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Preliminary communication

Unequivocal evidence for restricted rotation about a metal–arene bond caused by the steric effects of proximal ethyl groups; Crystal structure of dicarbonyltriphenylphosphine-(η^6 -1,3,5-triethyl-2,4,6-tris(trimethylsilylmethyl)benzene)molybdenum(0)

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Abstract

The crystal structure of dicarbonyltriphenylphosphine(η^6 -1,3,5-triethyl-2,4,6-tris(trimethylsilylmethyl)benzene)molybdenum(0), (**4**) shows that the complexed arene adopts a conformation in which the three trimethylsilylmethyl groups and one ethyl group are on the side of the benzene ring plane distal to the molybdenum while the other two ethyl groups are on the proximal side. Decoalescence phenomena are observed in the 75.47 MHz ^{13}C - $\{^1\text{H}\}$ NMR spectrum of **4** and, most notably, at 145 K two carbonyl resonances are resolved. The decoalescence phenomena are assigned to: (i) slowed ethyl group rotation; (ii) slowed rotation of the triphenylphosphine ligand about the Mo–P bond; (iii) slowed rotation about the arene–metal tripodal moiety bond.

It is now well-established that when hexaethylbenzene (heb) 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 [1,2,3]. Indeed, in at least one example, $[\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-heb})\text{Fe}]^+$, merely changing the balancing anion is sufficient to alter the conformation adopted by the complexed heb moiety in the crystal; thus $[\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-heb})\text{Fe}]\text{PF}_6$ has two ethyl groups proximal to the iron atom [4], whereas $[(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-heb})\text{Fe}]\text{BPh}_4$ has only one [5].

In the crystal, the coordinated heptahapto of dicarbonylthiocarbonyl(η^6 -hexaethylbenzene)chromium(0) (**1**) adopts a conformation in which three ethyl groups are proximal to the chromium atom [6]. At low temperatures, the solution $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of **1** is consistent with C_3 symmetry for the molecule [6,7]. Controversy has arisen concerning the interpretation of this low temperature NMR spectrum: McGlinchey et al. [6,8] have strongly advocated that the heptahapto conformation observed in the crystal is retained on dissolution, and that the C_3 symmetry results from slowed rotation about the metal-arene bond, a situation normally considered to arise only when there are exceptional electronic or steric factors [9], whereas one of us [2,7] has adopted the more conservative position that the case for slowed rotation about the (η^6 -heptahapto)-metal bond remains not proven, as dissolution of **1** may lead to a facile change of heptahapto conformation to one of C_3 symmetry, and that what was monitored was ethyl group rotation.

In an attempt to resolve this dichotomy we have prepared a series of complexes of 1,3,5-triethyl-2,4,6-tris(trimethylsilylmethyl)benzene (**2**), an arene for which the number of accessible stereoisomers is restricted by severe steric interactions between the alkyl substituents, and one of whose faces must be favoured over the other for metal complexation. Force field calculations [10] * for **2** reveal that attractive steric interactions should result in a ground state conformation in which the three trimethylsilylmethyl groups all project from the same side of the benzene ring plane. For one such group to project from the opposite side to the other two invokes such a large energy penalty that other than negligible populations of conformations with such an arrangement can be discounted. The ground state conformation of **2** therefore has all three ethyl groups projecting from the opposite side of the benzene ring plane to the trimethylsilylmethyl groups. However, the conformation with one ethyl group projecting from the same benzene ring face as the trimethylsilylmethyl groups is relatively low-lying at 27.6 kJ mol^{-1} above the ground state conformation and, although negligibly populated in the free arene, is a potential candidate to become the ground state conformation when **2** is hexahapto coordinated to a C_3 symmetrical metal-tripod moiety substituted with at least one sterically-demanding ligand. The other conformations of **2**, with two and three ethyl groups projecting from the same face as the trimethylsilylmethyl groups, lie respectively at 51.0 and 70.6 kJ mol^{-1} above the ground state energy calculated for the molecule and must therefore be considered inaccessible even with the arene bound to a sterically very demanding moiety. The $75.47 \text{ MHz } ^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of **2** in CDCl_2 solution was unchanged even at 145 K and entirely consistent with a ground state conformation with three equivalent trimethylsilylmethyl and three equivalent ethyl groups. The face of **2** from which the trimethylsilylmethyl groups project is inaccessible to a potentially coordinating tricarbonylmetal fragment, whereas the other face, from which project the ethyl groups should present similar steric hindrance to the approach of a ligated metal atom as does the ground state conformation of hexaethylbenzene [1]. Nevertheless, we were unable to synthesise and isolate an authentic chromium tricarbonyl complex of **2**, although tricarbonyl(η^6 -1,3,5-triethyl-2,4,6-tris(trimethylsilylmethyl)benzene)molybdenum(0) (**3**) was readily obtainable by simply refluxing **2** with an excess of hexacarbonylmo-

* Reference number with asterisk indicates a note in the list of references.

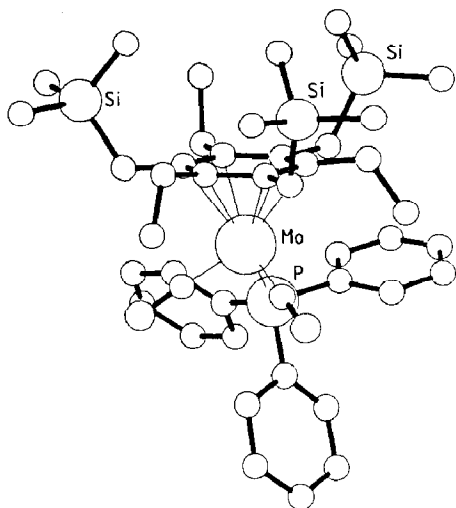


Fig. 1. Molecular structure of **4**, from data collected at 241 K.

lybdenum in *n*-heptane under nitrogen. The $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of **3** in CD_2Cl_2 (δ (ppm), 226.2 (carbonyls), 122.6 (arene), 111.9 (arene), 21.9 (CH_2), 21.4 (CH_2), 19.6 (CH_3), -0.6 ($\text{Si}(\text{CH}_3)_3$)) was unchanged even when the solution was supercooled to 153 K.

Photolysis of **3** with triphenylphosphine in toluene/heptane solution gave dicarbonyltriphenylphosphine(1,3,5-triethyl-2,4,6-tris-(trimethylsilylmethyl)benzene)-molybdenum(0) (**4**), which crystallised from benzene/cyclohexane at 0°C to give golden-yellow plates, unstable in air. Under nitrogen the crystals slowly decomposed at room temperature and underwent a phase transition at 163 K. However, an acceptable X-ray data set* was obtained at 241 ± 2 K and the molecular structure of **4** is shown in Fig. 1. 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 and the overall molecular symmetry is C_1 . In the analogous complex dicarbonyl(η^6 -hexaethylbenzene)triphenylphosphinechromium(0) (**5**) such interactions force all the ethyl groups on to the side of the arene distal to the metal [1]. Such an all distal alkyl group conformation is clearly inaccessible for **4**. The 75.47 MHz $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of **4** in CDFCl_2 solution (295 K, δ 235.3 ($J(^{31}\text{P}\text{-}^{13}\text{C})$ 15.3 Hz) (carbonyls), 139.4 ($J(^{31}\text{P}\text{-}^{13}\text{C})$ 34.3 Hz) (Ph_3P *ipso* carbons), 134.1

* Crystal data: $\text{C}_{44}\text{H}_{63}\text{MoO}_2\text{PSi}_3$, triclinic, space group P_1 , a 12.469(24), b 15.663(25), c 15.968(25) Å, α 74.59(13), β 87.50(14), γ 88.11(14)°, $Z = 2$, 7356 independent reflections were measured at 241(2) K on a modified STOE diffractometer, equipped with a NONIUS low temperature unit (Mo-K_α radiation (λ 0.71069 Å), of which 3308 were considered observed [$F \geq 4\sigma(F)$]. No absorption or extinction corrections were applied to the measured intensities. The structure was solved by the heavy atom method and refined by block least squares. In the final refinement, anisotropic thermal parameters were used for all non-hydrogen atoms. Two benzene molecules were located on special positions, but large peaks in the final difference Fourier map (largest peak, $1.35 \text{ e}\text{\AA}^{-3}$) suggest additional disordered benzene molecules. Final residual $R = 0.124$.

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

($J(^{31}\text{P}-^{13}\text{C})$ 11.4 Hz) (Ph_3P *ortho* carbons), 128.6 (Ph_3P *para* carbons), 127.7 ($J(^{31}\text{P}-^{13}\text{C})$ 7.6 Hz) (Ph_3P *meta* carbons), 115.3 (arene), 109.3 (arene), 24.5 (CH_2), 20.2 (CH_2), 17.9 (CH_3), 0.3 ($\text{Si}(\text{CH}_3)_3$) ppm) displays decoalescences at low temperatures in all the subspectra; most notably at 145 K two carbonyl resonances are observed (δ 238.1; 233.6 ppm) of approximately equal intensity. Decoalescences in the triphenylphosphine sub-spectrum can be assigned to restricted rotation about the metal–phosphorus bond, similar to that observed for **5** [11], while those in the alkyl subspectrum can be assigned to restricted ethyl group rotation. However, the decoalescence observed in the carbonyl resonance can only occur as a result of slowed rotation about the metal–arene bond. This is the first example of a molecule for which it can be unequivocally demonstrated that purely steric interactions between proximal ethyl groups and a metal tripodal moiety can slow such a process so that it is observable on the NMR timescale. It is difficult to determine a precise temperature for this decoalescence phenomenon as the carbonyl resonances are weak and remain collapsed into the background noise over quite a large temperature range. However, the carbonyl resonance is fully coalesced and exhibits splitting due to ^{31}P coupling at temperatures above 190 K. We estimate an approximate barrier of 35 kJ mol^{-1} to rotation about the metal–arene bond but line-shape fitting studies to give a more accurate estimate will require substantial ^{13}C enrichment to give a better signal to noise ratio.

While we have firmly established that slowed rotation about the arene–metal tripod bond can be caused by steric interactions, we note that **4** is an exceptionally-crowded molecule and yet even so the barrier is at the lower limit for a phenomenon observable on the NRM time-scale. We therefore still consider that the case remains not proven for attributing the behaviour of **1** and similar systems, to such effects without, perhaps, reinforcement arising from electronic influences.

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