattacharyya and co-workers [251] provides the only examples of maximally arylated or alkylated benzenes incorporating naphthalene. As often is the case, no fluxional details were cited for the [4+2] Diels–Alder cycloaddition products 2′,5′-dimethyl-4′-(2-naphthyl)-6′-phenyl-*m*-terphenyl (**186**), 2′,5′,6′-triphenyl-4′-(2-naphthyl)-*m*-terphenyl (**187**) and 2′,5′,6′-triphenyl-4′-(4-methoxy-1-naphthyl)-*m*-terphenyl (**188**). We note, however, the trends in 1-naphthyl rotational barriers (12 vs. 18 vs. 30 kcal mol^{-1}) as the buttressing effects increase (H vs. OH vs. Me) in **170**, **172**, and **171**, respectively, and anticipate that reduced flexibility in systems such as **183**, **184**, **187** and **188** will give rise to particularly interesting static and dynamic conformational networks (Scheme 41).

6.2. *Computational and structure correlation analyses*

C$_n$R$_n$ molecular propellers serve as a fundamental focal point for the study of static and dynamic stereochemical phenomena associated with large, conformationally flexible molecular systems, of which proteins are the archetypal example. While NMR spectroscopy provides an expansive window for the measurement of rotational isomerism in solution, both high-resolution X-ray crystallography and quantum mechanical calcula-



185 **186**

187: R$_1$ = 2-naphthyl
188: R$_1$ = 4-MeO-1-naphthyl

Scheme 41. Highly substituted arylbenzenes (**185**–**188**) containing naphthyl substituents.

Table 1
Experimentally determined activation parameters for C_n–ML_x and C_n–R rotation in C_nR_n (R = alkyl and aryl) fragments and/or their transition metal complexes, $(C_nR_n)ML_x$

Ring	ML_n	Complex [a]	Method [b]	$\Delta G^{\ddagger}$ (C_n–ML_x) [c] (kcal mol^{-1})	$\Delta G^{\ddagger}$ (C_n–R) [c] (kcal mol^{-1})	Reference
C_5 systems						
$C_4N(Ph)$-2,5-Ph_2-3,4-(C_6H_4 *o*-Me)		**19**	A		19.9	[93]
$C_4N(Ph)$-2,5-Ph_2-3,4-(C_6H_4 *m*-Me)			A		*a* (188 K)	[93]
$C_5(CF_3)_4O$	$Fe(CO)_3$		B	11.1 ± 0.5		[119]
$C_5(CF_3)_4O$	$Ru(CO)_3$		B	12.2 ± 0.5		[119]
C_5Ph_4O	$Fe(CO)_3$	**52**	B		*a* (167 K)	[117]
C_5Ph_4O	$Ru(CO)_3$		B		*a* (206 K)	[119]
C_5Ph_4O	$Os(CO)_3$		B		*a* (213 K)	[115]
C_5Ph_4O	$Mo(CO)_2$(dppe)	**49b**	B, C	11.6 (E_a)		[118]
C_5Ph_4O	$Mo(CO)_2$(dppm)	**49a**	C	*b*		[118]
C_5Ph_3-3-(Fc)O	$Fe(CO)_3$	**53**	B		12.5 ± 0.5	[117]
C_5Ph_3-3-(Fc)O	Rh(acac)	**55**	B		12.5 ± 0.5	[117]
C_5Ph_3-3-(Fc)-1-(OH)-1-(C_6F_5)		**57**	D		19 ± 1	[117]
C_5Ph_2-3,4-(C_6H_4 *o*-Me)$_2$O		**17**	A		21.8 ± 0.4	[92]
C_5Ph_2-2-(Ph,H)-3-(Fc,C_6F_5)O		**58**	D		21 ± 1	[120]
C_5-2,4-(mesityl)$_2$-3,5-Ph_2O	CoCp	**48**	A		Mesityl: *b* (303 K)	[79]
C_5Ph_2-3,4-(2-naphthyl)$_2$O	Rh(acac)	**177**	A		*b* (163 K)	[253]
C_5Ph_2-3,4-(2-naphthyl)$_2$O	Rh(acac)(PPh_3)	**178**	C		8.3	[253]
C_5-2,5-(C_6-3,5-Me_2H_3)$_2$-3,4-(2-naphthyl)$_2$O	Rh(acac)	**179**	A		*b* (163 K)	[253]
C_5-2,5-(C_6-3,5-Me_2H_3)$_2$-3,4-(2-naphthyl)$_2$O	Rh(acac)(PPh_3)	**180**	C		*b* (163 K)	[253]
$C_5(C_6H_4$-*o*-Me$)_4O$		**21**	A, B		α-ring: ∼15 β-ring: ∼20	[95], [96]
$C_5^iPr_5$	$Mo(CO)_3Me$	**71**	A		13.2	[125]
$C_5^iPr_5$	Co(Cp)PF_6	**69**	A		17.1 ± 0.2	[124]
C_5(neopentyl)$_5$	Co(Cp)PF_6	**70**	A		19.4 ± 0.2	[124]
$C_5(SiMe_2H)_5$	$Mn(CO)_3$	**72**	A		∼10	[126]
$[C_5^iPr_4H]_2$	Fe		A	13.6		[258]
$C_5(C_6F_5)_4H$	$Mn(CO)_3$	**61**	D		Outer ring: 8.0 β-ring: *b*	[121]
$C_5(C_6F_5)_4H$	$Re(CO)_3$	**62**	D		α-ring: 8.0 β-ring: *b*	[121]
$[C_5$-1,2,3-$(C_6F_5)_3H_2]_2$	Fe	**65**	A, D		Cp–Cp: *b* (223 K) Cp–outer C_6F_5: 9.2 Cp–inner C_6F_5: *a* (353 K)	[122]
$[C_5$-1,2,4-$(C_6F_5)_3H_2]_2$	Fe	**64**	A, D		Cp–Cp: 11.4 Cp–vicinal C_6F_5: *b* (223 K)	[122]
C_5-1,2,4-$(C_6F_5)_3H_2$	$Re(CO)_3$	**63**	A, D		Cp–vicinal C_6F_5: 8.4 Cp–isolated C_6F_5: *a* (173 K)	[122]
$[C_5$-1,2,4-$(CMe_3)_3H_2]_2$	Fe		A, B	13.2		[259]
$[C_5$-1,2,4-$(CMe_3)_3H_2]_2$	Ru		A, B	9.5		[259]
$[C_5$-1,2,4-$(CMe_2Et)_3H_2]_2$	Fe		A, B	13.6		[259]
$[C_5$-1,2,4-$(CMe_2Et)_3H_2]_2$	Ru		A, B	10.9		[259]
C_5Ph_5	Fe(CO)(COMe)(PMe_2Ph)	**46**	B	8.7 ± 0.3 (E_a)	11.7 ± 0.3 (E_a)	[113]
C_5Ph_5	Fe(CO)(PMe_3)Br	**26**	A, B		*a* (298 K)	[101]
C_5Ph_5	Fe(CO)(COEt)(PMe_3)		A, B		*a* (298 K)	[101]
C_5Ph_5	Fe(CO)(PMe_3)(Et)		A, B		*a* (298 K)	[101]
C_5Ph_5	Fe(CO)(PMe_3)(COH)		A, B		*a* (298 K)	[101]
C_5Ph_5	Fe(CO)(PMe_2Ph)(COEt)	**45**	B		*b* (163 K)	[101]
C_5Ph_5	$Mo(CO)_2L$ L = 2,3-bis(diphenylphosphino) maleic anhydride	**44**	E	*b*		[260]

Table 1 (*Continued*)

Ring	ML_n	Complex [a]	Method [b]	$\Delta G^{\ddagger}$ ($\mathrm{C}_n-\mathrm{ML}_x$) [c] (kcal mol^{-1})	$\Delta G^{\ddagger}$ ($\mathrm{C}_n-\mathrm{R}$) [c] (kcal mol^{-1})	Reference
$\mathrm{C_5Ph_5}$	$\mathrm{Ru(CO)(PPh_3)Br}$	**36**	A, B		*b* (298 K)	[88]
$\mathrm{C_5Ph_4H}$	$\mathrm{Mo(CO)_2L}$ L = 2,3-bis(diphenylphosphino) maleic anhydride		E		9.1	[261], [112]
$\mathrm{(C_5Ph_4H)_2}$	Fe	**40**	A	*a* (178 K)	β-ring: 9 ± 1	[108]
$\mathrm{(C_5Ph_4H)_2}$	$\mathrm{TiCl_2}$	**41**	A		β-ring: 9.8 ± 0.2	[109]
$\mathrm{(C_5Ph_4H)_2}$	Ru	**42**	A		*b* (est. ∼9)	[110]
$\mathrm{C_5Ph_4\text{-}1\text{-}(OH)\text{-}1\text{-}(C_6F_5)}$		**56**	B		20 ± 1	[120]
$\mathrm{2\text{-}(C_5Ph_4)\text{-}1\text{-}Cp\text{-}1\text{-}Ph\text{-}(CH_2)_2}$	$\mathrm{ZrCl_2}$	**43**	A		α-ring: *b* (213–233K) β-ring: *b* (233K)	[111]
$\mathrm{C_5Ph_4\text{-}1\text{-}[C_6\text{-}2,6\text{-}(OCH_3)_2H_3]\text{-}1\text{-}OH}$			B		20.8	[262]
$\mathrm{C_5Ph_4\text{-}1\text{-}[C_6\text{-}2,6\text{-}(OCH_3)_2H_3]\text{-}1\text{-}OMe}$			B		20.9	[262]
$\mathrm{C_5Ph_4[C_6\text{-}2,5\text{-}(OMe)_2H_3]}$	$\mathrm{Mo(CO)_3Br}$	**39**	A	*b* (260 K)	*b* (260 K)	[100]
$\mathrm{C_5Ph_4[C_6\text{-}2,5\text{-}(OMe)_2H_3]}$	$\mathrm{Mo(CO)_3PPh_4}$		A		*b* (260 K)	[100]
$\mathrm{C_5Ph_4[C_6\text{-}2,5\text{-}(OMe)_2H_3]}$	$\mathrm{MoO_2Br}$	**38**	A	*a*	16.4	[87]
$\mathrm{C_5Ph_4[C_6\text{-}2,5\text{-}(OMe)_2H_3]}$	$\mathrm{MoO_2(OR)}$ R = Me, Et, ^{i}Pr, ^{t}Bu	**22**	A		*a* (298 K)	[87]
$\mathrm{(C_5Ph_4[C_6\text{-}2,5\text{-}(OMe)_2H_3])_2}$	$\mathrm{Mo_2Br_2(CO)_2}$	**24**	A	*b* (260 K)	*b* (260 K)	[100]
$\mathrm{(C_5Ph_4[C_6\text{-}2,5\text{-}(OMe)_2H_3])_2}$	$\mathrm{Mo_2Br_4}$	**25**	A	*b* (260 K)	*b* (260 K)	[100]
$\mathrm{C_5Ph_4[C_6\text{-}3,5\text{-}(Me)_2H_3]}$	$\mathrm{Fe(CO)(PMe_3)Br}$	**47**	A, B	*b* (173 K)	*a* (173 K)	[113]
$\mathrm{[C_5\text{-}1,3\text{-}Ph_2H_3]_2}$	Fe		A, B	*a* (173 K)	*a* (173 K)	[259]
$\mathrm{C_6}$ systems						
$\mathrm{C_6Me_6}$		**87**	F		1.0	[165]
$\mathrm{C_6Me_6}$	$\mathrm{Cr(CO)_2(PPh_3)}$		B	*a* (158 K)	*a* (158 K)	[263]
$\mathrm{C_6Me_6}$	$\mathrm{Fe(CO)(SiCl_3)_2}$		A,B	*a* (153 K) (≤ ∼5.3)		[264]
$\mathrm{C_6Me_4\text{-}1,2\text{-}(neopentyl)_2}$			A, B		16.2	[169]
$\mathrm{C_6Me_4\text{-}1,2\text{-}(neopentyl)_2}$	$\mathrm{Cr(CO)_3}$		A, B		12	[169]
$\mathrm{C_6\text{-}2,3,5,6\text{-}Me_4\text{-}1,4\text{-}(COCCl_3)_2}$			A		*B*	[265]
$\mathrm{C_6\text{-}2,3,5,6\text{-}Me_4\text{-}1,4\text{-}(COCBr_3)_2}$			A		*B*	[265]
$\mathrm{C_6\text{-}2,4,5,6\text{-}Me_4\text{-}1,3\text{-}(COCCl_3)_2}$			A		*B*	[265]
$\mathrm{C_6\text{-}2,4,5,6\text{-}Me_4\text{-}1,3\text{-}(COCBr_3)_2}$			A		*B*	[265]
$\mathrm{C_6\text{-}2,4,6\text{-}Me_3\text{-}1,3\text{-}(COCCl_3)_2H}$			A		*A*	[265]
$\mathrm{C_6\text{-}2,4,6\text{-}Me_3\text{-}1,3\text{-}(COCBr_3)_2H}$			A		*B*	[265]
$\mathrm{C_6Et_6}$		**88**	F		11.8	[173]
$\mathrm{C_6Et_6}$		**88**	G		17.8	[266]
$\mathrm{C_6Et_6}$	$\mathrm{Cr(CO)_3}$	**94**	B		11.5 ± 0.6	[173]
$\mathrm{C_6Et_6}$	$\mathrm{Cr(CO)_2PMe_3}$		C		7.8–8.9	[267], [268]
$\mathrm{C_6Et_6}$	$\mathrm{Cr(CO)_2PEt_3}$		B, C		8.4–8.8	[268]
$\mathrm{C_6Et_6}$	$\mathrm{Cr(CO)_2PPh_3}$	**96**	B	*a**, *a* (158 K)**		*[180], **[263]
$\mathrm{C_6Et_6}$	$\mathrm{Cr(CO)_2P(OPh)_3}$		C		8.3–9.3	[268]
$\mathrm{C_6Et_6}$	$\mathrm{Cr(CO)_2CS}$	**97**	B	9.5	∼11.5	[180]
$\mathrm{C_6Et_6}$	$\mathrm{[Cr(CO)_2NO][BF_4]}$	**100**	B	9.5	∼11.5	[180]
$\mathrm{C_6Et_6}$	$\mathrm{Cr(CO)_2(maleic\ anhydride)}$		B		*b* (153 K)	[268]
$\mathrm{C_6Et_6}$	$\mathrm{[Cr(CO)(CS)(NO)][BF_4]}$	**99**	B	9.5	∼11.5	[180]
$\mathrm{[C_6Et_6]_2}$	$\mathrm{[Cr(CO)_2]_2(N_2)}$		B		11.0	[269]
$\mathrm{C_6Et_6}$	$\mathrm{[Fe(C_5H_5)][PF_6]}$		B		8.4–9.2	[178]
$\mathrm{C_6Et_6}$	$\mathrm{Mo(CO)_3}$	**95**	B		11.6 ± 0.2	[173]
$\mathrm{C_6Et_6}$	$\mathrm{Mo(CO)_2(CS)}$		B		*B*	[270]
$\mathrm{C_6Et_6}$	$\mathrm{Mo(CO)_2PEt_3}$		C		8.2–8.9	[268]
$\mathrm{C_6Et_6}$	$\mathrm{Mo(CO)_2(maleic\ anhydride)}$		B		8.5	[268]
$\mathrm{C_6Et_6}$	$\mathrm{[Ru(C_5H_5)][BF_4]}$		B		9.4	[198]
$\mathrm{C_6Et_5H}$		**105**	A, B		9.2 ± 0.1	[184]
$\mathrm{C_6Et_5Br}$		**106**	A, B		10.2 ± 0.1	[184]
$\mathrm{C_6Et_5(OCOMe)}$		**107**	A, B		9.4 ± 0.1	[184]
$\mathrm{C_6Et_5(OCOPh)}$		**108**	A, B		9.2 ± 0.1	[184]
$\mathrm{C_6Et_5(C_6Et_5)}$		**109**	B		8.6 ± 0.5	[271]
$\mathrm{C_6Et_5(COMe)}$		**110**	A, B		*a* (190 K)	[184]
$\mathrm{C_6Et_5(COMe)}$	$\mathrm{Cr(CO)_3}$	**98**	A, B	8.5–9.5	*b* (173 K)	[179]
$\mathrm{C_6Et_4\text{-}1,4\text{-}(Br)_2}$		**111**	A		9.5 ± 0.3	[185]
$\mathrm{C_6Et_4\text{-}1,4\text{-}(CH_2NHCOMe)_2}$		**112**	A		11.0 ± 0.3	[185]
$\mathrm{C_6Et_4\text{-}1,4\text{-}[(CH_2)_2CMe_3]_2}$		**104**	A		11.2 ± 0.3*	*[185], **[182]

Table 1 (*Continued*)

Ring	ML$_n$	Complex [a]	Method [b]	$\Delta G^{\ddagger}$ (C_n–ML_x) [c] (kcal mol^{-1})	$\Delta G^{\ddagger}$ (C_n–R) [c] (kcal mol^{-1})	Reference
					11.8 ± 0.3**	
C_6Et_4-1,4-[(CH$_2$)$_2$COCMe$_3$]$_2$		**101**	A		11.3 ± 0.3	[185], [181]
C_6Et_4-1,4-[(CH$_2$)$_2$NO$_2$]$_2$		**113**	A		11.2 ± 0.3	[185]
C_6Et_4-1,4-(CH$_2$Cl)$_2$		**114**	A		11.5 ± 0.3	[185]
C_6Et_4-1,4-(CH$_2$OMe)$_2$		**103**	A		9.4 ± 0.3* 8.9 ± 0.3**	*[185], **[182]
C_6Et_4-1,4-(CH$_2$SMe)$_2$		**115**	A		11.1 ± 0.3	[185]
C_6Et_4-1,4-(CH$_2$CN)$_2$		**116**	A		9.3 ± 0.3	[185]
C_6Et_4-1,4-(CH$_2$NH$_2$)$_2$		**117**	A		10.4 ± 0.3	[185]
C_6Et_4-1,4-[(CH$_2$)$_2$COCMe$_3$]$_2$	Cr(CO)$_3$	**101(Cr)**	B	9.5	11.5	[181]
C_6Et_4-1,4-[(CH$_2$)$_2$COCMe$_3$]$_2$	Mo(CO)$_3$	**101(Mo)**	B	6.7 ± 0.5	11.4 ± 0.5	[272]
C_6Et_4-1,4-(OMe)$_2$		**102**	A, B		7.7 ± 0.3	[182], [185]
C_6Et_4-1,4-(OMe)$_2$	Cr(CO)$_3$	**102(Cr)**	A, B		6.6 ± 0.3	[182]
C_6Et_4-1,4-(CH$_2$OMe)$_2$	Cr(CO)$_3$	**103(Cr)**	A, B		9.4 ± 0.3	[182]
C_6Et_4-1,4-(neohexyl)$_2$	Cr(CO)$_3$	**104(Cr)**	A, B		11.2 ± 0.3	[182]
C_6-3,4,5,6-(Et)$_4$-1,2-(^{i}Pr)$_2$			A, B		^{i}Pr: 16.6 ± 0.3	[273]
C_6Et_3-2,4,6-[CH$_2$(TMS)]$_3$			B		*a* (145 K)	[274]
C_6Et_3-2,4,6-[CH$_2$(TMS)]$_3$			F		Et: 12.8 CH$_2$(TMS): 17.2	[270]
C_6Et_3-2,4,6-[CH$_2$(TMS)]$_3$	Mo(CO)$_3$		B		*a* (153 K)*, (141 K)**	*[274], **[270]
C_6Et_3-2,4,6-[CH$_2$(TMS)]$_3$	Mo(CO)$_2$(CS)		B	9.3		[270]
C_6Et_3-2,4,6-[CH$_2$(TMS)]$_3$	Mo(CO)$_2$(η^2-*cis*-cyclooctene)		B	8.9		[270]
C_6Et_3-2,4,6-[CH$_2$(TMS)]$_3$	Mo(CO)$_2$PPh$_3$		B	~ 8.4*, 7.9**	*b* (153 K)*, 9.2**	*[274], **[270]
C_6-5,6-Et$_2$-1,2,3,4-(^{i}Pr)$_4$			A, B		Et: 11.9 ± 0.3 ^{i}Pr: 17.2 ± 0.3	[273]
C_6-1,2-(^{c}Pr)$_2$-3,4,5,6-(^{i}Pr)$_4$ ^{c}Pr = cyclopropyl			A, B		^{c}Pr: 10.9 ± 0.5 ^{i}Pr: 17.4 ± 0.3	[273]
C_6-1,2-(^{i}Pr)$_2$-3,4,5,6-(^{c}Pr)$_4$			A, B		^{c}Pr: 9.9 ± 0.5 ^{i}Pr: 12.7 ± 0.3	[273]
C_6-1,2,4-(^{i}Pr)$_3$-3,5,6-(^{c}Pr)$_3$			A, B		*b* (183 K)	[273]
C_6-1,2-(1-CH$_2$CH$_2$Br)$_2$ (^{i}Pr)$_4$		**83**	A		$\geq$ 24	[160]
C_6(CH$_2$CH$_2$Br)$_5$[C_6(CH$_2$CH$_2$Br)$_5$]			B		12.5	[275]
C_6(^{n}Pr)$_6$	Cr(CO)$_2$(PPh$_3$)		A	*a* (158 K)	*a* (158 K)	[263]
C_6(^{i}Pr)$_6$		**81**	A		$\geq$ 22	[157]
C_6(^{i}Pr)$_6$		**81**	F		35	[157]
C_6(CHCl)$_5$Cl			A		19.8, 20.3	[276]
C_6(SiMe$_2$H)$_6$		**82**	F		15.7	[159]
C_6(SiMe$_2$H)$_6$	Cr(CO)$_3$	**82(Cr)**	A		14.2	[159]
C_6Ph_6	Cr(CO)$_3$ Peripheral ring	**134**	B		12.2 ± 0.2	[196]
C_6(CH$_2$CH$_2$Ph)$_6$			A		*a* (181 K)	[277]
C_6(CH$_2$CH$_2$Ph)$_6$	[(C$_5$H$_5$)Fe][PF$_6$]		A		*a* (181 K)	[277]
C_6Ph_5Fc		**142**	A, B		*a* (188 K)	[205]
$C_6Ph_nPy_{6-n}$ Py = 2-pyridyl			A, B		*a* (343–423 K)	[278]
C_6Ph_4-1,2-(C$_6$H$_4$ *o*-Me)$_2$		**20**	A		38	[47]
C_6Ph_4-1-(C$_6$H$_4$ *o*-OMe)-2-(C$_6$H$_4$ *o*-Me)		**119**	A		33	[47]
C_6Ph_4-1,2-(C$_6$H$_4$ *m*-Me)$_2$		**122**	A		17.0	[48]
C_6Ph_4-1,2-(C$_6$H$_4$ *m*-OMe)$_2$		**121**	A		17.1	[48]
C_6Ph_3-1,2-(C$_6$H$_4$ *m*-Me)$_2$-5-H		**123**	A		15.5	[48]
C_6Ph_3-1,2-(C$_6$H$_4$ *m*-Me)$_2$-5-CHMe$_2$		**124**	A		16.8	[97]
C_6Ph_3-1,2-(C$_6$H$_4$ *m*-Me)$_2$-5-Me		**125**	A		16.2	[97]
C_6Ph_3-1,2-(C$_6$H$_4$ *m*-Me)$_2$-5-Et		**126**	A		16.1	[97]
C_6Ph_3-1,2-(C$_6$H$_4$ *m*-Me)$_2$-5-CH(OH)Me		**127**	A		16.4	[97]
C_6Ph_3-1,2-(C$_6$H$_4$ *m*-Me)$_2$-5-Cme$_3$		**128**	A		18.7	[97]
C_6-1,3,5-Ph$_3$H$_3$	Cr(CO)$_3$ Central ring	**130**	A, B		*a* (183 K)	[192]
C_6-1,3,5-Ph$_3$H$_3$	Cr(CO)$_3$ Peripheral ring	**131**	A, B		*a* (183 K)	[192]

Table 1 (*Continued*)

Ring	ML_n	Complex [a]	Method [b]	$\Delta G^{\ddagger}$ (C_n–ML_x) [c] (kcal mol^{-1})	$\Delta G^{\ddagger}$ (C_n–R) [c] (kcal mol^{-1})	Reference
C_6-1,3,5-Ph_3H_3	$[Cr(CO)_3]_2$ Peripheral ring	**132**	A, B		*a* (183 K)	[192]
C_6-1,3,5-Ph_3H_3	$[Cr(CO)_3]_3$ Peripheral ring	**133**	A, B		*a* (183 K)	[192]
C_6Ph_2-1-(C_6H_4 *o*-Me)-2-(C_6H_4 *o*-OMe)-3-(C_6H_4 *o*-Me)-4-(C_6H_4 *m*-Me)		**120**	A		33	[48]
C_6-3,4-Ph_2-1-(C_6H_4 *m*-OMe)-2-(C_6H_4 *m*-Me)-5-(C_6H_4 *m*-Me)-6-H			A		*a* (188 K)	[48]
C_6H_3-1,3,5-(C_6-2,5,6-Ph-3,4-$(PhOMe)_2)_3$		**129**	A		18.9	[191]
C_6H_3-1,3,5-(2-$C_{10}Ph_7)_3$		**181**	B		$26 > \Delta G^{\ddagger} > 20$	[191]
C_6-1,3,5-(1-naphthyl)$_3H_3$		**169**	B		12.0 ± 0.4	[246]
C_6-1,3-(1-naphthyl)$_2$-5-(2-naphthyl)H_3		**170**	B		1-Naphthyl: 12.0 ± 0.4 2-Naphthyl: < 9	[246]
C_6-1,3,5-Me_3-2,4,6-(1-naphthyl)$_3$		**171**	A, B		~ 30	[247]
C_6Ph_2-1,2-(C_6H_4 *o*-Me)$_2$-4,5-$(H)_2$		**18**	A		> 25.6	[92]
C_6-1-(OH)- 2,6-(1-naphthyl)$_2H_3$		**172**	A, B		18.0 ± 0.5	[248]
C_6-1-(O)-2-(1-naphthyl)-4,6-$(^tBu)_2H_2$	$Ta_2(\mu\text{-}CSiMe_3)_2$ $(CH_2SiMe_3)_3$	**173**	A, B		$> 18.0 \pm 0.5$	[248]
C_7 systems						
C_7Ph_7H		**146**	A, B		A rings: 9.1 B rings: 11.0 C rings: ~ 9	[221]
C_7Ph_6-1-(Fc)-2-(H)		**153**	A		Phenyl 7: 9.3 ± 0.5 Phenyl 4: 10.1 ± 0.5	[205]

Although this table is intended to provide a summary of the data provided in the current literature, the structural diversity of the topic has precluded an exhaustive search and there may be information that has been omitted inadvertently.

[a] Numbers are only provided if the complex is discussed in the text.

[b] Methods of barrier determination: (A) ^{1}H-NMR; (B) ^{13}C-NMR; (C) ^{31}P-NMR; (D) ^{19}F-NMR; (E) ESR; (F) theoretical calculations; (G) solid state ^{13}C-MAS NMR. In some cases, $\Delta G^{\ddagger}$ was calculated from the free enthalpies and entropies of activation provided in the text.

[c] In many cases, *a*, variable temperature experiments were conducted, but no changes were detected to the quoted temperature limit, or *b*, restricted rotation was detected on the timescale of the experiment, but no barrier was determined or quoted.

tions can yield reliable structural data. Concurrent with our experimental endeavours, we have employed HDFT computational methods to help rationalize and predict structures and properties of substituted hexaarylbenzenes. Ongoing studies are focused on the quantification of steric perturbations and the characterization of local regions of the PESs associated with this class of compounds [254]. In our tandem efforts to further understand the conformational subtleties of the less crowded C_5Ar_5 systems, we have employed Structure Correlation theory. As stated by Bürgi and Dunitz [255], “if a correlation can be found between two or more independent parameters describing the structure of a given molecular fragment in various environments, then the correlation function maps a minimum energy path in the corresponding parameter space” [256]. Accordingly, a succession of static X-ray structures of C_5Ar_4X ($X \neq Ar$) and C_5Ar_5 molecules has permitted us to survey the PES associated with peripheral aryl rotations or oscillations [257].

7. Concluding remarks

Beyond the aesthetic appeal of sterically crowded organometallic molecules, our interest in $(C_nR_n)ML_x$ cyclic arrays is educed from their potential transformation into functional molecular bevel gears. As both convergent and divergent domains for facial and peripheral metal binding, we seek to establish the precise substitution patterns (i.e. steric factors) that will enable control of their static structure and dynamic capabilities. Although challenging, our modular synthetic scheme is tolerant of many functional groups and has allowed us to expand the repertory of stereochemical data that is available for persubstituted Cp, arene and cycloheptatrienyl systems. Notwithstanding these advancements, the gap between propeller molecule and gear entity persists, attributable in part to the dichotomies of the iconic and analogic models. Central to this thematic shift is coupled torsional motion, an obligatory feature that is derived from the tight intermeshing of component parts. As confirmed by the rotational barrier trends in Table 1, the torsional itinerary is significantly influenced by the spatial disposition of the rotor axes ($5 < 6 < 7$ central rings), and the proximity and variations in 'tooth size' of the interacting n-fold rotors. Besides gear slippage, our design considerations are further governed by the parity restriction for dynamic gearing, which in effect limit us to the use of $n >$ two-fold rotors and C_5R_4X, C_6R_6 or C_7R_6X fragments, respectively. As immediate targets, it is possible that new details of rotary motion will be gleaned from maximally and differentially labelled C_nAr_n propeller fragments possessing both alkyl and aryl groups. By understanding the interplay between structure and energetics, we hope to achieve controllable rotational phenomena on the NMR time-scale in a chiral system that accommodates the essential steric and electronic features established in manifold areas of research over the past three decades. Ultimately, we must formulate methods of: (a) interlinking gears to enable the transmission of conformational information; and (b) interfacing the molecular arrays to the macroscopic world (i.e. on surfaces or at interfaces) to effect either parallel or serial concerted action.

Acknowledgements

Financial support from the Petroleum Research Fund (PRF), administered by the American Chemical Society, and from the Natural Sciences and Engineering Research Council (NSERC) of Canada, including NSERC postgraduate scholarships (SB, LEH), is gratefully acknowledged.

References

[1] J.A. Hirsch, Top. Stereochem. 1 (1967) 199.
[2] V. Pophristic, L. Goodman, Nature 411 (2001) 565.
[3] T.A. Albright, P. Hofmann, R. Hoffmann, J. Am. Chem. Soc. 99 (1977) 7546.
[4] T.A. Albright, R. Hoffmann, J.C. Thibeault, D.L. Thorn, J. Am. Chem. Soc. 101 (1979) 3801.
[5] T.A. Albright, R. Hoffmann, Y.-C. Tse, T. D'Ottavio, J. Am. Chem. Soc. 101 (1979) 3812.
[6] T.A. Albright, Acc. Chem. Res. 15 (1982) 149.
[7] M. Oki, Top. Stereochem. 14 (1983) 1.
[8] J.M. Chance, J.H. Geiger, K. Mislow, J. Am. Chem. Soc. 111 (1989) 2326.
[9] J. Clayden, J.H. Pink, Angew. Chem. Int. Ed. Engl. 37 (1998) 1937.
[10] A.A. Gakh, R.A. Sachleben, J.C. Bryan, Chemtech (1997) 26.
[11] L. Fabbrizzi, M. Licchelli, P. Pallavicini, Acc. Chem. Res. 32 (1999) 846.
[12] A.R. Pease, J.O. Jeppesen, J.F. Stoddart, Y. Luo, C.P. Collier, J.R. Heath, Acc. Chem. Res. 34 (2001) 433.
[13] Y. Kawaguchi, A. Harada, Org. Lett. 2 (2000) 1353.
[14] A.M. Brouwer, C. Frochot, F.G. Gatti, D.A. Leigh, L. Mottier, F. Paolucci, S. Roffia, G.W.H. Wurpel, Science 291 (2001) 2124.
[15] T.R. Kelly, M.C. Bowyer, K.V. Bhaskar, D. Bebbington, A. Garcia, F. Lang, M.H. Kim, M.P. Jette, J. Am. Chem. Soc. 116 (1994) 3657.
[16] T.C. Bedard, J.S. Moore, J. Am. Chem. Soc. 117 (1995) 10662.
[17] Z. Asfari, C. Naumann, G. Kaufmann, J. Vicens, Tetrahedron Lett. 39 (1998) 9007.
[18] K. Mislow, Chemtracts: Org. Chem. 2 (1989) 151.
[19] J.F. Stoddart, Acc. Chem. Res. 34 (2001) 409.
[20] R. Coontz, P. Szuromi, Science 290 (2000) 1523.
[21] R. Dagani, Chem. Eng. News 78 (2000) 27.
[22] T.T. Tidwell, Tetrahedron 34 (1978) 1855.
[23] K. Mislow, D. Gust, P. Finocchiaro, R.J. Boettcher, Fortschr. Chem. Forsch. 47 (1974) 1.
[24] K.P. Meurer, F. Vögtle, Top. Curr. Chem. 127 (1985) 3.
[25] D. Casarani, S. Grilli, L. Lunazzi, A. Mazzanti, J. Org. Chem. 66 (2001) 2757.
[26] S. Grilli, L. Lunazzi, A. Mazzanti, J. Org. Chem. 66 (2001) 5853.
[27] J.F. Blount, P. Finocchiaro, D. Gust, K. Mislow, J. Am. Chem. Soc. 95 (1973) 7019.
[28] J.F. Blount, P. Finocchiaro, D. Gust, K. Mislow, J. Am. Chem. Soc. 95 (1973) 7029.
[29] P. Finocchiaro, D. Gust, K. Mislow, J. Am. Chem. Soc. 96 (1974) 2165.
[30] S. Ito, N. Morita, T. Asao, Tetrahedron Lett. 44 (1992) 6669.
[31] S. Ito, N. Morita, T. Asao, Bull. Chem. Soc. Jpn. 68 (1995) 1409.
[32] R. Willem, C. Hoogzand, Org. Magn. Reson. 12 (1979) 55.
[33] R. Glaser, J.F. Blount, K. Mislow, J. Am. Chem. Soc. 102 (1980) 2777.
[34] J.A.S. Howell, M.G. Palin, P.C. Yates, P. McArdle, D. Cunningham, Z. Goldschimdt, H.E. Gottlieb, D. Hezroni-Langerman, J. Chem. Soc. Perkin Trans. II (1992) 1769.
[35] J.A.S. Howell, N. Fey, J.D. Lovatt, P.C. Yates, P. McArdle, D. Cunningham, E. Sadeh, H.E. Gottlieb, Z. Goldschimdt, M.B. Hursthouse, M.E. Light, J. Chem. Soc. Dalton Trans. (1999) 3015.
[36] R. Willem, H. Pepermans, K. Hallenga, M. Gielen, R. Dams, J. Org. Chem. 48 (1983) 1890.
[37] Z. Rappoport, S.E. Biali, Acc. Chem. Res. 30 (1997) 307.
[38] A.B. Lindner, F. Grynszpan, S.E. Biali, J. Org. Chem. 58 (1993) 6662.
[39] T. Selzer, Z. Rappoport, J. Org. Chem. 61 (1996) 7326.
[40] J. Sedó, N. Ventosa, M.A. Molins, M. Pons, C. Rovira, J. Veciana, J. Org. Chem. 66 (2001) 1567.
[41] J. Sedó, N. Ventosa, M.A. Molins, M. Pons, C. Rovira, J. Veciana, J. Org. Chem. 66 (2001) 1579.
[42] D. Gust, K. Mislow, J. Am. Chem. Soc. 95 (1973) 1535.
[43] K. Mislow, Acc. Chem. Res. 9 (1976) 26.
[44] R.J. Kurland, I.I. Schuster, A.K. Colter, J. Am. Chem. Soc. 87 (1965) 2279.
[45] D. Gust, K. Mislow, J. Am. Chem. Soc. 95 (1973) 1535.
[46] P. Finocchiaro, D. Gust, K. Mislow, J. Am. Chem. Soc. 96 (1974) 3198.
[47] D. Gust, J. Am. Chem. Soc. 99 (1977) 6980.
[48] D. Gust, A. Patton, J. Am. Chem. Soc. 100 (1978) 8175.
[49] H. Iwamura, K. Mislow, Acc. Chem. Res. 21 (1988) 175.
[50] U. Berg, T. Liljefors, C. Roussel, J. Sandström, Acc. Chem. Res. 18 (1985) 80.
[51] W.D. Hounshell, L.D. Iroff, D.J. Iverson, R.J. Wroczynski, K. Mislow, Isr. J. Chem. 20 (1980) 65.

[52] R.P. Feynman, Eng. Sci. 23 (1960) 22.
[53] Webster's New International Dictionary, G&C Merriam Co., Springfield, MA, 1938.
[54] R. Ballardini, V. Balzani, A. Credi, M.T. Gandolfi, M. Venturi, Acc. Chem. Res. 34 (2001) 445.
[55] M. Freemantle, Chem. Eng. News 77 (1999) 6.
[56] B. Yurke, A.J. Turberfield, A.P. Mills, Jr., F.C. Simmel, J.L. Neumann, Nature 406 (2000) 605.
[57] R.K. Soong, G.D. Bachand, H.P. Neves, A.G. Olkhovets, H.G. Craighead, C.D. Montemagno, Science 290 (2000) 1555.
[58] B.L. Feringa, Nature 208 (2000) 151.
[59] F.J. Nedelec, T. Surrey, A.C. Maggs, S. Leibler, Nature 389 (1997) 305.
[60] B. Alberts, Cell 92 (1998) 291.
[61] P.D. Boyer, Angew. Chem. Int. Ed. Engl. 37 (1998) 2296.
[62] K. Kitamura, M. Tokunaga, A.H. Iwane, T. Yanagida, Nature 397 (1999) 129.
[63] C. Mao, W. Sun, Z. Shen, N.C. Seeman, Nature 397 (1999) 144.
[64] V. Balzani, M. Gómez-López, J.F. Stoddart, Acc. Chem. Res. 31 (1998) 405.
[65] J.-P. Sauvage, Acc. Chem. Res. 31 (1998) 611.
[66] V. Balzani, A. Credi, F.M. Raymo, J.F. Stoddart, Angew. Chem. Int. Ed. Engl. 39 (2000) 3348.
[67] T.R. Kelly, I. Tellitu, J.P. Sestelo, Angew. Chem. Int. Ed. Engl. 36 (1997) 1866.
[68] T.R. Kelly, J.P. Sestelo, I. Tellitu, J. Org. Chem. 63 (1998) 3655.
[69] A.P. Davis, Angew. Chem. Int. Ed. Engl. 37 (1998) 909.
[70] T.R. Kelly, H. De Silva, R.A. Silva, Nature 401 (1999) 150.
[71] T.R. Kelly, R.A. Silva, H. De Silva, S. Jasmin, Y. Zhao, J. Am. Chem. Soc. 122 (2000) 6935.
[72] T.R. Kelly, Acc. Chem. Res. 34 (2001) 514.
[73] N. Koumura, R.W.J. Zijlstra, R.A. van Delden, N. Harada, B.L. Feringa, Nature 401 (1999) 152.
[74] N. Koumura, E.M. Geertsema, A. Meetsma, B.L. Feringa, J. Am. Chem. Soc. 122 (2000) 12005.
[75] B.L. Feringa, Acc. Chem. Res. 34 (2001) 504.
[76] C.A. Schalley, K. Beizai, F. Vögtle, Acc. Chem. Res. 34 (2001) 465.
[77] A.M. Stevens, C.J. Richards, Tetrahedron Lett. 38 (1997) 7805.
[78] C.J. Richards, D.C.D. Butler, Abstr. Pap.-Am. Chem. Soc., 221st, 2001, ORGN-367.
[79] M.D. Rausch, G.F. Westover, E. Mintz, G.M. Reisner, I. Bernal, A. Clearfield, J.M. Troup, Inorg. Chem. 18 (1979) 2605.
[80] A. Clearfield, P. Rudolf, I. Bernal, M.D. Rausch, Inorg. Chim. Acta 42 (1980) 17.
[81] M. Uno, K. Shirai, K. Ando, N. Komatsuzaki, T. Tanaka, M. Sawada, S. Takahashi, Chem. Lett. (1995) 7.
[82] T.J. Kealy, P.L. Pauson, Nature 168 (1951) 1039.
[83] G. Wilkinson, M. Rosenblum, M.C. Whiting, R.B. Woodward, J. Am. Chem. Soc. 74 (1952) 2125.
[84] R.B. King, M.B. Bisnette, J. Organomet. Chem. 8 (1967) 287.
[85] C. Janiak, H. Schumann, Adv. Organomet. Chem. 33 (1991) 291.
[86] J. Okuda, Top. Curr. Chem. 160 (1991) 97.
[87] W.M. Harrison, C. Saadeh, S.B. Colbran, D.C. Craig, J. Chem. Soc. Dalton Trans. (1997) 3785.
[88] H. Adams, N.A. Bailey, A.F. Browning, J.A. Ramsden, C. White, J. Organomet. Chem. 387 (1990) 305.
[89] J.A. Ramsden, D.J. Milner, H. Adams, N.A. Bailey, A.J. Smith, C. White, Organometallics 14 (1995) 2575.
[90] D. Matt, M. Huhn, J. Fischer, A. De Cian, W. Kläui, I. Tkatchenko, M.C. Bonnet, J. Chem. Soc. Dalton Trans. (1993) 1173.
[91] D. Matt, M. Huhn, M. Bonnet, I. Tkatchenko, U. Englert, W. Kläui, Inorg. Chem. 34 (1995) 1288.
[92] J. Haywood-Farmer, M.A. Battiste, Chem. Ind. (1971) 1232.
[93] M.W. Fagan, D. Gust, J. Org. Chem. 46 (1981) 1499.
[94] K. Möbius, Z. Naturforsch. A 20 (1965) 1117.
[95] R. Willem, H. Pepermans, C. Hoogzand, K. Hallenga, M. Gielen, J. Am. Chem. Soc. 103 (1981) 2299.
[96] R. Willem, A. Jans, C. Hoogzand, M. Gielen, G. Van Binst, H. Pepermans, J. Am. Chem. Soc. 107 (1985) 28.
[97] A. Patton, J.W. Dirks, D. Gust, J. Org. Chem. 44 (1979) 4749.
[98] C. Janiak, R. Weimann, F. Gõrlitz, Organometallics 16 (1997) 4933.
[99] S.B. Colbran, D.C. Craig, W.M. Harrison, A.E. Grimley, J. Organomet. Chem. 408 (1991) C33.
[100] C. Saadeh, S.B. Colbran, D.C. Craig, A.D. Rae, Organometallics 12 (1993) 133.
[101] P. Brégaint, J.-R. Hamon, C. Lapinte, Organometallics 11 (1992) 1417.
[102] L.D. Field, T.W. Hambley, P.A. Humphrey, A.F. Masters, P. Turner, Polyhedron 17 (1998) 2587.
[103] H. Schumann, A. Lentz, R. Weimann, J. Pickardt, Angew. Chem. Int. Ed. Engl. 33 (1994) 1731.
[104] A. Schott, H. Scott, G. Wilker, J. Brandt, H. Hoberg, E.G. Hoffmann, Liebigs Ann. Chem. (1973) 508.
[105] W.-Y. Yeh, S.-M. Peng, G.-H. Lee, J. Organomet. Chem. 572 (1999) 125.
[106] M.J. Hegg, R.H. Herber, C. Janiak, J.J. Zuckerman, H. Schumann, W.J. Manders, J. Organomet. Chem. 346 (1988) 321.
[107] L.D. Field, A.F. Masters, M. Gibson, D.R. Latimer, T.W. Hambley, I.E. Buys, Inorg. Chem. 32 (1993) 211.
[108] M.P. Castellani, J.M. Wright, S.J. Geib, A.L. Rheingold, W.C. Trogler, Organometallics 5 (1986) 1116.
[109] M.P. Castellani, S.J. Geib, A.L. Rheingold, W.C. Trogler, Organometallics 6 (1987) 2524.
[110] R.J. Hoobler, J.V. Adams, M.A. Hutton, T.W. Fransisco, B.S. Haggerty, A.L. Rheingold, M.P. Castellani, J. Organomet. Chem. 412 (1991) 157.
[111] B. Rieger, M. Steimann, R. Fawzi, Chem. Ber. 125 (1992) 2373.
[112] F. Mao, S.K. Sur, D.R. Tyler, J. Am. Chem. Soc. 111 (1989) 7627.
[113] L. Li, A. Decken, B.G. Sayer, M.J. McGlinchey, P. Brégaint, J.-Y. Thépot, L. Toupet, J.-R. Hamon, C. Lapinte, Organometallics 13 (1994) 682.
[114] J.A. Potenza, R.J. Johnson, R. Chirico, A. Efraty, Inorg. Chem. 16 (1977) 2354.
[115] M.R. Burke, T. Funk, J. Takats, V.W. Day, Organometallics 13 (1994) 2109.
[116] S. Yamazaki, Z. Taira, J. Organomet. Chem. 578 (1999) 61.
[117] H.K. Gupta, N. Rampersad, M.J. Stradiotto, M.J. McGlinchey, Organometallics 19 (2000) 184.
[118] H. Adams, N.A. Bailey, P.D. Hempstead, M.J. Morris, S. Riley, R.L. Beddoes, E.S. Cook, J. Chem. Soc. Dalton Trans. (1993) 91.
[119] L. Kruczynski, J. Takats, Inorg. Chem. 15 (1976) 3140.
[120] H.K. Gupta, M.J. Stradiotto, D.W. Hughes, M.J. McGlinchey, J. Org. Chem. 65 (2000) 3652.
[121] M.P. Thornberry, C. Slebodnick, P.A. Deck, F.R. Fronczek, Organometallics 20 (2001) 920.
[122] M.P. Thornberry, C. Slebodnick, P.A. Deck, F.R. Fronczek, Organometallics 19 (2000) 5352.
[123] J.-Y. Thépot, C. Lapinte, J. Organomet. Chem. 627 (2001) 179.
[124] B. Gloaguen, D. Astruc, J. Am. Chem. Soc. 112 (1990) 4607.
[125] H. Sitzmann, Chem. Ber. 123 (1990) 2311.
[126] K. Sünkel, J. Hofmann, Organometallics 11 (1992) 3923.
[127] H. Schumann, C. Janiak, E. Hahn, J. Loebel, J.J. Zuckerman, Angew. Chem. Int. Ed. Engl. 24 (1985) 773.
[128] H. Schumann, C. Janiak, E. Hahn, C. Kolax, J. Loebel, M.D. Rausch, J.J. Zuckerman, M.J. Heeg, Chem. Ber. 119 (1986) 2656.
[129] H. Schumann, C. Janiak, F. Gõrlitz, J. Loebel, A. Dietrich, J. Organomet. Chem. 363 (1989) 243.

[130] J.W. Chambers, A.J. Baskar, S.G. Bott, J.L. Atwood, M.D. Rausch, Organometallics 5 (1986) 1635.
[131] M.D. Rausch, W.-M. Tsai, J.W. Chambers, R.D. Rogers, H.G. Alt, Organometallics 8 (1989) 816.
[132] H. Schumann, C. Janiak, R.D. Köhn, J. Loebel, A. Dietrich, J. Organomet. Chem. 365 (1989) 137.
[133] P. Zanello, A. Cinquantini, S. Mangani, G. Opromolla, J. Organomet. Chem. 471 (1994) 171.
[134] H. Schumann, K. Sühring, R. Weimann, J. Organomet. Chem. 496 (1995) C5.
[135] W. Hübel, C. Hoogzand, Chem. Ber. 94 (1961) 2817.
[136] E.M. Arnett, J.M. Bollinger, J. Am. Chem. Soc. 86 (1964) 4729.
[137] K.P.C. Vollhardt, Acc. Chem. Res. 10 (1977) 1.
[138] J. Yang, J.G. Verkade, J. Am. Chem. Soc. 120 (1998) 6834.
[139] J. Yang, J.G. Verkade, Organometallics 19 (2000) 893.
[140] C.F.H. Allen, Chem. Rev. 62 (1962) 653.
[141] M.A. Ogliaruso, M.G. Romanelli, E.I. Becker, Chem. Rev. 65 (1965) 261.
[142] S. Ito, P.T. Herwig, T. Böhme, J.B. Rabe, W. Rettig, K. Müllen, J. Am. Chem. Soc. 122 (2000) 7698.
[143] S. Ito, J.D. Brand, L. Gherghel, K. Müllen, J. Am. Chem. Soc. 122 (2000) 7707.
[144] V. Enkelmann, G. Wegner, K. Müllen, J. Mater. Chem. 10 (2000) 879.
[145] F. Morgenroth, C. Kübel, K. Müllen, J. Mater. Chem. 7 (1997) 1207.
[146] F. Morgenroth, K. Müllen, Tetrahedron 53 (1997) 15349.
[147] F. Morgenroth, A.J. Berresheim, M. Wagner, K. Müllen, Chem. Commun. (1998) 1139.
[148] H.P. Dijkstra, P. Steenwinkel, D.M. Grove, M. Lutz, A.L. Spek, G. van Koten, Angew. Chem. Int. Ed. Engl. 38 (1999) 2186.
[149] H.P. Dijkstra, M.D. Meijer, J. Patel, R. Kreiter, G.P.M. van Klink, M. Lutz, A.L. Spek, A.J. Canty, G. van Koten, Organometallics 20 (2001) 3159.
[150] C. Kübel, S.-L. Chen, K. Müllen, Macromolecules 31 (1998) 6014.
[151] S. Kumar, S.K. Varshney, Angew. Chem. Int. Ed. Engl. 39 (2000) 3140.
[152] K. Kobayashi, T. Shirasaka, A. Sato, E. Horn, N. Furukawa, Angew. Chem. Int. Ed. Engl. 38 (1999) 3483.
[153] K. Kobayashi, T. Shirasaka, E. Horn, N. Furukawa, Tetrahedron Lett. 41 (2000) 89.
[154] L. Eshdat, A. Ayalon, R. Beust, R. Shenhar, M. Rabinovitz, J. Am. Chem. Soc. 122 (2000) 12637.
[155] E.M. Arnett, J.M. Bollinger, J. Am. Chem. Soc. 86 (1964) 4729.
[156] J. Siegel, K. Mislow, J. Am. Chem. Soc. 105 (1983) 7763.
[157] J. Siegel, A. Gutiérrez, W.B. Schweizer, O. Ermer, K. Mislow, J. Am. Chem. Soc. 108 (1986) 1569.
[158] S.E. Biali, A. Gutiérrez, K. Mislow, J. Org. Chem. 53 (1988) 1316.
[159] I.I. Schuster, W. Weissensteiner, K. Mislow, J. Am. Chem. Soc. 108 (1986) 6661.
[160] M.D. Singh, J. Siegel, S.E. Biali, K. Mislow, J. Am. Chem. Soc. 109 (1987) 3397.
[161] B. Kahr, S.E. Biali, W. Schaefer, A.B. Buda, K. Mislow, J. Org. Chem. 52 (1987) 3713.
[162] S.E. Biali, K. Mislow, J. Org. Chem. 53 (1988) 1318.
[163] J.M. Chance, B. Kahr, A.B. Buda, J.P. Toscano, K. Mislow, J. Org. Chem. 53 (1988) 3226.
[164] O. Ermer, Angew. Chem. Int. Ed. Engl. 22 (1983) 998.
[165] V. Melissas, K. Faegri, Jr., J. Almolöf, J. Am. Chem. Soc. 107 (1985) 4640.
[166] I. Bar, J. Bernstein, A. Christensen, Tetrahedron 33 (1977) 3177.
[167] H. Bock, W. Kaim, Chem. Ber. 111 (1978) 3552.
[168] M.P. Marsau, Acta Crystallogr. 18 (1965) 851.
[169] D.J. Iverson, K. Mislow, Organometallics 1 (1982) 3.
[170] C.S. Frampton, J.H. Gall, D.D. MacNicol, Acta Crystallogr. Sect. C 56 (2000) e22.
[171] M.J. McGlinchey, Adv. Organomet. Chem. 34 (1992) 285.
[172] G. Hunter, D.J. Iverson, K. Mislow, J.F. Blount, J. Am. Chem. Soc. 102 (1980) 5942.
[173] D.J. Iverson, G. Hunter, J.F. Blount, J.R. Damewood, Jr., K. Mislow, J. Am. Chem. Soc. 103 (1981) 6073.
[174] M.M. Maricq, J.S. Waugh, J.L. Fletcher, M.J. McGlinchey, J. Am. Chem. Soc. 100 (1978) 6902.
[175] G. Hunter, J.F. Blount, J.R. Damewood, Jr., D.J. Iverson, K. Mislow, Organometallics 1 (1982) 448.
[176] M.J. McGlinchey, J.L. Fletcher, B.G. Sayer, P. Bougeard, R. Faggiani, C.J.L. Lock, A.D. Bain, C.A. Rodger, E.P. Kuendig, D. Astruc, J.-P. Hamon, P. LeMaux, S. Top, G. Jaouen, J. Chem. Soc. Chem. Commun. 1 (1983) 634.
[177] M.J. McGlinchey, P. Bougeard, B.G. Sayer, R. Hofer, C.J.L. Lock, J. Chem. Soc. Chem. Commun. (1984) 789.
[178] G. Hunter, K. Mislow, J. Chem. Soc. Chem. Commun. (1984) 172.
[179] P.A. Downtown, B. Mailvaganam, C.S. Frampton, B.G. Sayer, M.J. McGlinchey, J. Am. Chem. Soc. 112 (1990) 27.
[180] B. Mailvaganam, C.S. Frampton, S. Top, B.G. Sayer, M.J. McGlinchey, J. Am. Chem. Soc. 113 (1991) 1177.
[181] K.V. Kilway, J.S. Siegel, J. Am. Chem. Soc. 113 (1991) 2332.
[182] K.V. Kilway, J.S. Siegel, J. Am. Chem. Soc. 114 (1992) 255.
[183] V. Marks, H.E. Gottlieb, S.E. Biali, J. Am. Chem. Soc. 119 (1997) 9672.
[184] H.E. Gottlieb, C. Ben-Ari, A. Hassner, V. Marks, Tetrahedron 55 (1999) 4003.
[185] K.V. Kilway, J.S. Siegel, Tetrahedron 57 (2001) 3615.
[186] M. Taha, V. Marks, H.E. Gottlieb, S.E. Biali, J. Org. Chem. 65 (2000) 8621.
[187] V. Marks, H.E. Gottlieb, A. Melman, G. Byk, S. Cohen, S.E. Biali, J. Org. Chem. 66 (2001) 6711.
[188] J.C.J. Bart, Acta Crystallogr. Sect. B 24 (1968) 1277.
[189] E.M. Larson, R.B. Von Dreele, P. Hanson, J.D. Gust, Acta Crystallogr. Sect. C 46 (1990) 784.
[190] A. Almenningen, O. Bastiansen, P.N. Skancke, Acta Chem. Scand. 12 (1958) 1215.
[191] L. Tong, D.M. Ho, N.J. Vogelaar, C.E. Schutt, R.A. Pascal, Jr., J. Am. Chem. Soc. 119 (1997) 7291.
[192] B. Mailvaganam, B.E. McCarry, B.G. Sayer, R.E. Perrier, R. Faggiani, M.J. McGlinchey, J. Organomet. Chem. 335 (1987) 213.
[193] T.A. Albright, Acc. Chem. Res. 15 (1982) 149.
[194] R.D. Rogers, J.L. Atwood, T.A. Albright, W.A. Lee, M.D. Rausch, Organometallics 3 (1984) 263.
[195] K.L. Malisza, L.C.F. Chao, J.F. Britten, B.G. Sayer, G. Jaouen, S. Top, A. Decken, M.J. McGlinchey, Organometallics 12 (1993) 2462.
[196] B. Mailvaganam, B.G. Sayer, M.J. McGlinchey, J. Organomet. Chem. 395 (1990) 177.
[197] P. Biagini, T. Funaioli, G. Fachinetti, F. Laschi, P.F. Zanazzi, J. Chem. Soc. Chem. Commun. (1989) 405.
[198] M. Crocker, M. Green, A.G. Orpen, D.M. Thomas, J. Chem. Soc. Chem. Commun. (1984) 1141.
[199] I.C. Quarmby, R.C. Hemond, F.J. Feher, M. Green, W.E. Geiger, J. Organomet. Chem. 577 (1999) 189.
[200] G.L. Ning, M. Munakata, L.P. Wu, M. Maekawa, T. Kuroda-Sowa, Y. Suenaga, K. Sugimoto, Inorg. Chem. 38 (1999) 1376.
[201] G.L. Ning, M. Munakata, L.P. Wu, M. Maekawa, Y. Suenaga, T. Kuroda-Sowa, K. Sugimoto, Inorg. Chem. 38 (1999) 5668.
[202] E.C. Constable, O. Eich, D. Fenske, C.E. Housecraft, L.A. Johnston, Chem. Eur. J. 6 (2000) 4364.
[203] A. Siegel, M.D. Rausch, Synth. React. Inorg. Met.-Org. Chem. 8 (1978) 209.
[204] M.D. Rausch, A. Siegel, J. Org. Chem. 33 (1968) 4545.

[205] H.K. Gupta, S. Brydges, M.J. McGlinchey, Organometallics 18 (1999) 115.
[206] K. Yasufuku, K. Aoki, H. Yamazaki, Inorg. Chem. 16 (1977) 624.
[207] K. Takeuchi, Y. Yokomichi, K. Okamoto, Chem. Lett. (1977) 1177.
[208] M.A. Battiste, J. Am. Chem. Soc. 83 (1961) 4101.
[209] C.D. Ritchie, H. Fleischaur, J. Am. Chem. Soc. 94 (1972) 3841.
[210] M. Lämsä, T. Suorsa, J. Pursiainen, J. Huuskonen, K. Rissanen, Chem. Commun. (1996) 1443.
[211] M. Lämsä, J. Pursiainen, K. Rissanen, J. Huuskonen, Acta Chem. Scand. 52 (1998) 563.
[212] M. Lämsä, S. Kiviniemi, E.-R. Kettukangas, M. Nissinen, J.P.K. Rissanen, J. Phys. Org. Chem. 14 (2001) 551.
[213] K. Yamamura, K. Nakatsu, K. Nakao, T. Nakazawa, I. Murata, Tetrahedron Lett. 52 (1979) 4999.
[214] R. Tsuji, K. Komatsu, K. Takeuchi, M. Shiro, S. Cohen, M. Rabinovitz, J. Phys. Org. Chem. 6 (1993) 435.
[215] O.S. Mills, N.J. Mooney, P.M. Robinson, C.I.F. Watt, B.G. Box, J. Chem. Soc. Perkin Trans. II (1995) 697.
[216] K. Komatsu, Eur. J. Org. Chem. 1 (1999) 1495.
[217] F. Pietra, Chem. Rev. 73 (1973) 334.
[218] M.L.H. Green, D.K.P. Ng, Chem. Rev. 95 (1995) 439.
[219] M. Tamm, K. Baum, R. Fröhlich, P. Saarenketo, Organometallics 20 (2001) 1376.
[220] M.A. Battiste, Chem. Ind. (1961) 550.
[221] L.C.F. Chao, H.K. Gupta, D.W. Hughes, J.F. Britten, S.S. Rigby, A.D. Bain, M.J. McGlinchey, Organometallics 14 (1995) 1139.
[222] S. Brydges, J.F. Britten, L.C.F. Chao, H.K. Gupta, M.J. McGlinchey, D.L. Pole, Chem. Eur. J. 4 (1998) 1201.
[223] E.A. Hill, R. Wiesner, J. Am. Chem. Soc. 91 (1969) 510.
[224] R. Gleiter, R. Seeger, H. Binder, E. Fluck, M. Cais, Angew. Chem. Int. Ed. Engl. 11 (1972) 1028.
[225] J.J. Dannenberg, M.K. Lavenberg, J.H. Richards, Tetrahedron 29 (1973) 1575.
[226] M.J. McGlinchey, L. Girard, R. Ruffolo, Coord. Chem. Rev. 143 (1995) 331.
[227] H. El Amouri, M. Gruselle, Chem. Rev. 96 (1996) 1077.
[228] G.R. Clark, G.J. Palenik, J. Organomet. Chem. 50 (1973) 185.
[229] M.J. Bennett, J.L. Pratt, K.A. Simpson, L.K.K. Li Shing Man, J. Takats, J. Am. Chem. Soc. 98 (1976) 4810.
[230] H. Knoche, Chem. Ber. 99 (1966) 1097.
[231] M. Tamm, B. Dreßel, R. Fröhlich, J. Org. Chem. 65 (2000) 6795.
[232] A. Roberts, M.W. Whiteley, J. Organomet. Chem. 458 (1993) 131.
[233] E. Schwed, H.-U. Hund, H.W. Bosch, H. Berke, Helv. Chim. Acta 74 (1991) 189.
[234] M. Tamm, B. Dreßel, R. Fröhlich, K. Bergander, Chem. Commun. (2000) 1731.
[235] M. Tamm, T. Bannenberg, B. Dressel, Organometallics 20 (2001) 900.
[236] W. Clegg, J.C. Lockhart, M.B. McDonnell, J. Chem. Soc. Perkin Trans. II (1985) 1019.
[237] J.C. Lockhart, M.B. McDonnell, W. Clegg, M.N.S. Hill, J. Chem. Soc. Perkin Trans. II (1987) 639.
[238] S. Ito, M. Fujita, N. Morita, T. Asao, Chem. Lett. (1995) 475.
[239] S. Ito, M. Fujita, N. Morita, T. Asao, Bull. Chem. Soc. Jpn. 68 (1995) 3611.
[240] C. Kiefl, Eur. J. Org. Chem. (2000) 3279.
[241] Z. Marcinow, P.W. Rabideau, J. Org. Chem. 55 (1990) 3812.
[242] M.V. Alfimov, Yu.B. Scheck, N.P. Kovalenkoy, Chem. Phys. Lett. 43 (1976) 154.
[243] Y.u.B. Scheck, N.P. Kovalenko, M.V. Alfimov, J. Lumin. 15 (1977) 157.
[244] J.H. Magill, A.R. Ubbelohde, Trans. Faraday Soc. 54 (1958) 1811.
[245] D.J. Plazek, J.H. Magill, J. Chem. Phys. 45 (1966) 3038.
[246] C.M. Whitaker, R.J. McMahon, J. Phys. Chem. 100 (1996) 1081.
[247] H.E. Katz, J. Org. Chem. 52 (1987) 3932.
[248] P.N. Riley, M.G. Thorn, J.S. Vilardo, M.A. Lockwood, P.E. Fanwick, I.P. Rothwell, Organometallics 18 (1999) 3016.
[249] R.W. Baker, M.A. Foulkes, J.A. Taylor, J. Chem. Soc. Perkin Trans. I (1998) 1047.
[250] B.A. Arbusov, J.A. Akmed-Zade, Zh. Obshch. Khim. 12 (1942) 1928.
[251] S.R. Samanta, A.K. Mukherjee, A.J. Bhattacharyya, Curr. Sci. 57 (1988) 926.
[252] M.D. Rausch, E.F. Tokas, E.A. Mintz, A. Clearfield, M. Mangion, F. Bernal, J. Organomet. Chem. 172 (1979) 109.
[253] L.E. Harrington, J.F. Britten, D.W. Hughes, A.D. Bain, M.J. McGlinchey, J. Organomet. Chem. (2002) accepted for publication.
[254] S. Brydges, K.K. Baldridge, M.J. McGlinchey (2002) manuscript in preparation.
[255] H.-B. Bürgi, J.D. Dunitz, Acc. Chem. Res. 16 (1983) 153.
[256] For a recent Structure Correlation study, refer to: E. Gur, M. Kaftory, S.E. Biali, Z. Rappoport, J. Org. Chem. 64 (1999) 8144.
[257] S. Brydges, M.J. McGlinchey, J. Org. Chem. (2002) submitted for publication.
[258] H. Sitzmann, J. Organomet. Chem. 354 (1988) 203.
[259] E.W. Abel, N.J.L. Long, K.G. Orrell, A.G. Osborne, J. Organomet. Chem. 403 (1991) 195.
[260] M. Fei, S.K. Sur, D.R. Tyler, Organometallics 10 (1991) 419.
[261] F. Mao, C.E. Philbin, T.J.R. Weakley, D.R. Tyler, Organometallics 9 (1990) 1510.
[262] K. Albert, J. Hambrecht, Z. Naturforsch. B 33 (1978) 94.
[263] G. Hunter, T.J.R. Weakley, W. Weissensteiner, J. Chem. Soc. Dalton Trans. (1987) 1545.
[264] V.H. Hansen, R.J. Batchelor, F.W.B. Einstein, J.L. Male, R.K. Pomeroy, M.J. Zaworotko, Organometallics 16 (1997) 4875.
[265] A.G. Pinkus, N. Kalyanam, J. Chem. Soc. Chem. Commun. (1978) 201.
[266] J.C. Barnes, J.A. Chudek, G. Hunter, A.J. Blake, P.J. Dyson, B.F.G. Johnson, W. Weissensteiner, J. Chem. Soc. Faraday Trans. 91 (1995) 2149.
[267] J.F. Blount, G. Hunter, K. Mislow, J. Chem. Soc. Chem. Commun. (1984) 170.
[268] G. Hunter, T.J.R. Weakley, K. Mislow, M.G. Wong, J. Chem. Soc. Dalton Trans. (1986) 577.
[269] S. Denholm, G. Hunter, T.J.R. Weakley, J. Chem. Soc. Dalton Trans. (1987) 2789.
[270] J.A. Chudek, G. Hunter, R.L. MacKay, P. Kremminger, W. Weissensteiner, J. Chem. Soc. Dalton Trans. (1991) 3337.
[271] V. Marks, H.E. Gottlieb, S.E. Biali, J. Am. Chem. Soc. 119 (1997) 9672.
[272] K.V. Kilway, J.S. Siegel, Organometallics 11 (1992) 1426.
[273] W. Weissensteiner, A. Gutiérrez, M.D. Radcliffe, J. Siegel, M.D. Singh, P.J. Tuohey, K. Mislow, J. Org. Chem. 50 (1985) 5822.
[274] J.A. Chudek, G. Hunter, R.L. MacKay, G. Färber, W. Weissensteiner, J. Organomet. Chem. 377 (1989) C69.
[275] N. Zuaretz, O. Golan, S.E. Biali, J. Org. Chem. 56 (1991) 2444.
[276] S.E. Biali, A.B. Buda, J. Org. Chem. 53 (1988) 135.
[277] M.J. Zaworotko, K.C. Sturge, L. Nunez, R.D. Rogers, Organometallics 10 (1991) 1806.
[278] G.R. Newkome, N.B. Islam, J.M. Robinson, J. Org. Chem. 40 (1975) 3514.