Observation of Slowed Rotation about the η^6-Arene–Chromium Bond in the Tripodal Chromium Complexes of the Trimers of Bicyclo[2.2.1]hept-2-yne: Intramolecular Rotational Barriers in Organometallic Complexes and their Correlation with Internal Non-bonding Interactions and Structural Changes

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The all-*syn* **1** and *syn-anti-syn* **2** trimers of bicyclo[2.2.1]hept-2-yne have been considered as realistic role models for some of the intramolecular rotational behaviour of hexaethylbenzene in its metal complexes. Both **1** and **2** complex to chromium as arenes rather than as cyclohexatrienes. The variable-temperature 75.5 MHz ^{13}C-{1 H} NMR spectra of a series of complexes [Cr(η^6-arene)(CO)$_2$L] (L = CO, CS, or PPh$_3$) have been observed and restricted rotation about the chromium–arene bond detected at very low temperatures only for the tricarbonyl complex of **2** and the dicarbonyl(triphenylphosphine) complex of **1**. A detailed structural analysis covering twenty-one metal complexes of **1**, **2**, hexaethylbenzene, 1,3,5-triethyl-2,4,6-tris(trimethylsilylmethyl)benzene, hexamethylbenzene, hexa-*n*-propylbenzene, and pentaethylacetophenone is reported and conclusions presented concerning the effects of intramolecular strain on ground-state structures and on internal mobility.

The barrier to rotation about a η^6-arene–metal bond is normally too low for that process to be observed directly by NMR spectroscopy.[1] However, exceptional electronic or steric factors may sufficiently raise the barrier so that rotation can be slowed on the observational time-scale at experimentally accessible temperatures.

Hoffmann and co-workers[1] calculated that completely localising the arene π system to one Kekulé resonance form (cyclohexatriene) raises the barrier from essentially zero to about 80 kJ mol^{-1}, and recently Nambu and Siegel[2] demonstrated experimentally the first example of restricted rotation in one arenemetal π complex due to the localised π character of the bound arene, *bent*-terphenylene (benzo-[3,4]cyclobuta[1,2-*a*]biphenylene). As to steric effects, there are but few examples of complexes in which restricted rotation about the η^6-arene–metal bond has been unequivocally demonstrated.[3] Indeed, for some time there has been controversy over the increase in barrier height caused by alkyl substitution of the benzene ring,[4,5] and only recently has it been established beyond reasonable doubt that the steric effects of the proximal ethyl groups of a six-co-ordinated arene can lead to slowed rotation about the η^6-arene–metal bond.[6,7]

To explore further the effect of steric hindrance on the Cr(η^6-arene) rotational barrier we have synthesised a series of complexes, [Cr(η^6-arene)(CO)$_2$L] (L = CO, CS, or PPh$_3$) of the sterically demanding and rigid all-*syn* **1** and *syn-anti-syn* **2** trimers of bicyclo[2.2.1]hept-2-yne, and observed their variable-temperature 74.49 MHz ^{13}C-{^{1}H} NMR spectra. As indicated in the preceding paper[8] we considered that some complexes of these arenes could be suitable as role models for some of the intramolecular rotations believed to occur in the metal complexes of hexaethylbenzene, **3**. A preliminary account of the crystal and molecular structures and ^{13}C-{^{1}H} NMR spectra of the chromium tricarbonyl complexes of the all-*syn* **6** and *syn-anti-syn* **7** isomers has already appeared.[9]

The present paper not only reports the intramolecular dynamics of the complexes of **1** and **2** but also compares the static stereochemistries of these complexes with those of a number of other alkyl-substituted arenes for which X-ray structural data are available (Fig. 1), and presents our conclusions regarding the ways in which M(η^6-arene) complexes can progressively adapt their molecular structures to relieve the effects of increasing steric strain and how intramolecular rotational barriers correlate with structural changes.

Results and Discussion

MM2(87) force-field calculations[10] for the uncomplexed trimers gave the molecular parameters recorded in Tables 1 and 3. The major prediction of these calculations is that neither arene should have any significant alternation in the carbon–carbon bond lengths of its unsaturated ring such as would happen for a cyclohexatriene system and thus there should be no anticipation of exceptional electronic factors to cause a significant barrier to rotation about the η^6-arene–chromium bond of their complexes. The molecular structures of the chromium tricarbonyl complexes **6** and **7** are shown in Fig. 2 and selected bond lengths in Table 1. As already predicted for the uncomplexed trimers, in neither complex is there any detectable alternation in the carbon–carbon bond lengths of the unsaturated rings, all of which fall within the range expected for a purely aromatic system. Although the individual bond lengths differ somewhat from each other, they do not alternate regularly as would be the case for a cyclohexatriene system. Indeed, *if* chemically equivalent bond lengths are averaged (**6**: 1–2, 3–4, 5–6, and 2–3, 4–5, 6–1) the differences become less than 0.01 Å. There is thus no evidence for localisation of the arene π system and therefore no exceptional electronic factor which could cause a significant barrier to rotation about the η^6-arene–chromium bond.

As might be expected, in both complexes **6** and **7** the metal co-ordinates to the less-crowded face of the arene. Thus in **6** the three methylene bridges are proximal to the chromium, the three

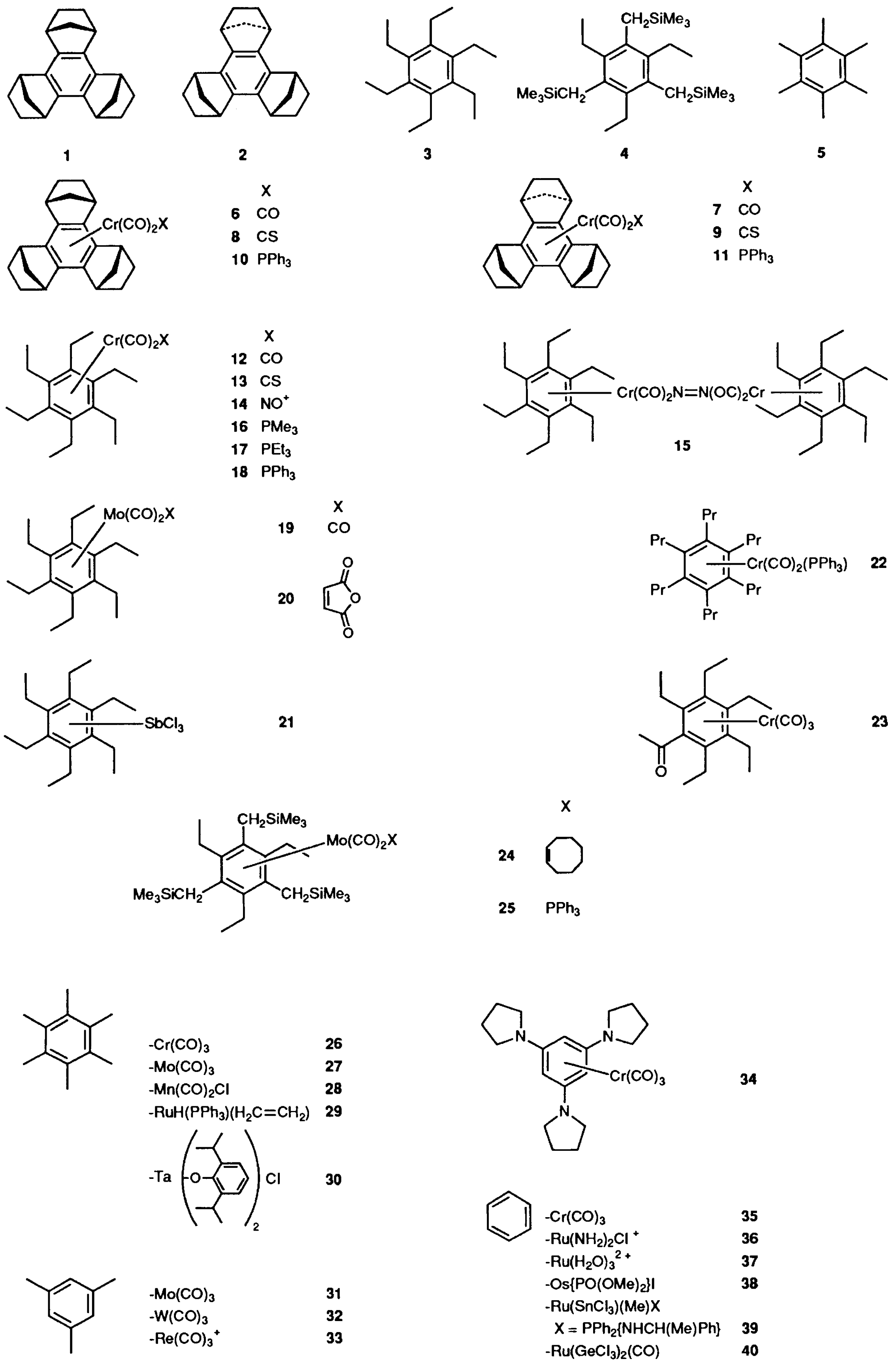

Fig. 1 The arenes and their metal complexes whose molecular structures are analysed

ethylene bridges distal; in **7**, two methylene and one ethylene bridge are proximal. The dicarbonylthiocarbonyl, **8** and **9**, and dicarbonyl(triphenylphosphine), **10** and **11**, analogues were prepared from the tricarbonyl complexes **6** and **7** and although their X-ray structures are unavailable it can be confidently anticipated that these substituted complexes also have the metal co-ordinated to the less-crowded faces of the arenes.

Table 1 Carbon–carbon bond lengths (Å) of the unsaturated rings, calculated for ligands **1** and **2** [MM2(87)] and found for complexes **6** and **7** (crystal structures)

	1	**2**	**6**^{a}	**7**^{a,b}	
C(1)–C(2)	1.395	1.395	1.426(6)	1.412(12)	1.419(12)
C(2)–C(3)	1.391	1.391	1.403(4)	1.410(11)	1.417(11)
C(3)–C(4)	1.395	1.395	1.411(4)	1.416(11)	1.414(13)
C(4)–C(5)	1.391	1.391	1.420(6)	1.416(12)	1.409(12)
C(5)–C(6)	1.395	1.395	1.411(4)	1.408(12)	1.423(11)
C(6)–C(1)	1.391	1.391	1.403(4)	1.407(12)	1.416(13)

[a] Standard deviations in parentheses. [b] Two molecules in the asymmetric unit.

Assignment of the observed ^{13}C-{^{1}H} NMR resonances was made by a combination of distortionless enhancements by polarisation transfer (DEPT) and heteronuclear correlation spectroscopy (COSY) and Table 2 lists chemical shifts for compounds **1**, **2** and **6**–**11**. Complexation of the all-*syn* arene **1** leads to upfield shifts for all the organic ligand resonances of complexes **6**, **8** and **10**. This is in contrast to the situation for the corresponding hexaethylbenzene complexes **12**,[11] **13**[4a] and **18**[11] where downfield shifts are observed on complexation of the arene.

As expected from its C_s molecular symmetry, three signals are observed for the aromatic carbons of the *syn-anti-syn* arene **2**, although their chemical shift differences are very small (< 1 ppm). However, complexation of **2** leads to much larger chemical shift differences for these signals (*e.g.* for **7**, 12.7 ppm), larger even than those observed for hexaethylbenzene complexes, despite the conformation of the metal tripod being staggered rather than eclipsed, and the lack of alternation of 'proximal' and 'distal' substituents to which such differences have been attributed.[4b] The signals arising from the carbon atoms of the methylene bridges can be unambiguously assigned, that from the proximal methylene bridges is shifted upfield, that

Table 2 ^{13}C NMR data for the all-*syn*- and *syn-anti-syn*-ligands and their complexes

			Chemical shifts^{a}					
Compound	Solvent	*T*/K	CO	C$_{ar}$	CH$_2$	CH	C$_2$H$_4$	PPh$_3$
1	CDCl$_3$	298	—	136.8	49.0	41.2	27.2	—
6	CDCl$_3$	298	236.1	110.9	47.5	39.3	26.8	—
	Solid state	298	237.8(1)^{b} 235.8(2)^{b}	112.0 111.5 111.3	—	—	—	—
8	CDFCl$_2$	210	235.1	116.3	48.2	39.2	26.0	—
10	CDFCl$_2$	180	245.6 (20.3)^{c}	108.5	45.1	39.1	27.2	146.1 (32.0)^{c} 133.5 (7.5)^{c} 128.5 127.6
2	CDCl$_3$	298	—	136.8 136.5 136.3	48.8(2)^{b} 48.6(1)^{b}	41.4 41.3 41.2	27.6(2)^{b} 27.2(1)^{b}	— —
7	CDCl$_3$	298	238.3	123.0 112.4 110.3	54.5(1)^{b,d} 47.3(2)^{b,e}	41.2(1)^{b} 39.8(2)^{b}	31.1 27.1 27.0	
	Solid state	298	239.5 238.5 237.4 236.5	120.4—121.5 114.0—109.0	—	—	—	—
9	CDFCl$_2$	190	235.0	116.7^{f} 115.2	53.2(1)^{b,d} 47.7(2)^{b,e}	40.7 39.6 29.2	31.2 26.5 25.9	—
11	CDFCl$_2$	289	245.2 (23.2)^{c}	117.8^{f} 109.2	57.7(1)^{b,d} 44.9(2)^{b,e}	42.3 40.4 39.7	29.9 28.3 27.6	140.5 (26.2)^{c} 134.0 (8.7)^{c} 128.6 127.5

[a] Chemical shifts are in ppm downfield from tetramethylsilane. [b] Relative intensity. [c] J_{PC}/Hz. [d] Distal. [e] Proximal. [f] Third signal obscured by solvent resonance.

Table 3 Selected *averaged* bond lengths, distances from the benzene least-squares plane (Å), and bond angles (°) for compounds **1**–**5**

				Distances from the benzene least-squares plane			
Compound	Source	C$_{ar}$–C$_{ar}$	C$_{ar}$–*C*	C$_{ar}$	–C$_{ar}$–*C*	C$_{ar}$–C–*C*	C$_{ar}$–C–R
1	Calculated^{a}	1.393	1.504	0.000	−0.036	0.807^{b} −1.436^{c}	—
2	Calculated^{c}	1.393	1.504	±0.001	−0.009	0.841^{b}, −0.862^{b} 1.382^{c}, −1.403^{c}	—
3	X-Ray	1.402	1.517	±0.003	0.028	1.444	112.8
3a	Calculated^{a}	1.408	1.524	±0.002	0.016	1.448	111.7
3h	Calculated^{a}	1.411	1.528	±0.020	−0.046	1.276	114.2
4	Calculated^{a}	1.408	1.523^{d} 1.522^{e}	±0.012	0.115^{d} −0.070^{e}	1.583^{d} −1.839^{e}	111.0^{d} 113.4^{e}
5	Calculated^{a}	1.405	1.516	±0.009	0.121	—	—

[a] MM2(87). [b] Methylene bridges. [c] Ethylene bridges. [d] Ethyl groups. [e] Trimethylsilylmethyl groups.

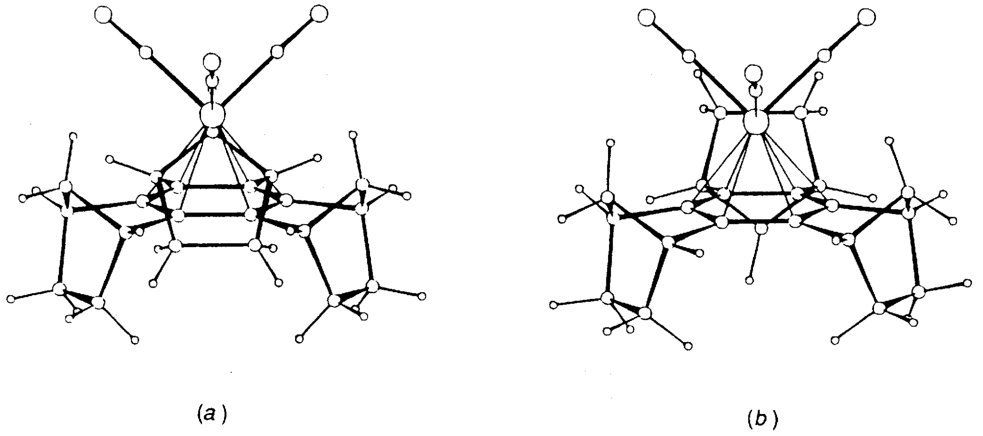
(a) (b)

Fig. 2 Molecular structures of complexes **6** (*a*) and **7** (*b*)[9]

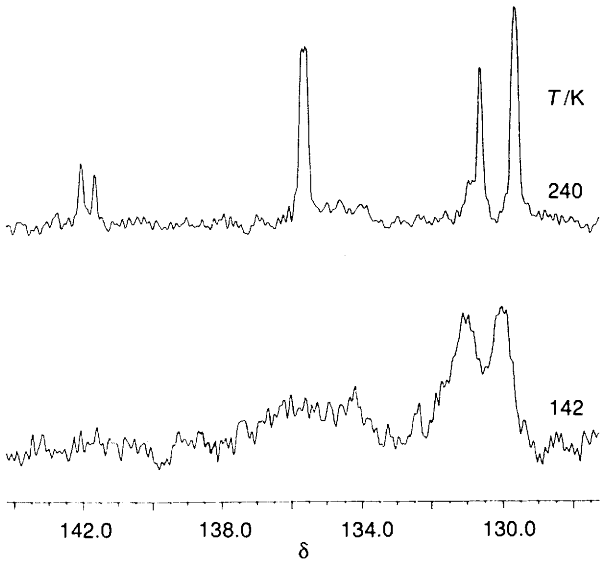

Fig. 3 Variable-temperature 75.5 MHz ^{13}C-{^{1}H} NMR triphenylphosphine carbon subspectrum of complex **10** dissolved in $CDFCl_2$

from the single distal methylene bridge downfield, on complexation (for the hexaethylbenzene complexes **12**–**14**,[12] *upfield* signals have been assigned to the carbon atoms of *distal* methyl groups). The signals of the carbon atoms of the ethylene bridges were not assigned to proximal and distal environments, although from comparisons with the chemical shifts of the unambiguously assigned all-*syn* complexes it is reasonable to speculate that the downfield signals can be attributed to the carbons of the proximal ethylene bridges of complex **2**. Whatever the correct assignment of signals to the carbons of the ethylene bridges, it is, however, clear that the observed upfield and downfield shifts of the signals unambiguously assigned to the carbon atoms of the proximal and distal methylene bridges of complexes **7**, **9**, and **11**, are in the opposite directions to those assigned by others to the methyl groups of their hexaethylbenzene analogues. Assignments of arene substituents to proximal and distal environments which are solely based on small chemical shift differences may not therefore be unambiguous.

Although the molecular symmetry of complex **6** closely approximates C_{3v}, the two resonances of relative intensities 1:2 observed for the carbonyl carbons in the solid-state ^{13}C-{^{1}H} NMR spectrum of this tricarbonyl complex of **1** are exactly as anticipated from the C_s site symmetry for the molecule in the crystal unit cell (space group *Pnma*, four molecules per unit cell). Its C_{3v} molecular symmetry, however, governs the appearance of the solution NMR spectrum of **6** and thus precludes direct observation by NMR spectroscopy of slowed tripodal rotation and, unsurprisingly, its ^{13}C-{^{3}H} NMR spectrum in $CDFCl_2$ was unchanged down to 142 K.

The C_s molecular symmetry anticipated for **8**, the dicarbonylthiocarbonyl complex of **1**, should potentially allow an observation of slowed tripodal rotation. That there was no change in the ^{13}C-{^{1}H} NMR spectrum of **8** dissolved in $CDFCl_2$ down to 140 K is evidence that the barrier to rotation about the η^6-arene–chromium bond is too low to bring that process on to the NMR time-scale. In contrast, in the spectrum of the dicarbonyl(triphenylphosphine) complex **10** in $CDFCl_2$ major line broadening, indicating exchange phenomena, occurred at temperatures below 157 K in both the triphenylphosphine and arene subspectra. The appearance of the decoalesced triphenylphosphine subspectrum (Fig. 3) is quite different to that of **18** and **22**, where a decoalescence was attributed to slowed rotation about the chromium–phosphorus bond while rotation about the *ipso*-C–P bonds remained rapid.[13] The case of **10** is similar to that of **25**[6] where we suspect that the latter rotation is also slowed, leading to a large number of overlapping resonances at low temperatures. That the alkyl and arene subspectra of **10** also decoalesce at about the same temperature as the triphenylphosphine subspectrum hints at slowed correlated rotation about the η^6-arene–chromium and chromium–phosphorus bands, but does not, of course, constitute proof. The barriers ($\Delta G^{\ddagger}_{200} = 26 \pm 5.4$ kJ mol^{-1}) are significantly lower than that for slowed rotation about the chromium–phosphorus bond in **18** ($\Delta G^{\ddagger}_{200} = 38$ kJ mol^{-1}).

In the crystal unit cell of complex **7** [space group *An*(9), eight molecules per unit cell] there are two independent molecules, and this is reflected in the four carbonyl carbon signals observed in the solid state ^{13}C-{^{1}H} NMR spectrum of this tricarbonyl complex of **2**. In contrast to **6**, the ^{13}C-{^{1}H} NMR spectrum of **7** in $CDFCl_2$ solution exhibited a decoalescence phenomenon involving only the carbonyl resonance: at 150 K this resonance was broadened compared to the other resonances in the spectrum; at 145 K it had become asymmetric, and at 142 K a definite shoulder had appeared on the resonance (Fig. 4). A fully decoalesced spectrum could not be observed as below the last temperature the solution froze. Nevertheless, this temperature-dependent decoalescence phenomenon can be unambiguously assigned to slowed rotation of the chromium tricarbonyl tripod in **7**. From line-shape fitting we estimate the rate of tripodal rotation at 142 K to be still about 250 s^{-1} giving a barrier with $\Delta G^{\ddagger}_{142} \approx 27$ kJ mol^{-1}, almost at the very lowest experimental limit for processes directly observable by variable-temperature NMR spectroscopy. The presence of a single proximal ethylene bridge does, however, provide sufficient steric interaction in this complex of the *syn-anti-syn* arene **2** to slow tripodal rotation, even though the rotational barrier must be significantly lower than that measured for the hexaethylbenzene complex **13**.

Down to 140 K no decoalescence was observed in the ^{13}C-{^{1}H} NMR spectrum of **9**, the dicarbonylthiocarbonyl complex

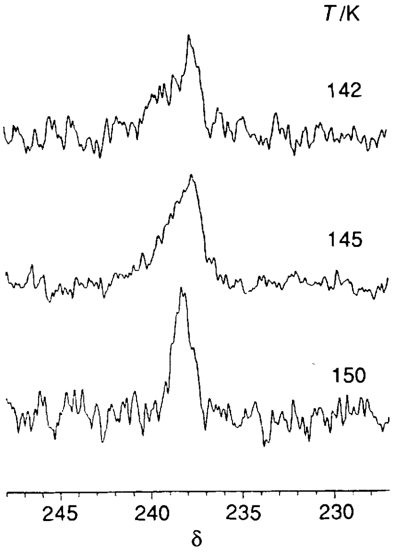

Fig. 4 Variable-temperature 75.5 MHz $^{13}C-\{^1H\}$ NMR carbonyl carbon subspectrum of complex **7** dissolved in $CDFCl_2$

Table 4 Numbers of proximal and distal arene substituents in the dicarbonylphosphine complexes

Compound	Proximal	Distal	%[a]
16c	2	4	80
16e	1	5	20
17e	1	5	50
17h	0	6	50
18e	1	5	33
18h	0	6	67
22	0	6	100
25	2	4	100

[a] Percentage of the conformer found in the crystal.

of **2**, dissolved in $CDFCl_2$. However, if the ground-state molecular conformation is of C_s symmetry, with asymmetric conformations of significantly higher energy and thus lowly populated, it is not surprising that slowed tripodal rotation was not observed for **9**. Likewise for **11**, the dicarbonyl(triphenylphosphine) complex of **2**, although a decoalescence was observed in the triphenylphosphine subspectrum below 180 K and attributed to slowed rotation about the chromium–phosphorus bond ($\Delta G^{\ddagger}_{200} \approx 35$ kJ mol^{-1}), no line broadening occurred in either the carbonyl or arene subspectra. Once again this is not too surprising as it is very unlikely that a molecular conformation of other than C_s symmetry is significantly populated for **11** and symmetry considerations would prevent the observation of slowed tripodal rotation.

Analysis of the Molecular Structural Parameters of M(η^6-arene) *Complexes*.—A whole body of information obtained from both solution and solid-state studies is now available for η^6-arenemetal carbonyl complexes, especially those of hexasubstituted benzenes. Our previous studies have concentrated on the overall molecular structures of the complexes and their intramolecular dynamic processes and some definite conclusions have already been summarised.[5] However, there are now available a significantly greater number of X-ray structural determinations of hexasubstituted benzene–metal carbonyl complexes, together with numerous more recent dynamic NMR studies and we shall here attempt to address more closely two general questions: (*i*) how do η^6-arenemetal carbonyl complexes minimise increasing intramolecular non-bonding interactions; and (*ii*) how do intramolecular rotational barriers correlate with structural changes?

(*i*) *Intramolecular non-bonding interactions and structural changes*. The present detailed structural analysis covers the twenty-one complexes **6**, **7**, **12**,[11] **13**,[4a] **14**,[12] **15**,[14] **16**,[15] **17**,[16] **18**, **19**,[11] **20**,[5] **21**,[17] **22**,[13a] **23**,[7a] **24**,[18] **25**,[6] **26**,[19] **27**,[20] **28**,[21] **29**[22] and **30**[23] involving the ligands **1**–**5**, hexa-*n*-propylbenzene (in **22**), and pentaethylacetophenone (in **23**). With the exception of **1** and **2**, only arenes without annelated rings have been considered. The analysis therefore deals mainly with η^6-arenemetal complexes of hexasubstituted benzenes with tricarbonyl- or dicarbonyl(ligand)-metal moieties, although reference is also made to complexes **21**, **29**, **30**, **31**,[20] **32**, **33**,[24] **34**,[25] **35**,[26] **36**,[27] **37**,[28] **38**,[29] **39**[30] and **40**,[31] where either the benzene is not hexasubstituted or the ligands substituting the metal are other than carbonyls.

To quantify the effects of complexation on an arene it is, of course, necessary first to analyse the geometry of the arene itself. Since hexaethylbenzene **3** is the only arene described in this analysis for which an X-ray structure is available,[11] we have resorted to empirical force-field calculations to provide the necessary molecular structural information for the other arenes. We have previously shown that such calculations accurately reproduce the structure of **3** and are therefore confident that they provide reliable predictions of the structural parameters of these relatively simple organic molecules.

Empirical force-field calculations were carried out using the Allinger MM2(87) program.[10b] Table 3 lists selected structural parameters calculated for arene ligands **1**–**5**. For comparison, the corresponding parameters obtained from the X-ray structure of **3** are also included.

For ligands **1**, **2** and **5** only a single minimum-energy conformation is found in each case, whereas **3** and **4** are able to adopt multiple minimum-energy conformations. For both **3** (eight conformations in total) and **4** (ten conformations in total) the conformation of lowest energy is that with the terminal groups of the benzene ring substituents alternating below and above the ring plane, whereas the conformation of highest energy is that with all substituents pointing on the same side of the benzene ring. The conformational energy differences, structures, and interconversion modes of **3** and **4** have been fully described in the preceding paper.[8] Data for only the lowest- and highest-energy conformers of **3** (**a** and **h**, respectively) and for the ground-state structure of **4** are listed in Table 3.

The benzene ring is essentially planar in all the conformers of ligands **1**–**5**. In the ground-state structures of the arenes the methyl groups of **5** and the methylene groups of **3** and **4** are alternately displaced above and below the benzene ring plane. Such alternating arrangements of groups directly attached to the ring have been found in many other hexasubstituted benzenes and are considered to be a regular deformation mode to avoid steric interactions between adjacent substituents.[32] It is of interest also that in the ground-state conformation of **3** and **4** there is a displacement of the methylene carbons away from the benzene ring plane in the direction towards their respective terminal methyl or trimethylsilyl (in **4**) groups. However, in conformation **h** of **3** the methyl and methylene groups are displaced to opposite sides of the benzene ring plane. In the ground-state structures of **3** and **4** the bond angles $C_{ar}-CH_2-CH_3$ or $C_{ar}-CH_2-Si$ range from 110.0 to 113.4°. The methine carbons of **1** are displaced slightly away from the benzene ring plane (0.036 Å) in the same direction as the ethylene bridges, whereas the corresponding carbons of **2** lie essentially in the plane of the benzene ring.

Complexation of an arene with a tripodal metal–ligand unit may cause gross changes in the arene conformation, especially if severe intramolecular steric interactions are introduced. Of all the arenes investigated so far, **3**, **4**, hexa-*n*-propylbenzene, and similar ligands show the most dramatic changes which are dependent on the nature of the tripodal moiety. In the $M(CO)_2L$ complexes **12**, **19**, **23** (L = CO), **13** (L = CS), **14** (L = NO), **15** (L = N_2), **20**, **24** (L = η^2-olefin), and also in the $SbCl_3$ complex **21**, the arenes retain the up-down conformation of their ground states, whereas this conformation is changed in the phosphine

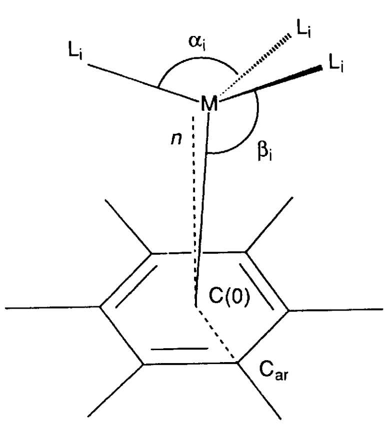

Fig. 5 Definition of the conformational parameters used in the structural analysis of the complexes

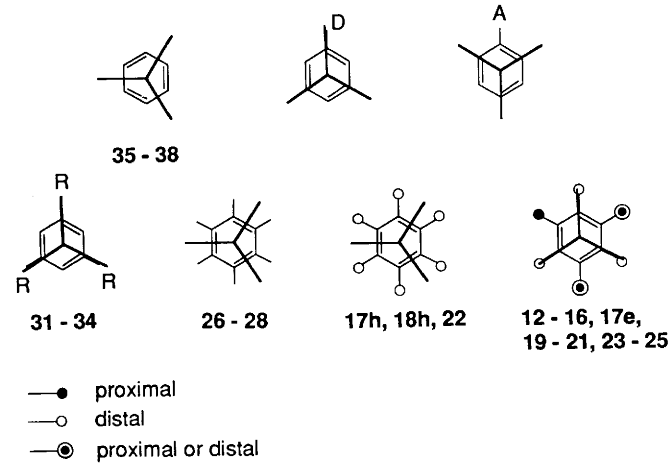

Fig. 6 View along the metal–arene bond axis for the complexes. D = Electron-donating arene substituent; A = electron-withdrawing arene substituent. Proximal (distal) indicates an alkyl group pointing towards (away from) the observer

complexes **16**–**18**, **22** and **25** (Table 4). We have previously pointed out that within a series of hexaethylbenzene complexes with different phosphine ligands substituting the metal, increasing the size (as indicated by the cone angle) of the phosphine increases the number of hexaethylbenzene distal substitutents.[5]

However, the number of distal groups is also related to the nature and size of the substituents on the arene itself. As discussed in detail in the preceding paper,[8] the hexaethylbenzene conformation **h**, with all methyl groups on the same side of the benzene ring, lies only 39.0 kJ mol^{-1} above the ground state, whereas in ligand **4** that conformation with two ethyl groups on the same side of the benzene ring as the three trimethylsilyl groups is as high as 44.2 kJ mol^{-1} above the ground state. Hence it is not too surprising that all the ethyl groups are forced into distal positions in complex **18**, whereas in **25**, the corresponding triphenylphosphine complex of **4**, there is found only one distal ethyl group.

In addition to gross conformational changes in the complexed arenes, several other structural changes may be anticipated and are indeed observed in complexes **6**, **7** and **12**–**30**.

Tripodal unit. The conformational parameters used in this analysis are defined in Fig. 5. In the ground state, M(η^6-arene)L_3 complexes may adopt staggered or eclipsed conformations about the metal–arene bond depending primarily on the number and nature of the benzene substituents and the axial symmetry of the arene. Where the arene exhibits six-fold axial symmetry, staggering is electronically favoured. Thus complexes of unsubstituted benzene, *e.g.* **35**–**38**, are normally staggered, the only known exceptions being the bimetallic species **39** and **40**. The hexamethylbenzene complexes **26**–**28** also adopt almost perfectly staggered conformations. The only known exceptions are **29**, in which the ligands differ very greatly in size with the result that the olefin eclipses a benzene carbon atom whereas the projection of the phosphorus atom bisects a benzene carbon–carbon bond, and **30**, in which the metal tripod is only approximately staggered. It should be noted, however, that in this latter complex the arene is puckered to such a degree that it is better considered to form a metallanorbornadiene rather than an η^6-arenemetal complex.[23] Complexes of other hexahomoalkyl-substituted benzenes can also be anticipated to adopt staggered structures if arene conformations of six-fold axial symmetry are energetically accessible. In **17h**, **18h** and **22** all of the arene substituents are distal and the view from the metal atom to the proximal side of the arene is now essentially the same as that with hexamethylbenzene, the complexes thus adopting staggered arrangements.

Arenes **1** and **2** lack six-fold symmetry but nevertheless their complexes are staggered. Steric effects, of course, are here dominant in determining the tripod conformation relative to the arene. In complex **6** the tripod conformation is perfectly staggered whereas in **7** one of the carbonyl groups is pushed away from the proximal ethylene bridges by about 5°. Normally, however, a reduction from six-fold axial symmetry in the arene inevitably leads to eclipsed conformations about the metal–arene bond. Even with arene substituents of low steric demand an eclipsed conformation is without exception found for complexes of monosubstituted arenes. In M(η^6-arene)(CO)$_3$ complexes an electron-donating group substituting the benzene leads to a conformation in which one carbonyl eclipses the arene substituent, whereas an electron-withdrawing substituent causes the arene hydrogen adjacent to that substituent to be eclipsed (Fig. 6). The arene hydrogens are also almost perfectly eclipsed in the symmetrically trimethyl-substituted mesitylene complexes **31**–**33**, with a maximum averaged deviation of only 1.8°. However, in the tris(pyrrolidine) complex **34** this deviation is much larger (17.1°), most probably the result of non-bonding interactions between one carbonyl group and one proximal pyrrolidine hydrogen.

For complexes of hexahomoalkyl-substituted benzenes with more sterically demanding arene substituents, energetically accessible arene conformations with one or more proximal alkyl groups force the tripod to adopt an eclipsed conformation in order to minimise non-bonding interactions between tripodal ligands and proximal substituents. The largest deviations from a perfectly eclipsed conformation are found in complexes **16c** and **25**. In **16c** the averaged deviation is 9.1° and results from repulsion between one methyl group of the trimethylphosphine and a proximal ethyl substituent (indeed, in the crystal unit cell of **16**, 20% of the molecules have this same ethyl group pushed to the distal side to give **16e**). An even larger deviation (averaging 17°) from perfect eclipsing is found in complex **25** where the arene adopts a conformation with two proximal (two ethyl) and four distal (one ethyl and three trimethylsilylmethyl) alkyl groups. In this case the repulsion arises from interaction between a phenyl ring of the triphenylphosphine ligand and one proximal ethyl group with the result that the ligated phosphorus is 20.1° from perfect eclipsing, pushing the two carbonyls closer to the proximal ethyl group. Unlike **16c**, however, the resulting strain cannot be relieved by turning a second ethyl group of the arene on to the distal side since such an arene conformation is energetically inaccessible.

The metal–arene bond distances of all the chromium complexes lie in the range 1.713–1.729 Å except for **7** (1.743 and 1.754 Å in the two independent molecules of the unit cell), the thiocarbonyl complex **13** (1.774 Å), the nitrosyl complex **14** (1.796 Å), and the pyrrolidine complex **34** (1.822 Å). In the molybdenum complexes all metal–arene distances are in the range 1.888–1.918 Å except for the maleic anhydride complex **20** (1.951 Å). Thiocarbonyl, nitrosyl, and maleic anhydride are all known to be good back-bonding ligands, and these observed

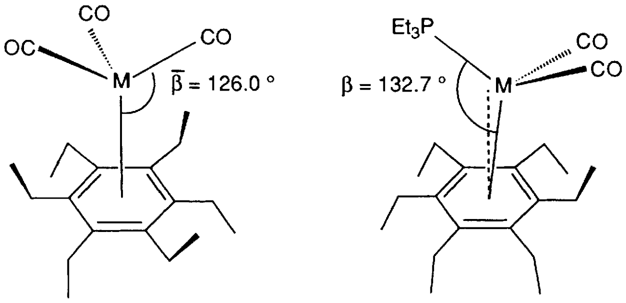

Fig. 7 The effects on bond angles and tilt angles by substituting a carbonyl group of hexaethylbenzene complex **12** with a triethylphosphine ligand to give complex **17e**

elongations in the metal–arene bonds are therefore not unexpected. Tris(pyrrolidinyl)benzene is an excellent electron donor and an observed elongation in the chromium–arene bond of **34** is also as expected. Only in **7** is there a larger than anticipated chromium–arene bond probably the result of *steric* interactions between the carbonyls and the proximal ethylene bridge.

Both the chromium- and molybdenum-carbonyl bonds show a similar dependence on the presence of phosphine ligands substituting the metal. The Cr–CO bond lengths of the tricarbonyl complexes **12**, **23**, **26**, **34** and **35** are in the range 1.823–1.841 whereas in the phosphine complexes **16**–**18** and **22** these bonds are somewhat shortened to between 1.800 and 1.824 Å. In the molybdenum complexes this trend is more pronounced; in the tricarbonyl complexes **19**, **27** and **31** the Mo–CO bond lengths are 1.944–1.966 Å whereas that of the triphenylphosphine complex **25** is 1.869 Å. Corresponding to shorter metal–carbonyl bonds, longer carbonyl (carbon–oxygen) bonds are found: in chromium tricarbonyl complexes, 1.151–1.163 Å (except for **34**, 1.172 Å) and in chromium dicarbonylphosphine complexes, 1.163–1.173 Å. In the molybdenum complexes no significant elongations are observed: tricarbonyls, 1.153–1.165; dicarbonylphosphine **25**, 1.154 Å. These findings are generally consistent with the concept that phosphines donate electron density to the metal, at the same time enhancing the back bonding of the carbonyls, with the result that the carbon–oxygen bonds are elongated whereas the metal–carbonyl bonds are shortened.

Interestingly, in complex **7** the individual chromium–carbonyl bond lengths in both the two independent molecules of the unit cell vary, from 1.817 to 1.826 and from 1.824 to 1.852 Å respectively. These variations (0.029 and 0.028 Å) are larger than observed in any of the other metal tricarbonyl complexes. In each independent molecule of the unit cell, the largest bond is that which is closest to the proximal ethylene bridge, indicating that this is probably the result of intramolecular interactions and provides some evidence for a correlation between increasing steric energy and bond elongations.

In all the tricarbonyl complexes the tilt angle of the tripodal unit is within the range 0.3–1.7°. Substituting more sterically demanding ligands for carbonyls increases the tilt angle, the maximum being found for **38** (3.6°). In general, however, the tilt angles remain small but their variation can be correlated with the size of the tripodal ligands and the substituents and conformation of the complexed arene. The largest tilt angles are found in complexes without proximal substituents and with a large ligand, for example triphenylphosphine (**18**, 2.5; **22**, 2.6°). The tripod is always tilted in such a way that the distance from the arene substituents to the largest ligand on the metal is maximised. A comparison of the structures of **17e** and **17h** shows the dependence of the tilt angle on the arene conformations: **17e** (one proximal ethyl group), 1.2; **17h** (all ethyl groups distal), 2.3°.

The bond angles α (ligand–metal–ligand) and β (ring centroid–metal–ligand) are defined in Fig. 5 and are, of course, strongly interrelated. For the chromium tricarbonyl complexes **6**, **7**, **12**, **23**, **26**, **34** and the ruthenium complex **36** the *averaged* values of α (89.3 ± 0.7°) and β (125.8 ± 0.4°) do not depend significantly on the arene, although individual values of α and β within a given complex may vary within a few degrees (for example, in the two independent molecules of the unit cell of **7**: Δα, 3.1; Δβ, 4.3° and Δα, 4.6; Δβ, 3.8°, respectively). Similar averaged values for α (88.0 ± 0.6°) and β (126.7 ± 0.5°) are found in the molybdenum tricarbonyl complexes **19**, **27** and **31**. Major changes, however, are observed in all the phosphine complexes **16**–**18**, **22**, **25** and **39**, where the averaged angle β is increased to 132.6 ± 0.5°, this value again being independent of both the arene and the metal. An increase in an individual angle β is accompanied by decreases in individual values for α and/or the remaining βs.

In the olefin complexes **20** and **24** the averaged carbonyl–metal–carbonyl bond angles are significantly smaller (84.5 ± 1.6°) than in the tricarbonyl complexes.

The result of the changes in the bond angles and the increased tilt angles induced by sterically demanding ligands substituting the metal is visualised for two hexaethylbenzene complexes, **12** and **17e**, in Fig. 7. The combined effects force the carbonyl groups of **17e** closer to the least-squares plane of the benzene ring than happens in the tricarbonyl complex **12**. Steric interactions between the arene and the sterically demanding ligand are thereby minimised. The *averaged* distances of the carbonyl carbons from the least-squares plane of the benzene ring are found to be 2.815 ± 0.032 Å for the chromium tricarbonyl complexes, 2.721 ± 0.027 Å for the chromium dicarbonylphosphine complexes, 3.080 ± 0.015 Å for the molybdenum tricarbonyl complexes and 2.889 Å in **25**.

Arene unit. Additional to their conformational variability, several other structural changes are found for complexes of hexaethylbenzene and similar arenes. In complexes of C_{3v} symmetry, for eclipsed structures there is no requirement for benzene-ring planarity and there can be no alternation of C_{ar}–C_{ar} bond lengths. Conversely, benzene-ring planarity is required of the staggered structures, and there is an expectation of C_{ar}–C_{ar} bond alternation. Both ring puckering and C_{ar}–C_{ar} bond variation might be anticipated for complexes of lower symmetry but, nevertheless, in actuality the arene rings are not very much affected by complexation. In general, bond lengths remain comparable with those of the free arene. Only in complex **25** is found an extreme bond length of 1.479 Å which could be the result of non-bonding interactions between the triphenylphosphine substituting the metal and one proximal ethyl group substituting the benzene. In most complexes the arene rings are essentially planar and any small deviations from planarity are not systematically dependent on the metal tripod. Two types of deformation are, however, typical for a few complexes. In **19** and **25**, and, to a lesser extent, in **12**, **17h** and **22**, the arene carbons are alternately displaced from the benzene least-squares plane, although these deviations are rather small (*e.g.* in **25**, ±0.025 Å). In complexes **18**, **28** and **36** the benzene rings are folded along an axis through the 1,4-carbons. An extreme case of puckering is found in **30** (±0.169 Å), although as mentioned above this is not regarded as an η^6-arenemetal complex.

Structural changes of more significance are found in the arene substituents. The C_{ar}–CH_3 and C_{ar}–CH_2 bond lengths in the free ligands **3**–**5** are in the range 1.516–1.528 Å (Table 3). The corresponding bond lengths in the hexamethylbenzene complexes **26**–**28** and **30**, are only slightly shorter at 1.500–1.521 Å. However, in **29**, that C_{ar}–CH_3 bond which is eclipsed by the olefin is elongated to 1.550 Å.

In the complexes of hexaethylbenzene and hexaethylbenzene-like arenes **12**–**23** the individual C_{ar}–CH_2 bond lengths vary over a wide range from 1.492 in **15** to 1.563 Å in **20**. Within a given complex the variation is much smaller although the bond lengths to the proximal methylene carbons are longer than to the distal methylene carbons. These differences in hexamethylbenzene complexes are quite small, the two largest being for **15**

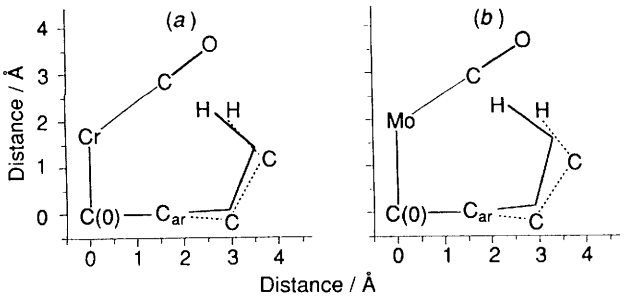

Fig. 8 The decrease in the distances of proximal substituents from the least-squares plane of the benzene ring on complexation of the arene. C(0) = Benzene ring centroid. (*a*) Complex **12** (- - - -) compared with arene **3** (——); (*b*) complex **24** (- - - -) compared with arene **4** (——)

Table 5 Closest possible distances (Å) * of tripodal CO and CS ligands from the hydrogen atoms of proximal arene substituents

Complex	C–H	O–H	S–H
6	1.99 (0.85)	1.90 (0.80)	—
7	1.99 (0.85)	1.90 (0.8)	—
	1.93 (0.79)	1.70 (0.6)	—
12	1.65 (0.51)	1.50 (0.40)	—
13	1.76 (0.62)	—	1.70 (0.30)
19	1.71 (0.61)	1.73 (0.63)	—

* Calculated by assuming rotation of the tripod about the η^6-arene–metal bond until the distances between the ligand atoms and the hydrogen atoms of the proximal arene substituents became as small as possible. Averaged values are reported. The effect of tripodal tilting was not taken into account. In parentheses are distances corrected for the van der Waals radii of the covalently bonded atoms (H, 0.37; O, 0.73; C, 0.77; S, 1.02 Å)

(0.036) and **20** (0.029 Å), but this trend is more pronounced for complexes of arene **4**. Individual C_{ar}–CH_2 bond lengths in complex **25** vary from 1.409 to 1.576 Å and the difference between bond lengths to the proximal and to the distal ethyl groups is as high as 0.054 Å.

The most significant structural changes occurring on complexation are, however, out-of-plane and angle deformations of the arene substituents. In the ground state the free arenes **3**–**5**, and hexa-*n*-propylbenzene have the substituents displaced alternately above and below the benzene ring with the carbons of a given alkyl group on the same side of the benzene ring plane. However, in complexes **12**–**20** and **22**–**25** all the methylene carbons of the proximal ethyl groups are pushed to the distal side. The least sterically strained hexaethylbenzene complex is **21** with the antimony located 2.962 Å from the benzene ring plane and in this molecule only the methylene carbons of two of the three proximal ethyl groups are forced on to the distal side. Methylene carbons of distal alkyl groups usually remain on the distal side of the benzene ring plane. Large tripodal ligands, such as phosphines, lead to very significant out-of-plane deviations of the methylene carbons of both proximal and distal substituents. If the tripod conformation is staggered the methylene carbons closest to the phosphines are most affected and deviations of up to 0.139 Å (**18**) occur. Eclipsing a methylene carbon by a phosphine ligand leads to its more significant displacement to the distal side. However, even larger displacements are found in the olefin complexes where non-bonding interactions between the olefin and adjacent *proximal* ethyl groups lead to very significant out-of-plane deformations of the methylene carbons of those particular groups (**20**, 0.225, 0.263; **24**-1, 0.242, 0.120; **24**-2, 0.160, 0.261 Å).

A similar effect is seen in complexes **6** and **7** where non-bonding interactions between proximal methylene or ethylene bridges and carbonyl ligands cause deformations in the arenes. The proximal groups are pushed away from the chromium tricarbonyl unit and as a result the methine carbons are pushed below the benzene ring plane (averaged values: 0.104, **6**; 0.143 Å, **7**). The largest effect is found at the proximal ethylene bridge of **7** where the methine carbons are out of plane by 0.217 and 0.245 Å.

In addition to the out-of-plane deformations significant changes in the C_{ar}–CH_2–CH_3 bond angles on complexation are found. The averaged bond angles of the proximal substituents are larger than either those of the distal ones or those found in the ligands (*e.g.* **16**, 118.3° proximal, 113.7° distal).

As a result of out-of-plane deformations and the increase in bond angles, the distances of proximal substituents from the least-squares plane of the benzene ring are decreased on complexation. Fig. 8(*a*) shows the difference between uncomplexed hexaethylbenzene and hexaethylbenzene in the chromium tricarbonyl complex **12**; Fig. 8(*b*) compares **4** with that arene in complex **24**-1. The methyl carbons of the proximal ethyl groups are 1.444 Å above the least-squares plane of the benzene ring in free hexaethylbenzene but only 1.261 Å in **12**. The extreme case is **4** compared with **24**-2 where the corresponding distances are 1.583 and 1.067 Å.

Even in complexes **6** and **7** where the complexed arenes are rigid these effects are very noticeable. In **6** the carbons of the proximal methylene bridges are found to be only 0.666 Å above the least-squares benzene ring plane compared with 0.807 Å in **1**. In **7** the methylene bridge carbons are 0.624 Å, those of the ethylene bridges 1.023 Å, above the benzene ring plane as compared with 0.841 and 1.382 Å in the free arene **2**.

(*ii*) *Molecular structure and internal rotations.* In tripodal η^6-arenemetal complexes three different intramolecular rotations have been identified which are potentially observable on the NMR time-scale: rotation of arene substituents causing their exchange between proximal and distal environments; rotation about tripodal ligand–metal bonds; and rotation about η^6-arene–metal bonds.

Rotation of arene substituents can lead to two different types of interconversion; homomerisation where there is interconversion between symmetry-equivalent structures, as happens in complexes **12**–**15**, **19**, **20** and **23**; and isomerisations where there is interconversion between two or more diastereomeric conformations, as happens in complexes **16**, **17** and **25**. In hexaethylbenzene complexes such as **12**, **13**, **15** and **19** with ligands of low steric demand the interconversion barriers range from 45.1 to 48.5 kJ mol^{-1}, only slightly lower than that calculated for hexaethylbenzene itself.[5,8] In the complexes with a phosphine ligand a significantly lower barrier (33–40 kJ mol^{-1}) is found, possibly the result of steric strain leading to an increase in ground-state energy relative to the transition-state energy. An even more pronounced effect is seen in **25** where a barrier of 38.7 kJ mol^{-1} was determined compared with a value of 53.6 kJ mol^{-1} calculated for the uncomplexed arene **4**.[8]

Slowed rotation about tripodal ligand–metal bonds has been monitored in several phosphine complexes, most notably those of triphenylphosphine, **10**, **11**, **18**, **22** and **25**.[13] Such slowed rotation is not limited to complexes of hexasubstituted benzenes but has also been observed, for example, in $[Cr(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)(CO)_2(PPh_3)]$. Whether such a rotation can be monitored depends on the substitution pattern of the benzene ring since if two adjacent positions are unsubstituted then rapid interconversion of the phenyl group environments of the triphenylphosphine ligand occurs even at the lowest experimentally accessible temperature. Barriers ($\Delta G^{\ddagger}_{200}$/kJ mol^{-1}) have been determined for **10** (26.0 ± 5.4), **11** ($\approx$35), **18** (38.2 ± 1.5), and **22** (33.7 ± 1.5).[33]

Slowed rotation about the η^6-arene–metal bond has now been demonstrated for a number of complexes. To date, electronic factors have been shown to be responsible for such slowed rotation only for the complexes $[Cr(p\text{-}MeC_6H_4CHR)(CO)_3]^+$ (R = Me or $C_6H_4Me\text{-}p$)[3c] and tricarbonyl(*bent*-terphenylene)chromium.[2] In all other cases, steric interaction between proximal arene substituents and the tripodal moiety is considered to be responsible for the observed phenomenon. Barriers [$\Delta G^{\ddagger}(T/\mathrm{K})/\mathrm{kJ\ mol^{-1}}$] have been determined for **7** [$\approx$27 (142)], **10** [$\approx$26 (200)], **13** [38.6 ± 1.0 (200)],[8] **24** [37.4 ± 0.6 (200)],[18] **25** [33.2 ± 2.7 (200)],[6,8] [$Mo(CO)_2CS$ complex of **4**] [39.1 ± 1.0 (200)],[8] and [$Ru(C_6H_4Bu^t{}_2$-1,4)$(CO)(SiCl_3)_2$] [$\approx$51 (248)].[3a] That non-bonding interactions are primarily responsible for the slowed rotation observed in these complexes is indicated by several pieces of evidence: the dicarbonylthiocarbonyl complexes **13** and $Mo(CO)_2CS$ with **4**, but not **8**, show slowed tripodal rotation. Table 5 lists values calculated for some of the complexes of the closest possible contacts between ligand atoms (C, O, S) and the hydrogens of proximal arene substituents achievable during rotation of the tripodal moiety about the η^6-arene–metal bond. The oxygen–hydrogen distance is significantly larger in complex **6** than in **12** or **13**, whether or not corrections for the van der Waals radii of the atoms are taken into account. Further, it is noteworthy that the sulphur–hydrogen distance in **13** is significantly longer than the oxygen–hydrogen distance in **12**, although when the larger van der Waals radius of sulphur is allowed for these distances become comparable. From a comparison of the closest oxygen–hydrogen contacts in the chromium tricarbonyl complexes **6**, **7** and **12** it can be concluded that the steric interactions of the ligands increase in the order **1** < **2** < **3**, explaining the non-observance of slowed tripod rotation for **8**. For the tripodal moiety, steric interactions decrease in the order $Cr(CO)_3 > Mo(CO)_3$; an increase in the size of the ligand increases the height of the η^6-arene–metal rotational barrier provided that the number of proximal substituents does not change. Slowed rotation is thus observed for the triphenylphosphine complex **10** but not for the corresponding thiocarbonyl complex **8**; even with triphenylphosphine, at least one proximal arene substituent is required to slow rotation about the η^6-arene–metal bond which is therefore observed for **25** but not for **18** or **22**; if the size of ligands is very large, *e.g.* the $SiCl_3$ ligand of [$Ru(C_6H_4Bu^t{}_2$-1,4)$(CO)(SiCl_3)_2$], even two proximal substituents in arene *para* positions are adequate to slow rotation about an η^6-arene–metal bond.

Conclusion

These and related studies on strained tripodal (η^6-arene) complexes have demonstrated that such molecules can provide exceptional insight into the effects of intramolecular strain on ground-state structures and on internal mobility. It is now clear that, in η^6-hexaethylbenzene-like complexes, increasing intramolecular strain can be initially accommodated by fairly minor structural changes, largely restricted to the tripodal tilt angle and the out-of-plane deformations and bond distances and angles of arene substituents, until the point is reached when, in the contemporary idiom, push becomes shove and the arene undergoes gross conformational change. Such changes clearly signal an increase in internal energy and hence reduction in molecular stability.

It is also clear that the molecular structure and structural change strongly influence intramolecular rotations and we conclude that: in the absence of exceptional electronic factors, proximal arene substituents are necessary to slow rotation about the η^6-arene–metal bond; increasing the size of the ligand has major effects and, depending on the arene, either the barrier to rotation about the η^6-*arene–metal* bond is increased or the number of proximal substituents is decreased; the effective size of the ligand substituting the metal increases in the order $CO \approx CS \approx NO^+ \approx$ *cis*-cyclooctene $< PMe_3 < PEt_3 < P(OEt)_3 < PPh_3$; rotation about the tripodal ligand–metal bond can be slowed even when all the arene substituents are distal, although this is dependent on the size of the ligand and the substitution pattern of the arene; if sterically demanding ligands are combined with sterically demanding arenes in the same molecule, as in complex **25**, rotations about the arene–substituent band, about the tripodal ligand–metal band, and about the η^6-arene–metal bond can all be slowed within an individual complex at experimentally accessible temperatures.

Experimental

Synthesis.—The all-*syn* **1** and *syn-anti-syn* **2** isomers were prepared by the method of Gassman and Gennick.[34]

Complexes. The complexes of the two isomeric arene ligands were synthesised using the same method for each complex. The tricarbonylchromium complexes were prepared by refluxing the arene, **1** or **2** (0.2 g, 0.7 mmol), and excess of hexacarbonylchromium (1.0 g, 4.5 mmol) in dibutyl ether–tetrahydrofuran (9:2, 20 cm^3) for 1 week. The solution was filtered and the solvent stripped off under reduced pressure. Unreacted [$Cr(CO)_6$] was removed by vacuum sublimation and the residue extracted with dichloromethane and the solution filtered. Slow evaporation of the solvent gave the required product as yellow crystals. Yields were typically 99%. Complex **6**: m.p. 240 °C (decomp.). IR (Nujol): 1840, 1926 and 1934 cm^{-1}. NMR: ^1H ($CDCl_3$), δ 0.98–1.28 (m, 9 H), 1.69–1.99 (m, 9 H) and 3.15 (s, 6 H); ^{13}C-{^1H} ($CDFCl_2$, 170 K), δ 26.13, 38.87, 47.52, 112.02 and 237.48. Mass spectrum [*m*/*z* (relative intensity)]: 412 (M^+, 8), 356 (M^+ − 2CO, 9) and 328 (M^+ − 3CO, 100) (Found: C, 69.7; H, 5.4. Calc. for $C_{24}H_{24}CrO_3$: C, 69.9; H, 5.8%). Complex **7**: m.p. 211 °C (decomp.). IR (Nujol): 1910 and 1928 cm^{-1}. NMR: ^1H ($CDCl_3$), δ 0.97–1.36 (m, 6 H), 1.58–2.11 (m, 12 H), 3.16 (s, 4 H) and 3.23 (s, 2 H); ^{13}C-{^1H} ($CDFCl_2$, 290 K) δ 26.95, 27.14, 31.14, 39.76, 41.16, 47.31, 54.50, 110.25, 112.36, 122.97 and 238.30. Mass spectrum [*m*/*z* (relative intensity)]: 412 (M^+, 7), 356 (M^+ − 2CO, 8) and 328 (M^+ − 3CO, 100) (Found: C, 69.8; H, 5.3. Calc. for $C_{24}H_{24}CrO_3$: C, 69.9; H, 5.8%).

The dicarbonylthiocarbonylchromium complexes were prepared by photolysis of the tricarbonylchromium complex **6** or **7** (0.2 g, 0.49 mmol) in benzene solution (100 cm^3) in the presence of *cis*-cyclooctene (2 cm^3, 1.5 mmol), followed by reaction with degassed carbon disulphide (100 cm^3) to give the η^2-CS_2 complex which was desulphurised with triphenylphosphine (0.13 g, 0.5 mmol). Filtration of the reaction mixture and removal of the solvents followed by chromatography on a silica column using hexane–ethyl acetate (7:1) as eluent gave the required product. Yields were typically 33%. Complex **8**: m.p. 220 °C (decomp.). IR (Nujol): 1860, 1869 and 1914 cm^{-1}. NMR: ^1H ($CDCl_3$), δ 0.84–1.25 (m, 9 H), 1.53–1.88 (m, 9 H) and 3.15 (s, 6 H); ^{13}C-{^1H} ($CDFCl_2$, 210 K), δ 25.99, 39.24, 48.22, 116.30 and 235.05. Mass spectrum [*m*/*z* (relative intensity)]: 428 (M^+, 12), 372 (M^+ − 2CO, 100) and 328 (M^+ − 2CO − CS, 41) (Found: C, 67.2; H, 5.8. Calc. for $C_{24}H_{24}CrO_2S$: C, 67.3; H, 5.6%). Complex **9**: m.p. 178 °C (decomp.). IR (Nujol): 1856, 1870 and 1916 cm^{-1}. NMR: ^1H ($CDCl_3$), δ 0.71–2.16 (m, 18 H), 3.07 (s, 2 H), 3.16 (s, 2 H) and 3.20 (s, 2 H); ^{13}C-{^1H} ($CDFCl_2$, 190 K), δ 25.86, 26.50, 31.17, 39.21, 39.55, 40.73, 47.71, 53.16, 115.70, 116.67 and 235.03. Mass spectrum [*m*/*z* (relative intensity)]: 428 (M^+, 12), 372 (M^+ −2CO, 100) and 328 (M^+ − 2CO − CS, 35) (Found: C, 67.1; H, 5.5. Calc. for $C_{24}H_{24}CrO_2S$: C, 67.3; H, 5.6%).

Dicarbonyl(triphenylphosphine)chromium complexes were prepared by photolysis of the tricarbonylchromium complex **6** or **7** (0.2 g, 0.49 mmol) with triphenylphosphine (0.13 g, 0.50 mmol) in toluene for 2 h, followed by removal of the solvent and chromatography of the residue [silica, eluent hexane–ethyl acetate (7:1)] gave the required product. Yields were typically 38%. Complex **10**: m.p. 168–172 °C (decomp.). IR (Nujol): 1814, 1829 and 1873 cm^{-1}. NMR: ^1H ($CDCl_3$), δ 0.79–1.94 (m, 18 H), 2.74 (s, 6 H) and 7.04–7.55 (m, 15 H); ^{13}C-{^1H} ($CDFCl_2$, 180 K), δ 27.23, 39.06, 45.08, 108.47, 127.49, 128.42, 133.34 and 139.33 ($^1J_{PC}$ = 29.44 Hz). Mass spectrum [*m*/*z* (relative intensity)]: 646 (M^+, 0.8), 590 (M^+ − 2CO, 9), 276 ($C_{21}H_{24}{}^+$, 43) and 262 ($PPh_3{}^+$, 100) (Found: C, 75.9; H, 5.9. Calc. for $C_{41}H_{39}CrO_2P$: C, 76.2; H, 6.0%). Complex **11**: m.p. 163–168 °C (decomp.). IR (Nujol): 1803 and 1861 cm^{-1}. NMR: ^1H ($CDCl_3$), δ 0.56–2.12 (m, 12 H), 3.06 (s, 2 H), 3.20 (s, 2 H), 3.26 (s, 2 H) and 7.04–7.60 (m, 15 H); ^{13}C-{^1H} ($CDFCl_2$, 28.9 K), δ 27.63, 28.34, 29.94, 39.68, 40.38, 42.29, 44.92, 55.72, 109.21, 117.83, 127.51, 128.58, 133.99, 140.47 ($^1J_{PC}$ = 28.0 Hz) and 245.38. Mass spectrum [m/z (relative intensity)]: 590 (M^+ −2CO, 0.4), 328. (M^+ − 2CO − PPh_3, 2.4), 276 ($C_{21}H_{24}^+$, 7) and 262 (PPh_3^+, 100) (Found: C, 76.1; H, 5.8. Calc. for $C_{41}H_{39}CrO_2P$: C, 76.2; H, 6.0%).

Physical Measurements.—Infrared spectra were recorded between NaCl plates using a Perkin-Elmer model 377 spectrometer, mass spectra using a Varian MAT-CH-7 spectrometer. Melting points were obtained with a Kofler apparatus. Solution and solid-state NMR spectra were obtained using a Bruker AM300WB instrument operating at 300 MHz (^1H) and 75.5 MHz (^{13}C). Liquid samples were filtered under N_2 through a grade 3 glass sinter, freeze-thaw degassed, and sealed in 10 mm (outside diameter) tubes. The concentrations of the sample solutions were in the range 65–125 mmol dm^{-3} and for low-temperature measurements all samples were dissolved in $CDFCl_2$.

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