Synthesis of octamethyltetrasila[2.2]paracyclophane: a high yielding Würtz coupling reaction using $Cr(CO)_3$ templates

Paul J. Dyson,* Alexander G. Hulkes and Priya Suman

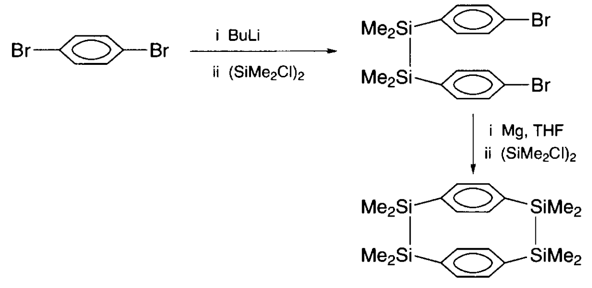
Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, UK SW7 2AY

Octamethyltetrasila[2.2]paracyclophane and [2.2]paracyclophane are prepared in high yield from the Würtz coupling reaction of $[Cr(CO)_3\{\eta^6\text{-}C_6H_4(SiMe_2Cl)_2\text{-}1,4\}]$ and $[Cr(CO)_3\{\eta^6\text{-}C_6H_4(CH_2Br)_2\text{-}1,4\}]$, respectively.

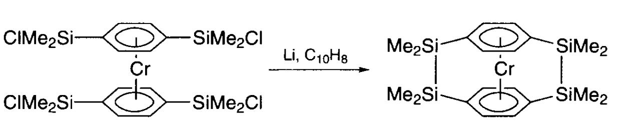
There is considerable interest in the synthesis and reactivity of cyclophanes.[1,2] The $[2_n]$cyclophanes have been of particular interest due to the unusual chemical and physical properties they display as a result of the close proximity of their aromatic decks. The π-orbitals are forced to overlap resulting in an internal molecular strain which causes a lengthening of the aliphatic bridges and a deviation of the rings from planarity.[3] The intramolecular π–π repulsions which make these compounds so interesting also hinder their preparation with most $[2_n]$cyclophanes only being prepared in low yield, and often requiring several synthetic steps. This paper reports a new synthetic approach to octamethyltetrasila[2.2]paracyclophane and [2.2]paracyclophane which is superior to those previously reported.

The original methods used in the preparation of [2.2]cyclophanes employ Würtz coupling reactions on appropriate arene precursors, which are known to result in low yields.[4] Octamethyltetrasila[2.2]paracyclophane has been prepared by a number of different methods, the best of these (with only a 1.6% yield) is shown in Scheme 1.[5] An alternative route to this compound involves the metal atom vapour synthesis of $[Cr\{\eta^6\text{-}C_6H_4(SiMe_2Cl)_2\text{-}1,4\}_2]$ followed by coupling of the rings (Scheme 2).[6] Despite the fact that the rings are held in close proximity in the precursor complex, the yield is still very low, *ca.* 3.5%. Presumably this is due to the presence of the chromium atom between the aromatic decks which inhibits the reaction in some way.

The strategy reported herein involves the Würtz reductive coupling reaction of $C_6H_4(SiMe_2Cl)_2\text{-}1,4$ when coordinated to a $Cr(CO)_3$ fragment (Scheme 3). The $Cr(CO)_3$ has two important functions; first it reduces π-electron density on one face of the arene precursor which facilitates direct face-to-face coupling, and second it stabilises radical formation which is necessary in the reductive coupling step.



Scheme 1



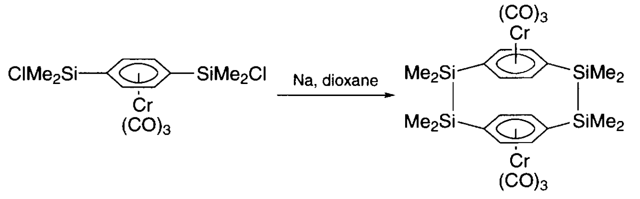
Scheme 2

The complex, $[Cr(CO)_3\{\eta^6\text{-}C_6H_4(SiMe_2Cl)_2\text{-}1,4\}]$, in dioxane, was added dropwise to a refluxing solution of dioxane containing sodium (2 mol equiv.). The resulting bright yellow reaction mixture was filtered and the filtrate evaporated to dryness under reduced pressure. The yellow solid was redissolved in diethyl ether and stored at −20 °C for several days. During this period, yellow crystals were obtained which were characterised spectroscopically as $[\{Cr(CO)_3\}_2$(octamethyltetrasila[2.2]paracyclophane)] (50%). The ^1H NMR spectrum recorded in $CDCl_3$ comprises two singlets at δ 3.60 and 0.30, which are readily assigned to the aromatic and methyl group protons, respectively.

It has been shown previously that tricarbonylchromium groups may be removed by oxidation using oxygen and light,[7] and using this method, followed by Soxhlet extraction, octamethyltetrasila[2.2]paracyclophane was obtained in quantitative yield from the bis$[Cr(CO)_3]$ complex.

Using the same procedure as that outlined above, $[Cr(CO)_3\{\eta^6\text{-}C_6H_4(CH_2Br)_2\text{-}1,4\}]$ was used to prepare $[\{Cr(CO)_3\}_2$([2.2]paracyclophane)] and after removal of the tricarbonyl chromium fragments [2.2]paracyclophane was isolated in 36% yield. There are many methods available for the preparation of this compound,[8–10] and while this method does not give the highest yield reported, it is probably the most convenient from a synthetic viewpoint.

The bis(tricarbonylchromium) cyclophane complexes are interesting in their own right. In the case of [2.2]paracyclophane, $[Cr(CO)_3$([2.2]paracyclophane)] may be prepared in high yield from direct reaction with hexacarbonylchromium in a high boiling light petroleum.[11] The structure was established some years ago and is interesting in that the distance between the rings is less than in the free ligand due to the presence of the electron withdrawing tricarbonylchromium group.[12] The preparation of $[\{Cr(CO)_3\}_2$([2.2]paracyclophane)] requires even higher boiling solvents and only takes place in low yield.[13] Clearly, the route described in this paper is a far more effective method. As far as we are aware, tricarbonylchromium complexes of octamethyltetrasila[2.2]paracyclophane are not known. However, since the C–Si and Si–Si bond lengths are longer than the corresponding C–C bonds in the bridges of [2.2]paracyclophane, the molecule is less strained and as such, we anticipate that both the mono- and bis-tricarbonylchromium complexes could be made by direct reaction with $Cr(CO)_6$. From our studies it would appear that $[\{Cr(CO)_3\}_2$(octa-



Scheme 3

methyltetrasila[2.2]paracyclophane)] is more stable than the corresponding [2.2]paracyclophane species.

We intend to carry out a series of other related reactions to those described herein, including the preparation of *ortho*- and *meta*-cyclophanes as well as those containing other Group IV elements in their bridges or substituents on the ring.

We gratefully acknowledge The Royal Society for a University Research Fellowship (P. J. D.) and the EPSRC for financial support (P. S.).

References

1 F. Vögtle, *Cyclophane Chemistry*, Wiley, Chichester, 1993.

2 Recent papers covering aspects of cyclophane chemistry include: (*a*) Y. Sakamoto, N. Miyoshi and T. Shinmyozu, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 549; (*b*) K. Albrecht, D. C. R. Hockless, B. König, H. Newmann, M. A. Bennett and A. de Meijere, *Chem. Commun.*, 1996, 543; (*c*) C.- K. Chan, K-, K. Cheung and C.- M. Che, *Chem. Commun.*, 1996, 227.

3 H. Hope, J. Bernstein and K. N. Trueblood, *Acta Crystallogr, Sect. B.*, 1972, **28**, 1733.

4 M. M. Pellegrin, *Rec. Trav. Chim. Pays-Bas*, 1899, **18**, 457.

5 H. Sakurai, S. Hoshi, A. Kamiya, A. Hosomi and C. Kabuto, *Chem. Lett.*, 1986, 1781.

6 C. Elschenbroich, J. Hurley, W. Massa and G. Baum, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 684.

7 G. Jaouen, S. Top, A. Laconi, D. Couturier and J. Brocard, *J. Am. Chem. Soc.*, 1984, **106**, 2207.

8 For a review see: V. Boekelheide, *Top. Curr. Chem.*, 1983, **113**, 87.

9 H. Higuchi, K. Tani, T. Otsubo, Y. Sakata and S. Misumi, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 4027.

10 S. Kawakami, S. Iwaki, A. Yu, M. Nakada and T. Yamaguchi, *Chem. Lett.*, 1990, 893.

11 D. J. Cram and D. I. Wilkinson, *J. Am. Chem. Soc.*, 1960, **82**, 5721.

12 Y. Kai, N. Yasnoka and N. Kasai, *Acta Crystallogr., Sect B*, 1978, **34**, 2840.

13 H. Ohno, H. Horita, T. Otsubo, Y. Sakata and S. Misumi, *Tetrahedron Lett.*, 1977, **18**, 265.

Received, 5th July 1996; Com. 6/04706H