

Restricted Rotation about a Metal–Arene Bond caused by the Steric Effects of Proximal Ethyl Groups: Stereodynamics of Some Complexes of 1,3,5-Triethyl-2,4,6-tris(trimethylsilylmethyl)benzene

John A. Chudek,^a Geoffrey Hunter,^{a,*} Regina Louise MacKay,^a Peter Kremminger^b and Walter Weissensteiner^{*,b}

^a Department of Chemistry, The University, Dundee DD1 4HN, UK

^b Institut für Organische Chemie, Universität Wien, Währinger Strasse 38, A-1090 Wien, Austria

1,3,5-Triethyl-2,4,6-triethylbenzene **5** and 1,3,5-triethyl-2,4,6-tris(trimethylsilylmethyl)benzene **6** are considered as realistic role models for the intramolecular rotational behaviour of hexaethylbenzene in its metal complexes. Empirical force-field calculations are reported for the ten diastereomeric conformers of **5** and **6** which fall into four sets depending on the number of *syn* interactions. Variable-temperature 75.5 MHz ¹³C-¹H NMR spectra have been recorded for dicarbonylthiocarbonyl-, dicarbonyl(η²-*cis*-cyclooctene- and dicarbonyl(triphenylphosphine)-[η⁶-1,3,5-triethyl-2,4,6-tris(trimethylsilylmethyl)benzene]molybdenum(0). Decoalescence phenomena are observed for the three complexes and line-shape-fitting studies gave the barriers for rotation about molybdenum–arene bond.

It is well established that when hexaethylbenzene **1** is π-complexed to a metal the up-down ethyl conformation(s) actually adopted by the arene are critically dependent on the steric effects of the other ligands attached to the metal atom.^{1–3} Indeed, in at least one example, [Fe(η⁵-C₅H₅)(η⁶-C₆Et₆)]⁺, merely changing the balancing anion is sufficient to alter the conformation adopted by the complex C₆Et₆ moiety in the crystal: thus [Fe(η⁵-C₅H₅)(η⁶-C₆Et₆)]PF₆ has two ethyl groups proximal to the iron atom,⁴ whereas [Fe(η⁵-C₅H₅)(η⁶-C₆Et₆)]BPh₄ has only one,⁵ the energy difference between the two conformations being small enough to be overcome by even subtle packing effects in the solid state. The structural evidence therefore supports our prior assertion that this complex cation exists as three interconverting stereoisomers in equilibrium in solution at low temperatures.² There are other examples in which compensatory destabilisation, whereby non-bonding repulsive interactions between proximal ethyl groups of the C₆Et₆ moiety and another ligand substituting the metal balance unfavourable *syn* interactions between neighbouring ethyl groups whose methyls are located on the same side of the benzene ring plane, tends to equalise the internal energies of the stereoisomeric C₆Et₆ complexes.²

In the crystal, the co-ordinated C₆Et₆ of dicarbonyl(η⁶-hexaethylbenzene)thiocarbonylchromium(0), **2** adopts a conformation in which three ethyl groups are proximal to the chromium atom.⁶ At low temperatures the solution ¹³C-¹H NMR spectrum of **2** displays two apparent decoalescence phenomena with the ultimate slow-exchange spectrum consistent with C_s symmetry for the molecule.^{6,7} Controversy has arisen concerning the interpretation of the low-temperature NMR spectrum. McGlinchey *et al.*^{6,8} have strongly advocated that the C₆Et₆ conformation observed in the crystal is retained on dissolution and that the C_s symmetry results from an initial slowed rotation about the arene–ethyl bond ($\Delta G_{200}^{\ddagger} = 45.1 \pm 1.4$ kJ mol⁻¹, this work) followed by slowed rotation about the η⁶-arene–metal bond ($\Delta G_{200}^{\ddagger} = 38.6 \pm 1.0$ kJ mol⁻¹, this work), although this latter situation is normally considered to arise only when there are exceptional electronic or steric factors.⁹ By analogy, it was suggested that similar slowed tripodal rotation also occurs in [Cr(η⁶-C₆Et₆)(CO)₃], a molecule whose C_{3v} symmetry precludes direct observation of

this process by NMR spectroscopy.^{6,8} One of us, however, had adopted the more conservative position that the case for slowed rotation about the η⁶-C₆Et₆–M bond remained not proven, as dissolution of compound **2** may lead to a facile change of the C₆Et₆ conformation to one of C_s symmetry, and what had been monitored was solely ethyl-group rotation, for which line-shape-fitting studies gave a barrier of $\Delta G_{200}^{\ddagger} = 37.6 \pm 2.5$ kJ mol⁻¹.^{2,7} Arguments based solely on considerations of molecular symmetry do not therefore allow unequivocal diagnosis of slowed metal tripodal rotation in the C₆Et₆ complexes.

In principle, the solution stereochemistries of the complexes can be determined by measuring the nuclear Overhauser enhancement of the carbonyl ¹³C NMR signals by proximal methyl group protons, thus permitting an unequivocal assignment of the alkyl group resonances to proximal or distal environments. However, no such enhancement of the carbonyl signals by protons of any of the alkyl groups could be detected in ¹³CO isotopically enriched **2** or in [Cr(η⁶-C₆Et₆)(CO)₃].¹⁰ Moreover, our previous attempt to determine the rate constants for the tripodal rotation by variable-temperature T₁ measurements of the carbonyl carbons in [Cr(η⁶-C₆Et₆)(CO)₃] foundered on the inability to separate the rotational and molecular tumbling components to the tripodal reorientation barrier and, contrary to other comments,¹¹ we could therefore make no claim to have measured this rotational barrier.¹ However, by analogy with similar systems, we considered that it was unlikely to exceed about 20 kJ mol⁻¹.

When such direct approaches failed it became necessary to study related molecules as models for C₆Et₆. Such models cannot, of course, in a strict sense either prove or disprove the C₆Et₆ case, but if chosen with care should provide very strong circumstantial evidence as to the intramolecular rotational behaviour of the prototype complexes. A realistic model arene for C₆Et₆ in a M(η⁶-C₆Et₆) complex must fulfil certain basic requirements: the proximal face presented to the metal must be sterically very similar to that presented by C₆Et₆; the energy difference between the interconverting isomers must be high enough for it to be incredible that substitution of one of the metal tripod carbonyls by another, relatively sterically undemanding, ligand (*e.g.* thiocarbonyl) will change the model arene conformation, and also that dissolution of the complex

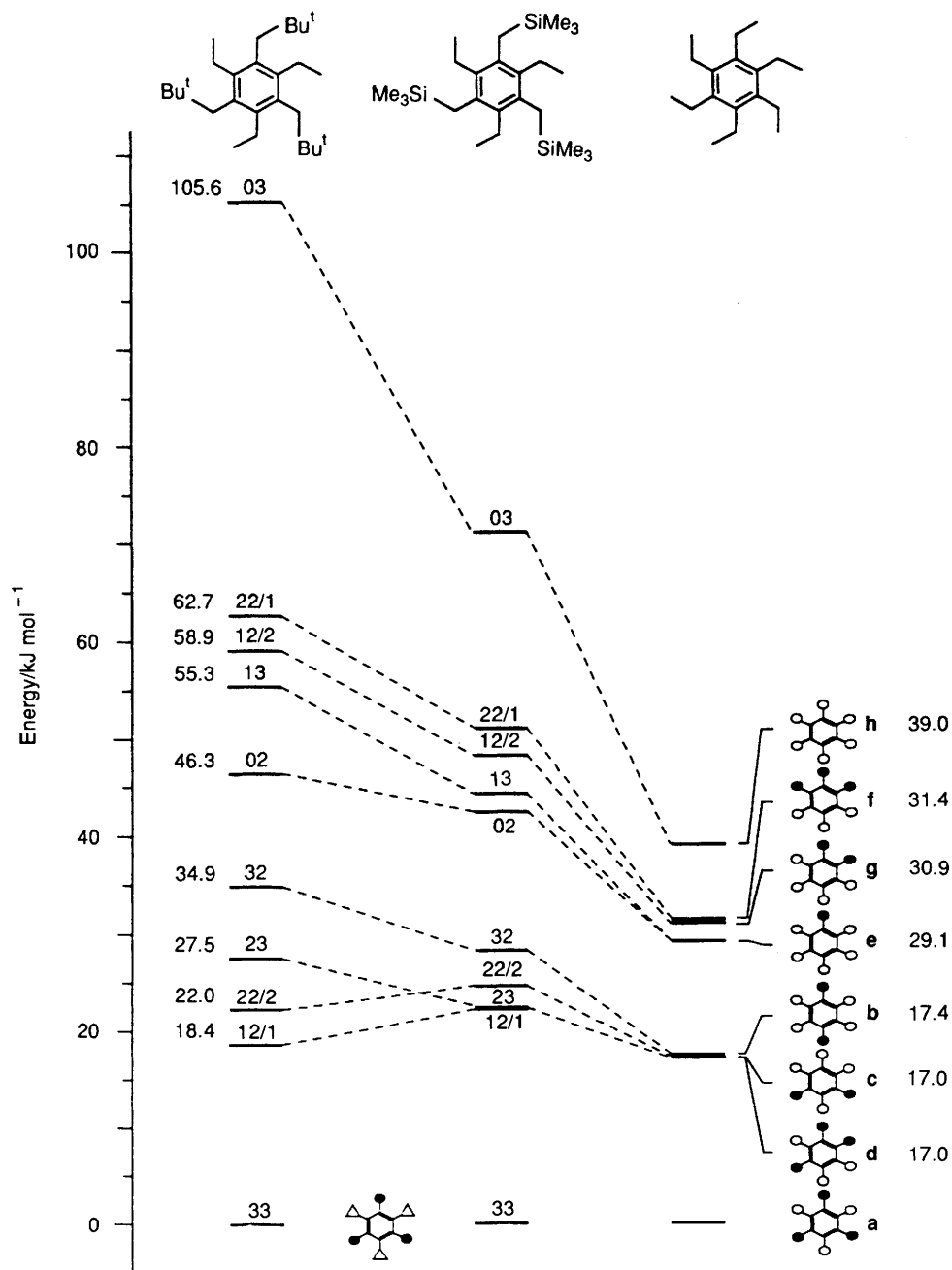


Fig. 1 The calculated [MM2(87)¹⁷] energies of the stereoisomers of hexaethylbenzene **1** and of 1,3,5-triethyl-2,4,6-trineopentylbenzene **5**. [Calculated energies for 1,3,5-triethyl-2,4,6-tris(trimethylsilylmethyl)benzene **6** are shown in Fig. 4.] Filled (open) circles represent ethyl groups above (below) the benzene ring plane; filled (open) triangles represent neopentyl or trimethylsilylmethyl groups above (below) the benzene ring plane

will allow a change in the arene conformation from that observed in the crystal; additional electronic factors unavoidably introduced to the model arene and which might unduly influence the η^6 -arene-metal rotational barrier should be minimal. In this last respect the very recent report of unequivocal evidence for slowed tripod rotation in the chromium tricarbonyl complex of pentaethylacetophenone describes the intramolecular rotational behaviour of a less than optimal model for C_6Et_6 .¹¹ Substitution of an acetyl for an ethyl group reduces the arene molecular symmetry to C_s , which requires that the ring edges fall into four symmetry non-equivalent sets of one, two, two and one. The strongly electron-withdrawing carbonyl group of the acetyl moiety is likely to reinforce the inevitable local differences in the π -electron distribution of an arene of C_s symmetry and thus may substantially alter the electronic contribution to the overall η^6 -

arene-metal rotational barrier. In extreme examples of localised π character, Hoffmann and co-workers¹² have calculated that completely localising the benzene π system to one Kekulé resonance form (cyclohexatriene) raises this barrier from essentially zero to about 80 kJ mol⁻¹, and recently Nambu and Siegel¹³ demonstrated experimentally the first example of slowed rotation in a $M(\eta^6\text{-arene})$ complex due to the localised π character of the bound arene *bent*-terphenylene (benzo-[3,4]cyclobuta[1,2-*a*]biphenylene).

We have investigated two types of hexaalkylbenzenes as role models for C_6Et_6 : (a) the *syn-anti-syn* **3** and all-*syn* **4** trimers of bicyclo[2.2.1]hept-2-yne. The intramolecular rotational behaviour of hexahapto metal complexes of these sterically demanding and rigid arenes have been briefly described¹⁴ and are more fully discussed in the following paper;¹⁵ (b) 1,3,5-triethyl-2,4,6-trineopentylbenzene **5** and 1,3,5-triethyl-2,4,6-

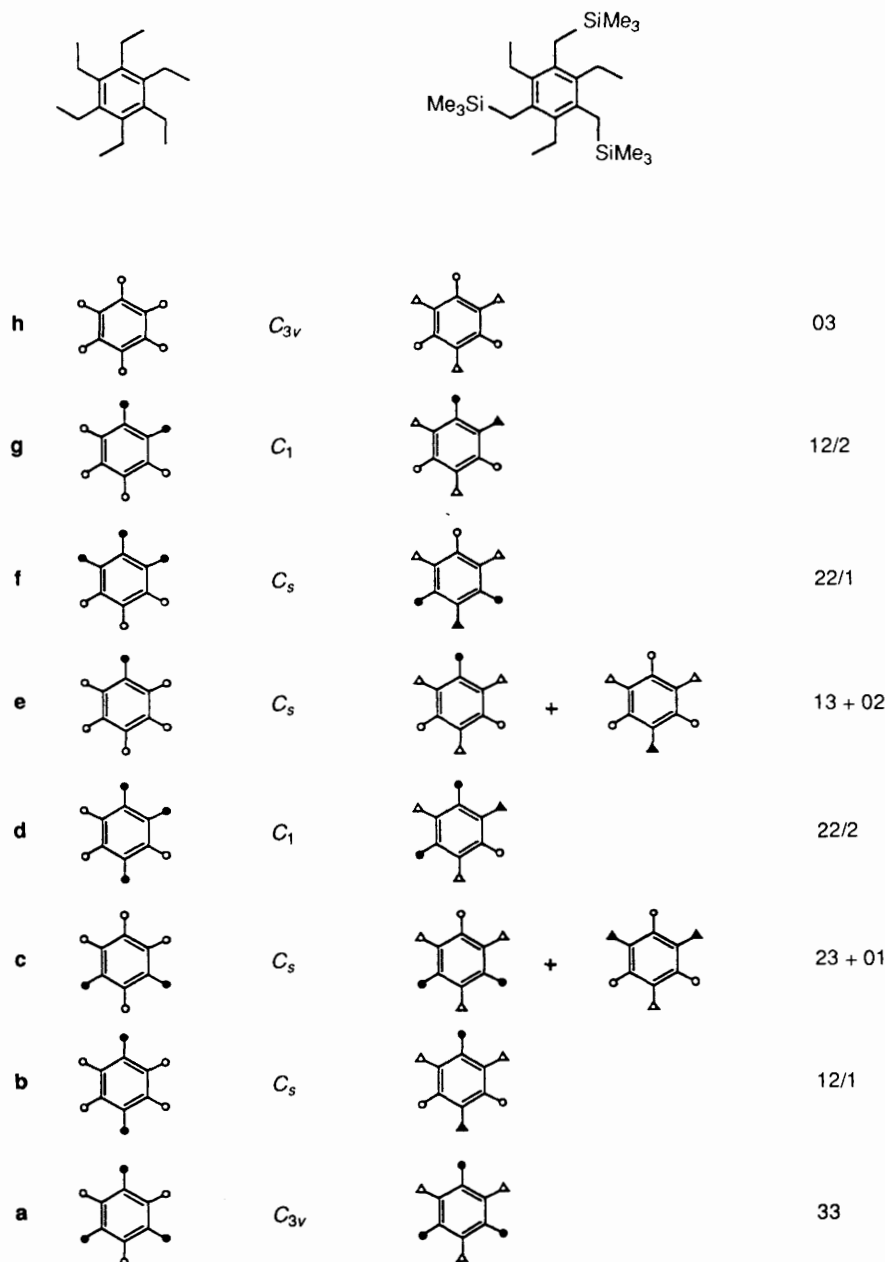


Fig. 2 The corresponding stereoisomers and their descriptors for compounds 1 and 6

tris(trimethylsilylmethyl)benzene **6**. The present paper discusses the suitability of these two arenes as role models for the intramolecular rotational behaviour of C_6Et_6 in its metal complexes, and describes the static and dynamic stereochemistries of a number of hexahapto metal complexes of **6**. A preliminary account of the crystal structure of dicarbonyl[η^6 -1,3,5-triethyl-2,4,6-tris(trimethylsilylmethyl)benzene](triphenylphosphine)molybdenum(0) and of its variable-temperature ^{13}C - $\{^1H\}$ NMR spectrum has previously appeared.¹⁶

Results and Discussion

Empirical Force-field Calculations for Compounds 1, 5 and 6.—All calculations were performed using the Allinger MM2(87) force field.¹⁷ To give a better comparison between the three arenes, the eight up-down structures were recalculated for C_6Et_6 as this program uses some new arene parameters. The new results do not differ significantly from our previously published calculations for this molecule which have shown that the eight up-down stereoisomers can be partitioned into four sets of increasing energy according to the number of *syn*

interactions between neighbouring *ortho* positions whose methyl groups are located on the same side of the benzene ring. The calculated ground state is of D_{3d} molecular symmetry with alternating ethyl groups (stereoisomer **a**). Rotation of one ethyl group of **a** from one side of the benzene ring to the other results in **c** (molecular symmetry C_s) which is calculated to be 17.0 kJ mol⁻¹ higher in energy than **a**. The highest-energy stereoisomer **h** (with all ethyl groups on the same side of the benzene ring) lies 39.0 kJ mol⁻¹ above the ground state. Our calculations indicate that it is very unlikely that attractive non-bonding interactions play a significant role in stabilising minimum-energy conformations of C_6Et_6 .¹⁸ Rotation of the ethyl groups of C_6Et_6 has been found to be completely uncorrelated, *i.e.* only one ethyl group may move at a time from an up to a down position, with the favoured rearrangement pathway being **a** \rightarrow **c** \rightarrow **d** \rightarrow **b** \rightarrow **d** \rightarrow **c** \rightarrow **a**. The rate-limiting step is **a** \rightarrow **c**, with the transition state lying 49.4 kJ mol⁻¹ above the ground-state stereoisomer **a**.^{1,18} As with C_6Et_6 , the ground-state structures for compounds **5** and **6** are the up-down conformers with the ethyl groups on one side of the benzene ring plane and the neopentyl groups of **5** or the trimethylsilyl-

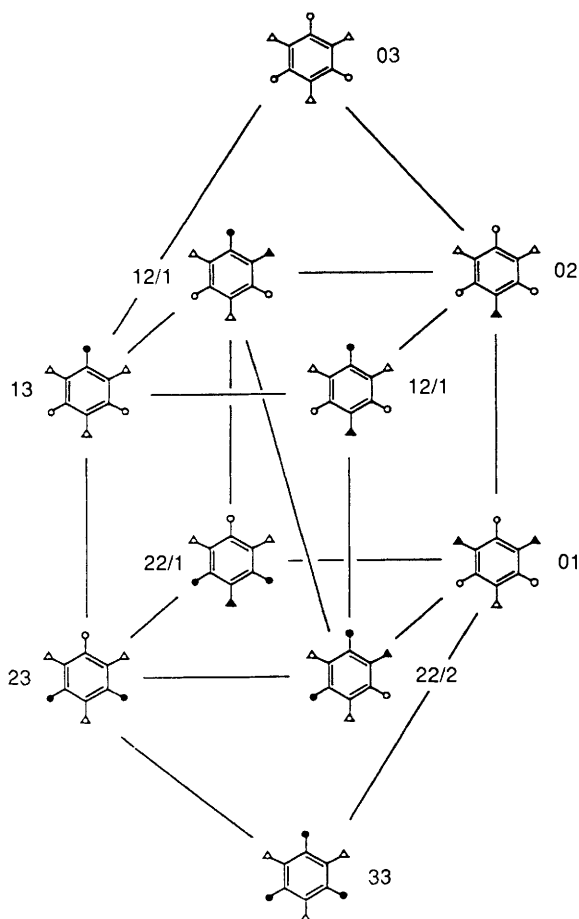


Fig. 3 Basic interconversion graph for the ten stereoisomers of compounds 5 and 6

methyl groups of 6 on the other. 1,3,5-Trineopentylbenzene itself adopts a ground-state conformation with all three neopentyls located on the same side of the benzene ring plane, it having been argued that attractive non-bonding interactions between the *tert*-butyl groups stabilise such a conformation.¹⁹ It should be further noted that the C_{3v} molecular symmetry of the ground-state stereoisomers of 5 and 6 requires that the benzene ring edges are symmetry-equivalent and that, like C_6Et_6 , there can be no alternation of $C_{ar}-C_{ar}$ bond lengths but there is no requirement for $(C_{ar})_6$ ring planarity.

Like the conformers of C_6Et_6 , the ten possible diastereomeric conformers of compounds 5 and 6 fall into four sets depending on the number of *syn* interactions (0,2,4,6). This qualitative classification holds better for 6 than for 5. These ten stereoisomers are, of course, related to the eight of C_6Et_6 and the relationship is shown in Fig. 1. The stereoisomer labelling adopted differentiates between ethyl and the other alkyl group and indicates the side of the benzene ring plane on which the group occurs (Fig. 2). For example, 6/23 to the stereoisomer of arene 6 which has two ethyl groups above and three trimethylsilylmethyl groups below the ring plane as seen from the viewpoint of the observer. Where this system would give the same label to two diastereomers they are further differentiated, e.g. 6/22/1 and 6/22/2.

We have previously postulated that only stereoisomers **a**, **c**, **e**, and **h** are energetically favoured for tripodal $M(\eta^6-C_6Et_6)L_3$ complexes,¹ and it can be further postulated that as is found with 3 and 4, metal complexation will only occur on the less-crowded face of the benzene ring plane of 5 and 6. Moreover, it should be energetically highly unfavourable for one or more of the bulkier alkyl groups to occur on the face of the arene proximal to the complexed metal. Hence of the ten stereoisomers of the two model arenes, only 5/33 (6/33), 5/23 (6/23), 5/13 (6/13) and 5/03 (6/03), which respectively correspond to **a**,

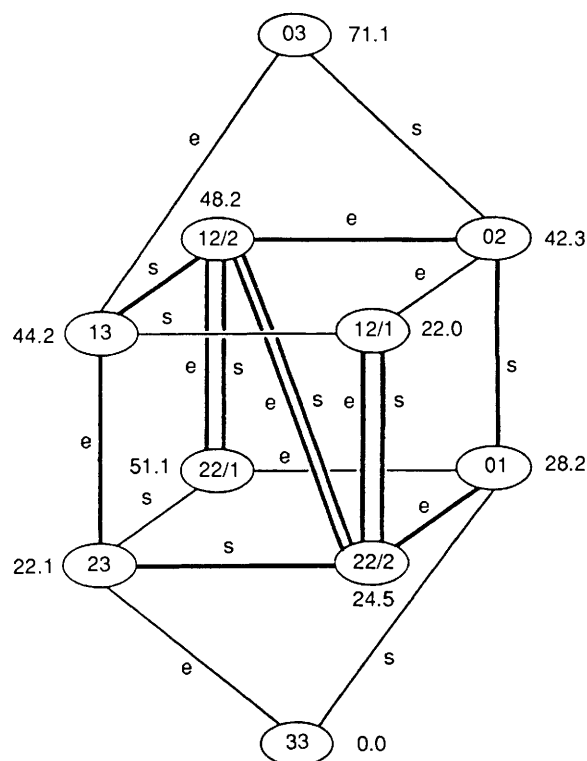


Fig. 4 Interconversion graph for compound 6 indicating (bold lines) the diastereomeric pathways depending on the sense of alkyl group rotation. Each pathway is labelled according to whether the two connected stereoisomers (energies in kJ mol^{-1} adjacent to each stereoisomer) are interconverted by an ethyl group rotation (e) or a trimethylsilylmethyl group rotation (s)

c, **e**, and **h** of C_6Et_6 , can be considered plausible candidates to complex a metal-tripodal moiety. The energy gap between their ground-state stereoisomers and 5/23 and 6/23 (27.5 and 22.1 kJ mol^{-1} respectively) is substantially greater than that between stereoisomers **a** and **c** of C_6Et_6 . To move two ethyl groups from one side of the benzene ring to the other (*i.e.* 5/13 and 6/13) requires very much more energy (55.3 and 44.2 kJ mol^{-1} respectively) than for the corresponding C_6Et_6 stereoisomer **e** (29.1 kJ mol^{-1}). These energy differences for 5 and 6 are greater even than the difference between **a** and **h**, the highest-energy stereoisomer of C_6Et_6 . The highest-energy stereoisomers, 5/03 and 6/03, are 105.6 and 71.1 kJ mol^{-1} respectively above their ground states.

The ten diastereomeric conformations of compounds 5 and 6 can interconvert by rotation of either type of alkyl group. Our calculations indicate that correlated alkyl group rotation can be discounted, and Fig. 3 shows the basic interconversion graph for the model arenes, assuming rotation of one group at a time. It is, however, preferable to double some edges to indicate that interconversion of two stereoisomers can occur *via* diastereomeric pathways.^{18,20} For example, stereoisomer 5/23 (6/23) can interconvert by rotation of a single ethyl group to give stereoisomers 5/33 (6/33) or 5/13 (6/13). Assuming ideal C_s symmetry for stereoisomer 5/23 (6/23) it makes no difference if its single distal ethyl group which lies on the plane of symmetry rotates either clockwise or counterclockwise, the pathways leading to 5/33 (6/33) are enantiomeric and equal in energy. However, rotation of one of the proximal ethyl groups of 5/23 (6/23) which gives 5/13 (6/13) can occur on diastereomeric pathways depending on the sense of rotation. Fig. 4 also shows the interconversion graph for 6, but now indicates the diastereomeric pathways. Each pathway is labelled according to whether the two connected stereoisomers can be interconverted by an ethyl group rotation (e) or by a trimethylsilylmethyl group rotation (s).

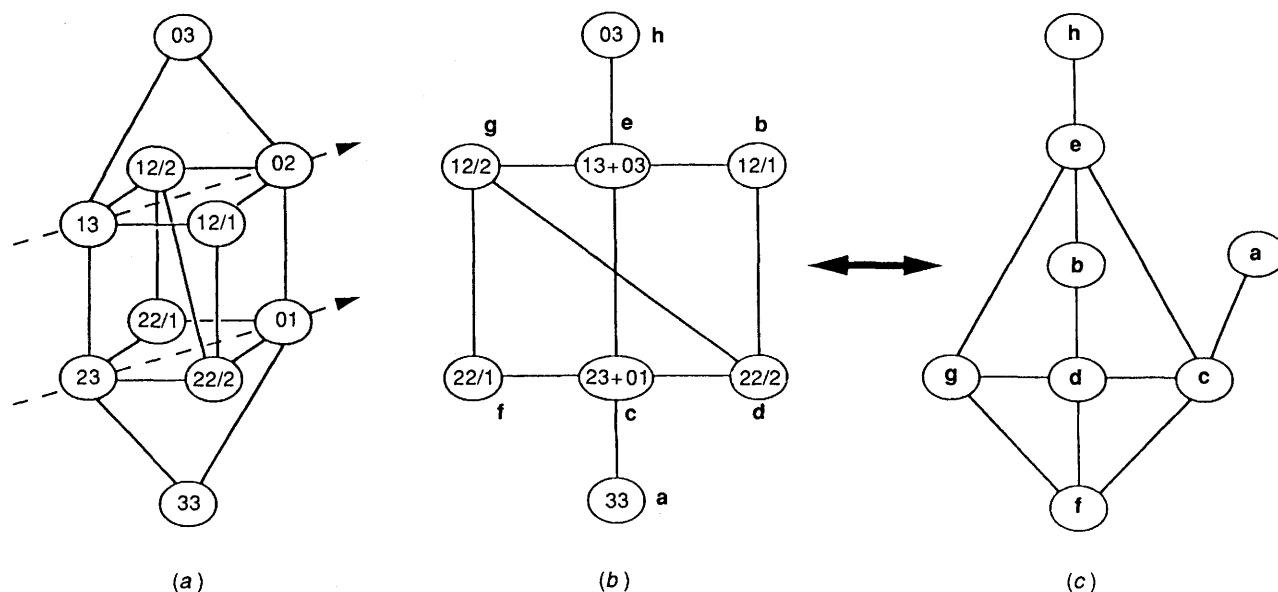


Fig. 5 (a) Interconversion graph for compound **6**. (b) Projection of the vectors connecting vertices 13 and 02 or 23 and 01 on to a plane normal to these vectors. (c) Interconversion graph for compound **1**⁸

Since the two faces of compound **6** are diastereotopic an interconversion which corresponds to a homomerisation of the free arene (*i.e.* the three ethyl groups and the three trimethylsilylmethyl groups exchange faces) leads to isomerisation of an $M(\eta^6\text{-arene})$ complex. Therefore if the ground-state stereoisomer of the free arene is retained on complexation an ethyl or trimethylsilylmethyl group rotation can only be detected if at least one other diastereomer is significantly populated. This is in contrast to the situation for C_6Et_6 where ethyl group rotation can be detected even if its ground-state stereoisomer (except for **h**) is uniquely populated in the complex. If arene **6** complexes as a stereoisomer with C_s symmetry then rotation of its ethyl groups is potentially detectable by NMR spectroscopy even if that is the only diastereomer to be significantly populated.

Starting from its ground state, the ethyl group rotational barrier for compound **6** is calculated to be 53.6 kJ mol⁻¹, rather higher than that calculated for C_6Et_6 , whereas a trimethylsilylmethyl group rotation requires 72.0 kJ mol⁻¹. This is also the lower limit for a homomerisation of the ground-state stereoisomer of **6**. Not only are the stereoisomers of C_6Et_6 and **5** and **6** related to each other, but so are their interconversion graphs. Fig. 5 shows how a projection of the vectors connecting vertices **6/13** and **6/02** or **6/23** and **6/01** on to a plane normal to these vectors results in an interconversion graph analogous to that of C_6Et_6 and which requires only minor redrawing to correspond exactly with that previously published for the latter arene.¹⁸

We therefore consider that both compounds **5** and **6** should behave as realistic models for the intramolecular rotational behaviour of C_6Et_6 in a $M(\eta^6-C_6Et_6)$ complex: a metal tricarbonyl moiety will bind to the less-crowded face of the benzene ring, and in the ground state all ethyl groups will be proximal to the metal atom; the energy penalty involved in forcing one ethyl group from the proximal to the distal side of the complexed model arene is significantly higher than for C_6Et_6 and changing one of the carbonyls for, say, thiocarbonyl is very unlikely to change the arene conformation; although replacement of three ethyl by either neopentyl or trimethylsilylmethyl groups inevitably introduces different electronic distributions at the two different sets of three ring carbon atoms, this difference is likely to be very small and, furthermore, there is the requirement that the π -electron density be three-fold symmetrically distributed in the ground-state stereoisomers of these arenes.

The neopentyl-substituted arene **5** could only be synthesised with great difficulty and in very poor yield. In contrast, the trimethylsilylmethyl-substituted arene **6** was obtained in reasonable yield without undue difficulty and all subsequent metal complex studies were performed with this ligand.

Hexahapto Metal Complexes of Compound 6.—The preparation of compound **6** has been described elsewhere.²¹ The 75.5 MHz ¹³C-¹H NMR spectrum (Table 1) of this molecule displays the two expected arene carbon resonances at δ 133.2 and 132.5, the very small chemical shift difference confirming that there is only a very small difference in the electronic distributions at the two different sets of three ring carbon atoms. We were unable to synthesise an authentic chromium tricarbonyl complex of **6**, although tricarbonyl[η^6 -1,3,5-triethyl-2,4,6-tris(trimethylsilylmethyl)benzene]molybdenum(0) **7** was readily obtainable by simply refluxing **6** with an excess of hexacarbonylmolybdenum in heptane under nitrogen. No decoalescence was observed in the 75.5 MHz ¹³C-¹H NMR spectrum of **7** dissolved in $CDCl_2$ down to 141 K.²¹ Photolysis of **7** in *cis*-cyclooctene, removal of solvent cyclooctene and treatment of the residue with carbon disulphide and triphenylphosphine dissolved in benzene gave dicarbonylthiocarbonyl[η^6 -1,3,5-triethyl-2,4,6-tris(trimethylsilylmethyl)benzene]molybdenum(0) **8** as a yellow crystalline solid. The 75.5 MHz ¹³C-¹H NMR spectrum of **8** was observed down to 153 K in CD_2Cl_2 solution, and down to 141 K in $CDCl_2$. Only a single decoalescence phenomenon, starting at about 190 K and essentially complete at 175 K, was observed and which involved both the alkyl (Fig. 6) and arene (Fig. 7), but not the carbonyl or thiocarbonyl, subspectrum. The decoalesced alkyl and arene subspectra were entirely consistent with C_s molecular symmetry for **8**. We consider it extremely unlikely that steric interactions with the thiocarbonyl substituent would be sufficient to overcome the energy penalty involved in forcing one of the ethyl groups on to the distal face of the co-ordinated arene which must therefore retain the three proximal ethyl groups of the ground-state stereoisomer of **6**. The observed decoalescence phenomenon can thus only be attributed to the onset of slowed rotation about the η^6 -arene-molybdenum bond. Line-shape fitting studies of the arene carbon subspectrum (Fig. 7) gave $\Delta G_{200}^\ddagger = 39.1 \pm 1.0$ kJ mol⁻¹ for this process, the exchange being treated as a three-site problem with the same single rate constant successfully simulating the appearance of both groups of arene resonances at a given temperature.

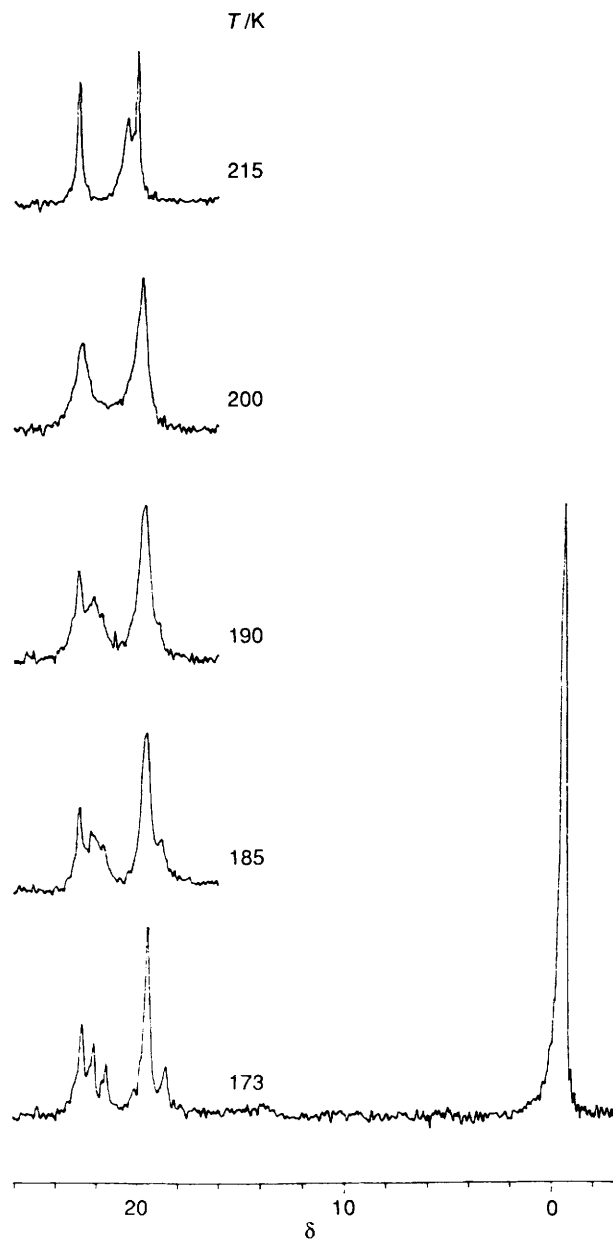


Fig. 6 Variable-temperature 75.5 MHz $^{13}\text{C}\{-^1\text{H}\}$ NMR alkyl carbon subspectrum of complex **8** dissolved in CDFCl_2

There is no significant difference in the $M(\eta^6\text{-arene})$ rotational barriers for complexes **8** and **2** although it might have been anticipated that the larger metal atom of **8** would lead to reduced steric interactions between the proximal ethyl groups of the arene and the ligands of the metal tripod. There is some evidence that this may happen with the molybdenum analogue of **2** for which we have observed only one decoalescence phenomenon, unequivocally attributed to slowed ethyl group rotation, in its 90.6 MHz $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum in CD_2Cl_2 solution. Down to 153 K, the only additional change in the spectrum of this complex was a broadening of one of the arene carbon resonances at δ 126.0, all the other signals remaining sharp and the spectrum consistent with averaged C_{3v} molecular symmetry. While the non-occurrence of a second decoalescence phenomenon attributable to slowed rotation about the $\eta^6\text{-arene-metal}$ bond may simply be due to accidental isochrony, it is also suggestive of the lower barrier anticipated on changing the metal from chromium to molybdenum. If the latter is the case, it would seem either that a proximal ethyl group of **6** has greater steric requirements, perhaps through a more restricted rocking motion about its mean position, than does an ethyl group of C_6Et_6 , or that substitution of trimethylsilylmethyl

for three of the ethyl groups of C_6Et_6 causes a greater than anticipated enhancement of the electronic contribution to the barrier to rotation about the $\eta^6\text{-arene-metal}$ bond.

The two crystal and molecular structures found for dicarbonyl($\eta^2\text{-cis-cyclooctane}$)[$\eta^6\text{-1,3,5-triethyl-2,4,6-tris(trimethylsilylmethyl)benzene}$]molybdenum(0) **9** have been described elsewhere.²¹ In both structures the co-ordinated *cis*-cyclooctene and arene moieties adopt conformations which are very similar to those calculated to be the ground states of the free molecules. Both types of crystal have identical $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra in CD_2Cl_2 solution and at ambient temperature all of the signals anticipated for a conformationally mobile molecule were observed. Cooling the solution caused decoalescences in all of the subspectra. That due to the carbonyl carbon atoms broadened at 156 K, and at 152 K two signals of approximately equal intensity were clearly observed despite a very small separation of only 16.7 Hz. Provided that only one stereoisomer of **9** is significantly populated, then the diastereotopic carbonyl groups are clearly indicative of C_1 molecular symmetry. The *cis*-cyclooctene alkene carbon signal at δ 60.6 broadened and collapsed at 175 K but none of its component signals reappeared down to the lowest temperature observed. In the alkyl carbon subspectrum the signals attributable to *cis*-cyclooctene and the arene substituents decoalesced such that at least twelve signals were observed at 152 K, and it was not possible to distinguish unequivocally from which moiety a given methylene carbon signal originated. However, using the distortionless enhancements by polarisation transfer (DEPT) pulse sequence it was possible to identify three signals at δ 19.5, 16.5 and 15.6 which arose from the decoalescence of the signal at δ 17.3 in the ambient-temperature spectrum and assigned to the methyl carbons of the arene methyl groups, providing further evidence for C_1 molecular symmetry.

At 160 K the two arene carbon signals of the ambient-temperature spectrum had each decoalesced into three signals of approximately equal intensity (Fig. 8). Particularly informative as to the number of intramolecular exchanges responsible for these spectral changes was the decoalescence of the signal at δ 119.0 in the ambient-temperature spectrum. The two outer components of the decoalesced signal had very similar chemical shifts from the centre signal at δ 118.8 (67.0 and 55.1 Hz at 156 K) but nevertheless the spectral collapse initially involved only the centre and right-hand components (δ 118.9, 118.2). The decoalescence was simulated as a general three-site exchange which requires a set of three rate constants for each temperature. If all three of a set were the same then the entire simulated spectrum collapsed on the centre component. It required two significantly different rate constants in each set satisfactorily to simulate the observed spectral changes. At the corresponding temperatures the same sets of rate constants also successfully simulated the decoalescence of the other arene signal at δ 109.3 (Fig. 8). Therefore, despite their very similar energies, the evidence is quite unambiguous that there are at least two independent intramolecular exchange processes and these occur in a sequence whereby the apparent molecular symmetry, initially C_{3v} , reduces to C_s , and ultimately to C_1 , as the exchanges slow.

There are two possible explanations for the spectral changes observed for complex **9**. (i) The arene stereoisomer changes on dissolution to that with one distal and two proximal ethyl groups (*i.e.* **6/23** of the free arene) and the higher-energy intramolecular exchange corresponds to slowed ethyl group rotation. The diastereotopicities of the carbonyl and proximal ethyl groups result from subsequent slowed exchange within the fluxional and unsymmetrically twisted *cis*-cyclooctene moiety. Such slowed exchange has been observed for both *cis*-cyclooctene itself ($\Delta G_{298}^\ddagger = 26.2 \pm 2.7$ kJ mol $^{-1}$) and tetracarbonyl($\eta^2\text{-cis-cyclooctene}$)iron(0) ($\Delta G_{298}^\ddagger = 32.9 \pm 4.2$ kJ mol $^{-1}$),²² and in **9** would correspond to a restricted twisting motion about the C(31)–C(32) bond. The decoalescences observed in the *cis*-cyclooctene methylene carbon subspectrum

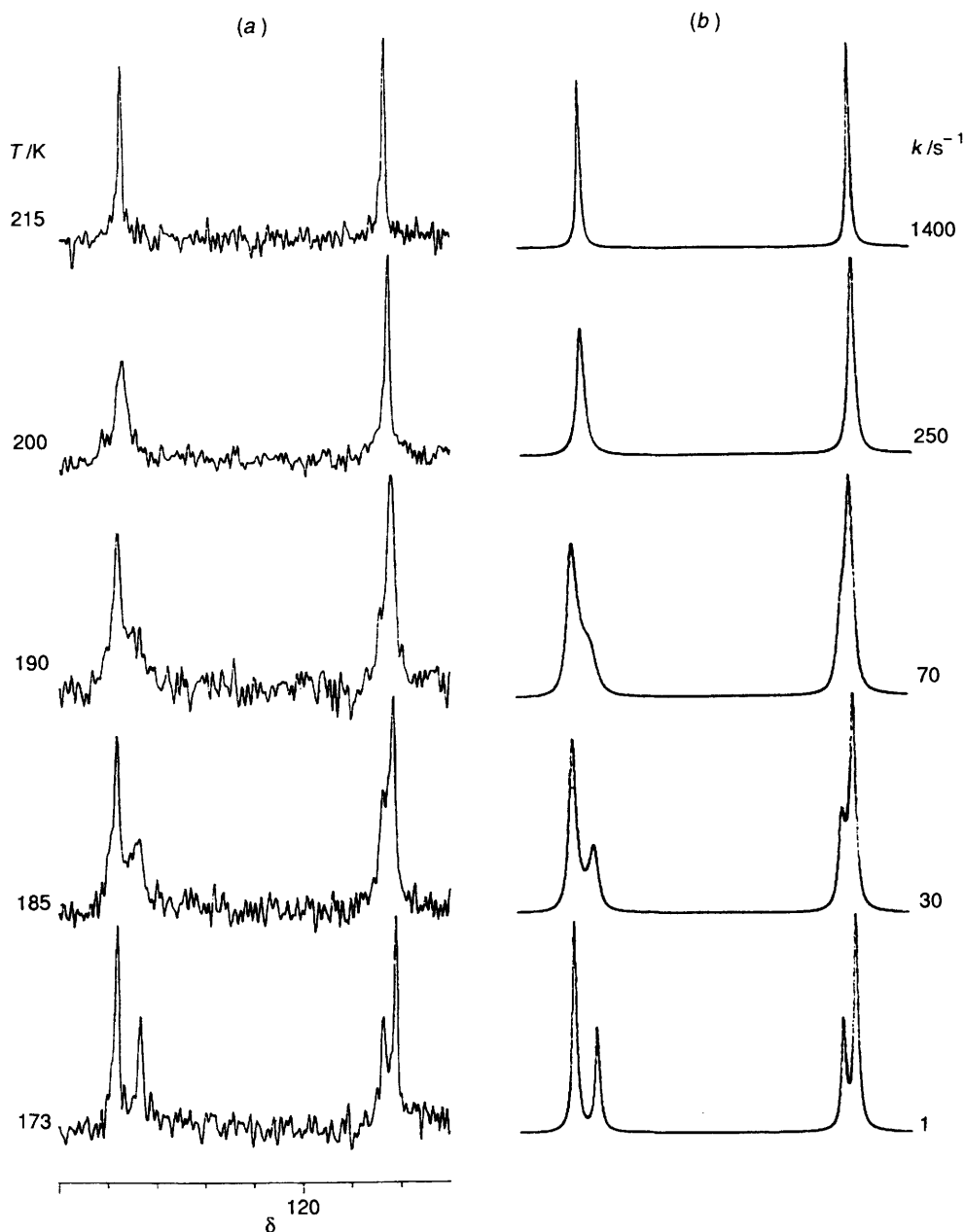


Fig. 7 Variable-temperature 75.5 MHz $^{13}\text{C}\{-^1\text{H}\}$ NMR arene carbon subspectrum of complex **8** dissolved in CDFCl_2 : (a) observed, (b) calculated

confirm that exchange is slowed within that moiety in **9**. Slowed rotation about the η^6 -arene-metal bond is not therefore required in this explanation of the observed diastereotopicities, provided that there is a change in the arene stereoisomer to one of C_3 symmetry on dissolution of the complex. The alternative explanation, (ii) assumes that the complex retains the arene conformation of the solid state on dissolution. The higher-energy exchange corresponds to slowed rotation about the η^6 -arene-metal bond and C_1 molecular symmetry ultimately results from subsequent slowed exchange within the *cis*-cyclooctene moiety as described in (i).

In view of our findings for complex **8** we consider that (ii) is the more plausible explanation for the fluxional behaviour of **9**. However, it is of interest that two of the positively identified methyl carbon signals of **9** have chemical shifts (δ 16.5, 15.6) firmly within the range assigned by other workers^{8,11} to distal carbon atoms {*c.f.* for $[\text{Mo}(\eta^6\text{-C}_6\text{Et}_6)(\text{CO})_3]$ the methyl carbon signals at δ 14.4 and 23.4 have been respectively assigned to distal and proximal environments} but, whichever explanation of the fluxional behaviour is correct, it seems incredible to us that the co-ordinated arene can adopt a conformation with more than a distal ethyl group.

Photolysis of complex **7** with triphenylphosphine in toluene-heptane solution gave dicarbonyl $[\eta^6\text{-1,3,5-triethyl-2,4,6-tris(trimethylsilylmethyl)benzene}](\text{triphenylphosphine})\text{molybdenum}(0)$ **10**, the crystal structure of which is shown in Fig. 9.¹⁶ Repulsive steric interactions between the ligated triphenylphosphine and the ethyl groups force the complexed arene to adopt a conformation in which two of the ethyl groups are proximal and one ethyl group distal to the molybdenum atom (*i.e.* stereoisomer **6/23** of the free arene), the tripodal ligands eclipse the trimethylsilylmethyl groups, and the overall molecular symmetry is C_1 . The 75.5 MHz $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of **10** in CDFCl_2 solution displayed decoalescences at low temperatures in all the subspectra. At 145 K two carbonyl resonances [δ 238.1, 233.6; $J(^{31}\text{P}\text{-}^{13}\text{C})$ 17.5, 13.1 Hz, respectively] of approximately equal intensity were observed. We consider that the decoalescence in the carbonyl signal can only occur as a result of slowed rotation about the η^6 -arene-metal bond. Substantial ^{13}C O enrichment, however, was necessary to give a signal-to-noise ratio adequate for line-shape fitting which gave a barrier $\Delta G_{200}^\ddagger = 33.2 \pm 2.7$ kJ mol⁻¹ for this rotation (Fig. 10).

The two arene resonances observed at δ 109.3 and 115.3 in

Table 1 Selected ^{13}C - $\{^1\text{H}\}$ NMR spectral data (δ values, J_{PC} in Hz)

Compound	Solvent	T/K	$\text{Si}(\text{CH}_3)_3$	CH_3	CH_2	C_{arene}	CO	Tripod substituent
C_6Et_6^a	CD_2Cl_2	Ambient		15.5	21.6	137.2		
$[\text{Cr}(\eta^6\text{-C}_6\text{Et}_6)(\text{CO})_3]^a$	CD_2Cl_2	202		14.2, 20.1	19.4, 22.8	108.8, 117.2	235.4	
$[\text{Cr}(\eta^6\text{-C}_6\text{Et}_6)(\text{CO})_2(\text{CS})]^b$	CD_2Cl_2	163		13.2, 13.6, 17.8, 18.5	19.9, 20.7, 21.7	112.8, 113.4, 119.9, 121.7	234.7	347.1 ^c
$[\text{Cr}(\eta^6\text{-C}_6\text{Et}_6)(\text{CO})_2(\text{PPh}_3)]^a$	CD_2Cl_2	189		15.9	22.4	109.2	243.5 (22.0) ^d	139.9 (29.6), ^{e,f} 133.4 (10.6), ^{e,g} 127.6 (8.0), ^{e,h} 128.5 ^c
$[\text{Mo}(\eta^6\text{-C}_6\text{Et}_6)(\text{CO})_3]^a$	CD_2Cl_2	205		14.4, 23.4	19.5, 22.8	114.7, 121.6	225.1	
$[\text{Mo}(\eta^6\text{-C}_6\text{Et}_6)(\text{CO})_2(\text{CS})]$	CD_2Cl_2	178		13.9, 22.1	19.8, 22.0	119.8, 126.0	224.8	331.7 ^c
6	CD_2Cl_2	Ambient	-0.2	13.3	17.9, 23.3	132.5, 133.2		
7	CD_2Cl_2	Ambient	-0.6	19.6	21.4, 21.9	111.9, 122.6	226.2	
8	CD_2Cl_2	Ambient	0.4	20.6	21.3, 23.7	117.2, 127.5	226.1	332.4 ^c
	CD_2Cl_2	173	-0.3	18.9, 19.8	19.8, 21.9, 22.5, 23.0	116.5, 117.1, 127.0, 128.0	226.3	332.8 ^c
9	CD_2Cl_2	Ambient	0.4	17.3	20.4, 24.1	109.3, 119.0	238.2	26.7, ^{i,j} 31.7, ^{i,j} 33.5, ^{i,j} 60.6 ^{i,k}
	CDFCl_2	156	0.5	15.6, 16.5, 19.5		106.2, 110.7, 111.3, 118.2, 118.9, 119.8	238.0, 238.2	
10	CD_2Cl_2	Ambient	0.3	17.6	19.8, 24.2	109.3, 115.3	235.3 (15.4) ^d	139.4 (34.9), ^{e,f} 134.1 (11.6), ^{e,g} 128.6, ^e 127.7 ^e
	CDFCl_2	155	0.3	17.0, 17.6, 18.1			238.1 (17.5) ^d 233.6 (13.1) ^d	

^a Data from ref. 1. ^b Data from ref. 6. ^c CS. ^d $^2J_{\text{PC}}$. ^e PPh_3 . ^f $^1J_{\text{PC}}$. ^g $^2J_{\text{PC}}$. ^h $^3J_{\text{PC}}$. ⁱ *cis*-cyclooctene. ^j CH_2 . ^k $\text{HC}=\text{CH}$.

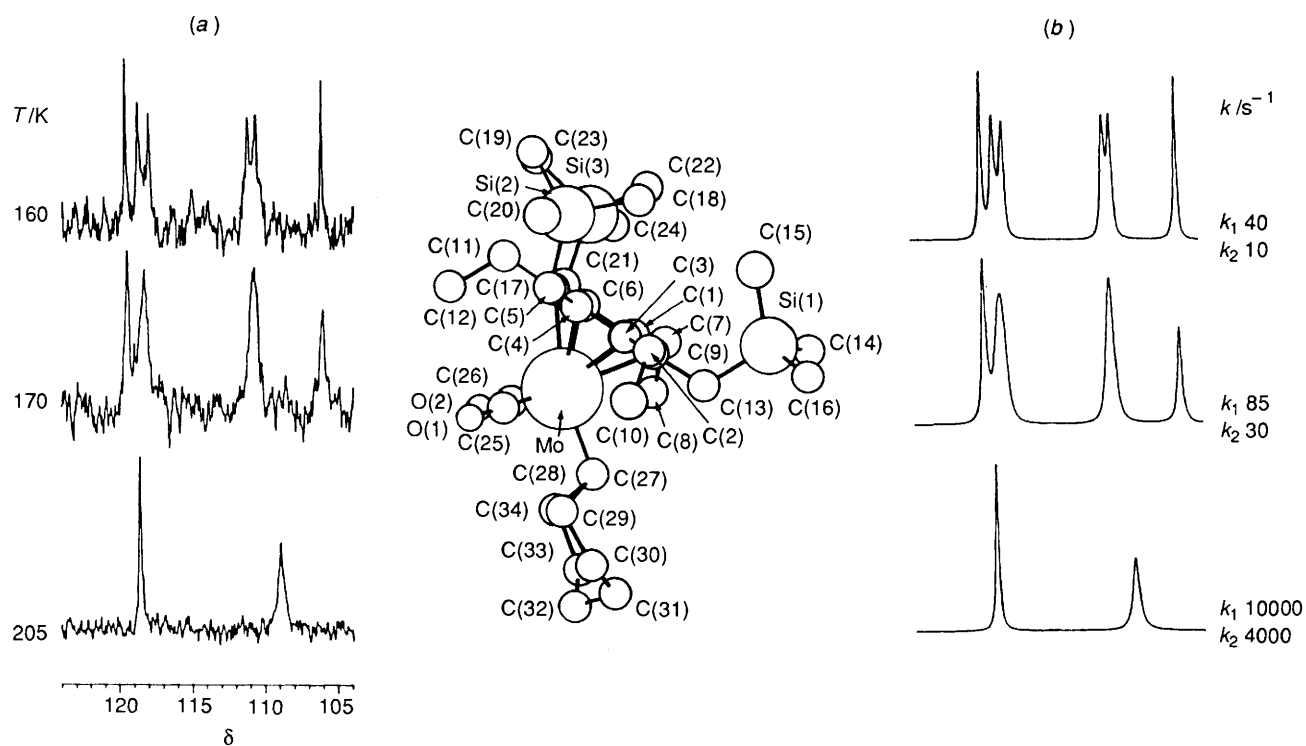


Fig. 8 Variable-temperature 75.5 MHz ^{13}C - $\{^1\text{H}\}$ NMR arene carbon subspectrum of complex **9** dissolved in CD_2Cl_2 : (a) observed; (b) calculated

the ambient-temperature spectrum collapsed at temperatures below 220 K but did not reappear down to 155 K. In the alkyl subspectrum the signal at δ 17.6, positively identified as arising from the methyl carbons of the ethyl groups, underwent two apparent decoalescences ultimately to give three signals at δ 18.1, 17.6 and 17.0. If the stereoisomer observed in the crystal is retained on dissolution then these decoalesced signals must arise from one distal and two proximal methyl groups. However, the greatest difference in their chemical shifts is only 1.1 ppm, demonstrating once again that perhaps assignment to proximal or distal environments on the sole basis of chemical shift values is unreliable.^{2,8}

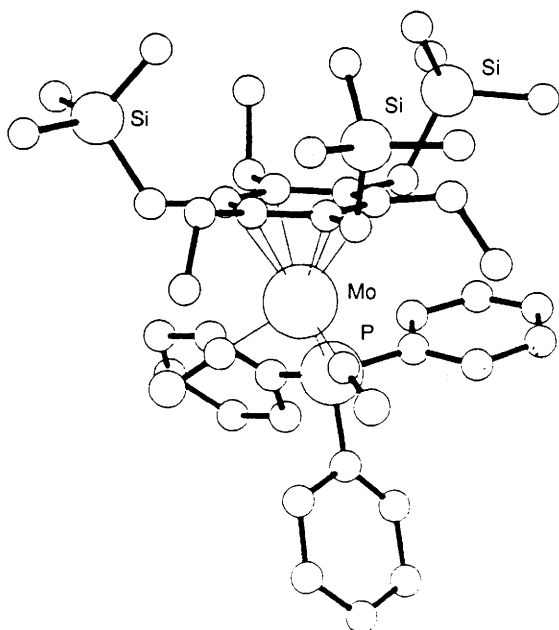
The decoalescence of the methyl carbon signal was treated as

a three-site exchange and, as with the arene carbon subspectrum of complex **9**, two significantly different rate constants in each set of three were necessary satisfactorily to simulate the observed spectral changes, despite the close internal chemical shift differences (37.8 and 45.3 Hz at 155 K) of the decoalesced signals. At each temperature, satisfactory simulation was achieved using as the higher of the two rate constants that which satisfactorily simulated the decoalescence of the carbonyl subspectrum (Fig. 11). The slower (higher-energy) exchange was assigned to ethyl group rotation.

There is also a decoalescence observed in the triphenylphosphine subspectrum (Fig. 12) but the appearance of the decoalesced subspectrum is quite different to that of $[\text{Cr}(\eta^6\text{-C}_6\text{Et}_6)(\text{CO})_2(\text{PPh}_3)]$.

Table 2 Barriers to intramolecular exchange

Compound	Exchange process identified	$\Delta G_{200}^\ddagger/\text{kJ mol}^{-1}$
C_6Et_6 ^a	Ethyl group rotation ^b	49.4
$[\text{Cr}(\eta^6\text{-C}_6\text{Et}_6)(\text{CO})_3]$ ^a	Ethyl group rotation	48.1 ± 2.5
$[\text{Cr}(\eta^6\text{-C}_6\text{Et}_6)(\text{CO})_2(\text{CS})]$	Ethyl group rotation	45.1 ± 1.4
	$\text{M}(\eta^6\text{-arene})$ rotation	38.6 ± 1.0
$[\text{Mo}(\eta^6\text{-C}_6\text{Et}_6)(\text{CO})_3]$ ^a	Ethyl group rotation	48.5 ± 0.8
6	Ethyl group rotation ^b	53.6
	Trimethylsilylmethyl group rotation ^b	72.0
8	$\text{M}(\eta^6\text{-arene})$ rotation	39.1 ± 1.0
9	$\text{M}(\eta^6\text{-arene})$ rotation	37.4 ± 0.6
	$\eta^2\text{-cis-cyclooctene}$ twist	34.3 ± 2.5
10	Ethyl group rotation	38.7 ± 1.3
	$\text{M}(\eta^6\text{-arene})$ rotation	33.2 ± 2.7

^a Ref. 1. ^b Calculated.**Fig. 9** Molecular structure of complex **10**¹⁶

$\text{C}_6\text{Et}_6(\text{CO})_2(\text{PPh}_3)]$ where a decoalescence was attributed to slowed rotation about the Cr–P bond while rotation about the *ipso*-C–P bonds remained rapid.²³ In the case of complex **10** we suspect that the latter rotation is also slowed, leading to a large number of overlapping resonances giving a quite different appearance to the subspectrum at low temperatures.

Conclusion

We consider that the above results, in conjunction with those recently reported by McGlinchey and co-workers,¹¹ establish beyond reasonable doubt that the steric effects of the ethyl groups of a hexahapto co-ordinated arene can lead to slowed rotation about the η^6 -arene–metal bond. However, complexes **8**–**10** are exceptionally crowded molecules and yet, despite reinforcement by electronic influences, the barriers are at the lower limit for a phenomenon observable on the NMR time-scale. Moreover, the η^6 -arene–metal rotational barrier for **10** is quite similar to its ethyl group rotational barrier. The latter barrier is significantly smaller than that calculated for a free arene **6**, and this difference is probably a reflection of a more highly strained ground state for the complex. Caution must still therefore be exercised, not only in predicting whether slowed rotation about the η^6 -arene–metal bond will be observed for

any given complex at experimentally accessible temperatures, but also in positively identifying what exchange process is responsible for any observed spectral changes.

Experimental

Synthesis.—1,3,5-Triethyl-2,4,6-tris(trimethylsilylmethyl)benzene **6**, tricarbonyl[η^6 -1,3,5-triethyl-2,4,6-tris(trimethylsilylmethyl)benzene]molybdenum(0) **7**, and dicarbonyl(η^2 -cis-cyclooctene)[η^6 -1,3,5-triethyl-2,4,6-tris(trimethylsilylmethyl)benzene]molybdenum(0) **9** were prepared as described elsewhere.²¹

Dicarbonylthiocarbonyl[η^6 -1,3,5-triethyl-2,4,6-tris(trimethylsilylmethyl)benzene]molybdenum(0) **8**. A freeze-thaw degassed solution of complex **7** (2.0 g, 3.3 mmol) in benzene and *cis*-cyclooctene (10 cm³) was irradiated with UV light for 2 h. Carbon disulphide (10 cm³) was added to the orange-yellow solution which was then heated for 2 h at 50 °C. Triphenylphosphine (1.05 g, 40 mmol) was added to the cooled solution and the resulting mixture allowed to stand for 12 h at room temperature. The brown solution was filtered under N₂ and the solvent and excess of *cis*-cyclooctene and carbon disulphide evaporated under reduced pressure. The residue was purified twice by medium-pressure liquid chromatography (230–400 mesh silica gel, eluent hexane–2% ethyl acetate) under N₂. Removal of the solvent gave orange-yellow crystals of complex **8** (0.365 g, 0.59 mmol, 18%) (Found: C, 52.8; H, 7.7. Calc. for C₂₇H₄₈MoO₂SSi₃: C, 52.6; H, 7.8%).

Dicarbonyl[η^6 -1,3,5-triethyl-2,4,6-tris(trimethylsilylmethyl)benzene](triphenylphosphine)molybdenum(0). A freeze-thaw degassed solution of complex **7** (0.50 g, 0.83 mmol) and triphenylphosphine (0.22 g, 0.83 mmol) in toluene–heptane was irradiated with UV light for 2 h. The orange solution was filtered under N₂ and the solvent evaporated under reduced pressure. The residue was purified twice by medium-pressure liquid chromatography (230–400 mesh silica gel, eluent hexane–2% ethyl acetate) under N₂. Removal of the solvent gave yellow crystals of complex **10** (0.33 g, 0.39 mmol, 47%) (Found: C, 63.1; H, 7.2. Calc. for C₄₄H₆₃MoO₂PSi₃: C, 63.3; H, 7.6%).

¹³CO Labelling Experiments.—Following the method of Strohmeier and Hobe,²⁴ a solution of complex **7** (0.33 g, 0.55 mmol) in toluene (35 cm³) was frozen in a liquid-nitrogen bath, and the reaction vessel was evacuated. After thawing the reaction mixture, ¹³CO (MSD Isotopes, 99.3% isotopically pure) was bled into the system. The pressure of the ¹³CO was adjusted to 1 atm (ca. 10⁵ Pa), and the magnetically stirred reaction mixture was irradiated with UV light for 2 h. Little decomposition was observed. Nitrogen was then bubbled through the solution to remove dissolved carbon monoxide, triphenylphosphine (0.14 g, 0.55 mmol) added, and the mixture photolysed for 2 h. The orange solution was filtered under N₂, the solvent evaporated under reduced pressure, and the residue

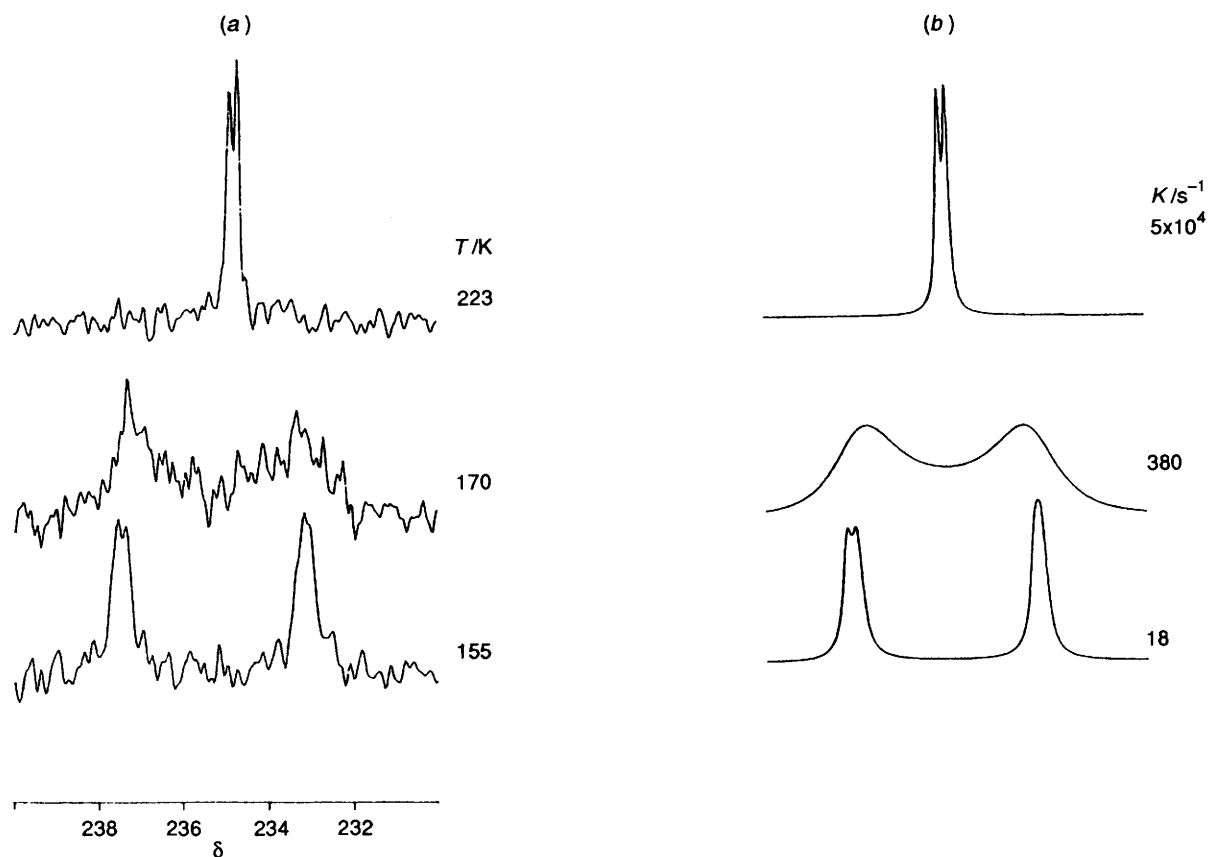


Fig. 10 Variable-temperature 75.5 MHz $^{13}\text{C}\{-^1\text{H}\}$ NMR carbonyl carbon subspectrum of complex **10** enriched in ^{13}C ($\approx 10\%$) and dissolved in CDCl_2 : (a) observed; (b) calculated

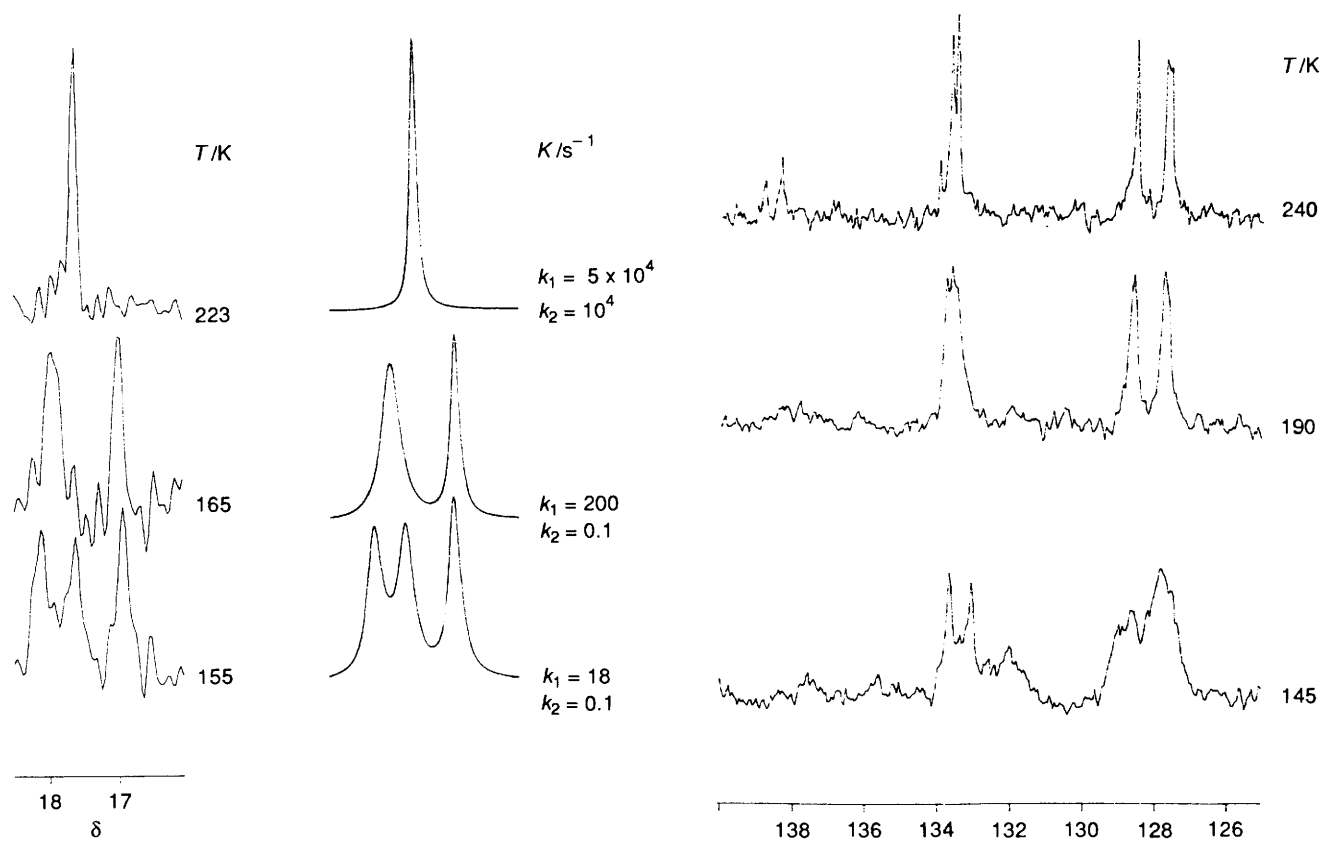


Fig. 11 Variable-temperature 75.5 MHz $^{13}\text{C}\{-^1\text{H}\}$ NMR methyl subspectrum of complex **10** dissolved in CDCl_2 : (a) observed, (b) calculated

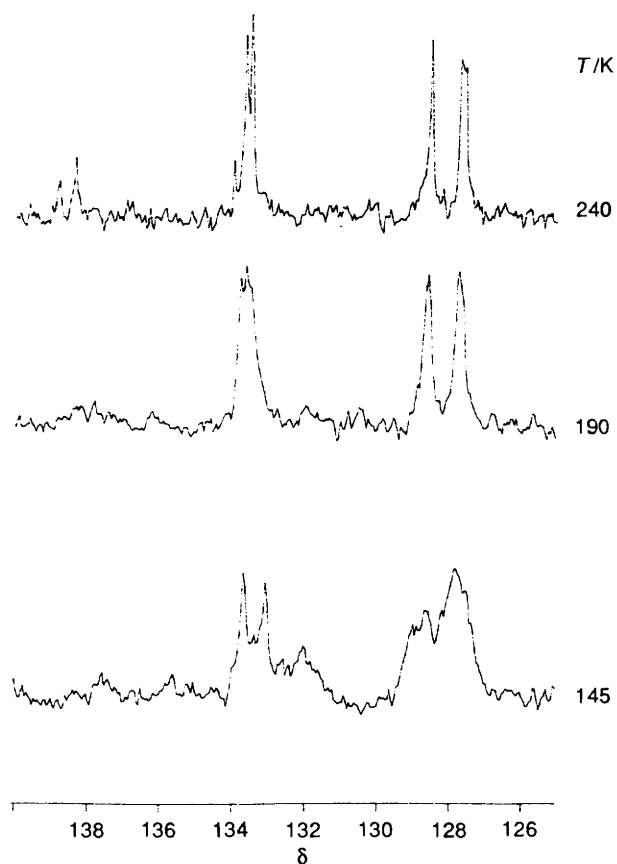


Fig. 12 Variable-temperature 75.5 MHz $^{13}\text{C}\{-^1\text{H}\}$ NMR triphenylphosphine carbon subspectrum of complex **10** dissolved in CDCl_2

purified as described for **10** above. Of the total carbonyl content, 12% was ^{13}C , as determined by mass spectroscopy.

Variable-temperature NMR Measurements.—All variable-temperature NMR spectra were recorded at 75.5 MHz (^{13}C) on a Bruker AM300WB spectrometer. All samples were filtered under N_2 through a grade 3 glass sinter, freeze-thaw degassed, and sealed in 10 mm (outside diameter) tubes. Concentrations of the sample solutions were in the range 65–125 mmol dm^{-3} . Provided that they were carefully filtered, degassed, and the sample tube sealed, it was usually possible to supercool the CD_2Cl_2 solutions to at least 20 °C below the nominal freezing of that solvent, the samples remaining liquid for several hours at these temperatures.

Spectral simulations were performed using a version of the DNMR3 program²⁵ modified to handle single-spin, n -site exchange. Satisfactory fit of simulated to observed spectra was judged by visual comparison. The ΔG^\ddagger values were calculated using the Eyring equation.

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