Tetrahedron Letters No. 39, pp 3421 - 3424, 1977. Pergamon Press. Printed in Great Britain.

Cyclotrimerization of Cyclic Diynes via Metal Atom Cocondensation; Revised Structure for the Reported "Percyclophane-4"

J. A. Gladysz,* J. G. Fulcher, Sung J. Lee, and A. B. Bocarsley

Contribution No. 3818
Department of Chemistry
University of California
Los Angeles, California 90024

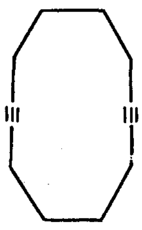
(Received in USA 13 June 1977; received in UK for publication 9 August 1977)

SUMMARY A compound previously assigned the "percyclophane-4" structure 3 has been shown to be the triyne 2.

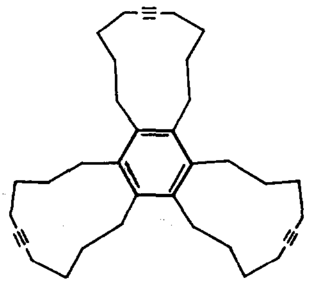
Metal atoms are readily produced high chemical potential species which give a wealth of chemistry when cocondensed with organic compounds.[1] Direct π complex formation,[2] oxidative additions,[3] and deoxygenations[4] are among the reaction types commonly observed.

In connection with an ongoing program directed at using metal atoms as templates for the construction of highly connected carbocyclic cage compounds, our attention was drawn to the recent work of Stephens.[5] Upon treatment of 1,7-cyclododecadiyne (1) with dimesitylcobalt[6] acetylene cyclotrimerization catalyst, a 70% yield of a trimer was reported, to which was assigned the structure 3 and the name "percyclophane-4." Presumably reaction occurred via intermediate triyne 2. Trimesitylchromium was also found to catalyze trimerization of 1, but 1,6-cyclotridecadiyne and 1,8-cyclotetradecadiyne afforded no tractable products.[5]

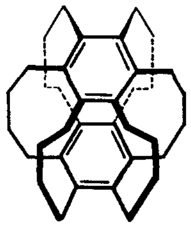
Reports from Skell's group indicate that acetylene cyclotrimerization can be effected by metal atom cocondensation.[7] 2-butyne was converted to hexamethylbenzene upon codeposition with chromium atoms, and terminal acetylenes could be cyclized as well.[7b] While no bis(arene)chromium(0) complexes were formed in these reactions,[8] it seemed plausible to us that a chromium atom would be bound to each arene ring immediately after its formation. From this premise, chromium atoms would be expected to react with diyne 1 to form intermediate 2 with a metal bound to the central ring. Although a general mechanism for acetylene cyclotrimerization remains to be



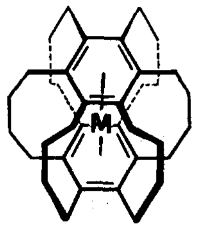
1



2



3



4

established,[9] it appeared possible that a second cyclization might occur, at least part of the time, to afford the novel caged chromium species 4 (M=Cr). The transannular distance in 3 should compare closely[10] with the 3.22 Å found in bis(benzene)chromium(0)[11] and allow sufficient room for the entrapped metal atom depicted in 4.

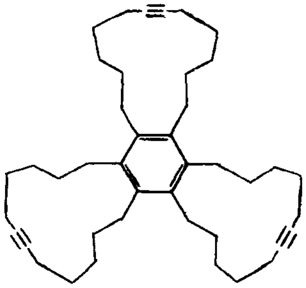
Chromium atoms (1-2 mmol) were cocondensed with 1 (20-25 mmol) at 77°K and $\leq 10^{-4}$ torr in the type of metal atom reactor employed by Skell and Klabunde.[1-3] After sublimation of unreacted 1 from the cocondensation matrix, the residue was analyzed by mass spectroscopy. No evidence for a species such as 4 (M=Cr) was observed, but a trimer of 1 was clearly present.

The reactor residue was continuously extracted with ether and the trimeric material (typically 80-120 mg/run) separated from polymeric by-products by extensive column chromatography.[12] The product mass spectrum showed a parent ion at m/e 480 ($C_{36}H_{48}$) and no fragment peaks greater than 10% of the molecular ion intensity. Proton nmr ($CDCl_3$; broad resonances centered at δ 1.70, 2.33, and 2.88, area 2:1:1), ir ($CHCl_3$, cm^{-1}; 2981 (m), 2918 (m), 2848 (m), 2830 (m), 1472 (w), 1450 (m), 1438 (m), 1422 (m), 1410 (w), 1332 (w), 1320 (w), 1050 (w), 898 (w)), uv (95% EtOH; λ max 272 nm, ε max ca. 1,000), and melting point (237.5 - 238.5 in sealed evacuated tube) data concurred with those reported by Stephens for "percyclophane-4" (3). As a final check, we prepared an authentic sample of "percyclophane-4" by Stephens' method[5,13] and found it to be identical to our trimer in all respects.

Additional characterization of the "percyclophane-4" material, however, has shown the structural assignment 3 to be incorrect. The ^{13}C nmr spectrum ($CDCl_3$, TMS internal standard) indicates the presence of four types of aliphatic carbons (30.5, 30.0, 26.7, 18.9 ppm), one type of acetylenic carbon (81.4 ppm), and one type of arene carbon (137.4 ppm). Only three resonances would be expected from a structure such as 3. This data is consistent only with the partially cyclized trimer structure 2.

Chemical evidence that "percyclophane-4" has the structure 2 was obtained by hydrogenation. Over PtO_2 in 1:1 HOAc/EtOAc under 5 atm pressure, 6 equiv H_2 was absorbed at room temperature during the course of 4 hr. The product was isolated in 97% crude yield by extraction and subsequent chromatography (mp 140.5 - 142 after $CHCl_3/CH_3OH$ recrystallization). The mass (molecular ion at m/e 492, $C_{36}H_{60}$, with no other significant fragments ($\geq$ 10%) above m/e 100), ^1H nmr ($CDCl_3$; resonances at δ 2.66 and 1.53, area 1:4), ^{13}C nmr ($CDCl_3$, TMS internal standard: 137.8, 29.6, 29.0, 28.1, 23.4 ppm; area 1:1:2:1:1) and ir ($CHCl_3$, cm^{-1}; 2933 (s), 2867 (m), 2853 (m), 1607 (w), 1446 (m)) spectra clearly indicate the hydrogenated material to be 1,2:3,4:5,6-tricyclododecabenzene. Although Stephens reported no reaction between 2 and Br_2/CCl_4, we find that decolorization occurs over the course of ten minutes. Diyne 1 reacts about 20 times faster. There is, however, no sign of an acetylenic absorption in the ir spectrum of 2.

1,8-cyclotetradecadiyne is also cyclotrimerized upon chromium atom cocondensation, although in somewhat lower yield than 1. The product 5 (mp 166-166.5 after $CHCl_3$/hexane recrystallization) was isolated by a purification scheme similar to that used for 2. The ^{13}C nmr spectrum ($CDCl_3$, TMS internal standard: 137.6, 80.7, 31.1, 30.7, 29.7, 26.6, 18.2 ppm) unequivocally eliminates a percyclophane type of structure. Other spectral data (mass spectrum parent ion at m/e 564, $C_{42}H_{60}$; ^1H nmr resonances ($CDCl_3$) at 2.62, 2.20, and 1.63 δ, area ratio 1:1:3; ir absorbances ($CHCl_3$) at 2945 (s), 2871 (m), 1611 (w), 1491 (w), 1469 (w), 1451 (m), 1425 (w), 1357 (w), 1270 (m), 1148 (w), 1113 (w), 1018 (m) cm^{-1}) support the structural assignment 5.



5

Notably, conventional cyclotrimerization catalysts have been reported to yield only intractable products from 1,8-cyclotetradecadiyne,[5,14] making 5 uniquely accessible via cocondensation methodology.

These results add to the growing body of useful synthetic transformations which can be accomplished with metal atom techniques. Physical and chemical properties of triynes 2 and 5 are under current investigation. Cage compounds such as 3 and 4, however, remain yet unattained synthetic targets, and work directed at their preparation is in progress.

ACKNOWLEDGEMENT

We thank the National Science Foundation, the Jane Coffin Childs Memorial Fund for Medical Research, the Research Corporation, and the UCLA Research Committee for support of this work.

REFERENCES AND NOTES

1. For recent reviews encompassing reactions, mechanisms, and experimental techniques, see "Cryochemistry," M. Moskovits and G. A. Ozin, Eds., John Wiley & Sons, New York, N.Y. (1976).
2. P. S. Skell and M. J. McGlinchey, *Angew. Chem. Int. Ed. Engl.*, 14, 195 (1975).
3. K. J. Klabunde, *Acc. Chem. Res.*, 8, 393 (1975).
4. J. A. Gladysz, J. G. Fulcher, and S. Togashi, *J. Org. Chem.*, 41, 3647 (1976); J. A. Gladysz, J. G. Fulcher, and S. Togashi, *Tetrahedron Lett.*, 521 (1977).
5. R. D. Stephens, *J. Org. Chem.*, 38, 2260 (1973).
6. M. Tsutsui and H. Zeiss, *J. Am. Chem. Soc.*, 83, 825 (1961).
7. a) P. S. Skell, J. J. Havel, D. L. Williams-Smith, and M. J. McGlinchey, *J. Chem. Soc., Chem. Commun.*, 1098 (1972).

   b) P. S. Skell, D. L. Williams-Smith and M. J. McGlinchey, *J. Am. Chem. Soc.*, 95, 3337 (1973).
8. Bis(hexamethylbenzene)chromium(0) is known: G. Wilke and M. Kröner, *Angew. Chem.*, 71, 574 (1959). That complexes are not formed in the cocondensations raises the possibility the cyclotrimerization is heterogeneously catalyzed by small chromium aggregates.
9. P. M. Maitlis, *Acc. Chem. Res.*, 9, 93 (1976), and D. R. McAlister, J. E. Bercaw, and R. G. Bergman, *J. Am. Chem. Soc.*, 99, 1666 (1977).
10. The average carbon-carbon transannular distance in [3.3]paracyclophane is about 3.25 Å: P. K. Gantzel and K. N. Trueblood, *Acta Crystallogr.*, 18, 958 (1965).
11. E. Keulen and F. Jellinek, *J. Organomet. Chem.*, 5, 491 (1966).
12. Purification is rendered difficult in that the various polymeric by-products are both more polar and less polar than the desired trimer, as indicated by analytical thin layer chromatography. ^{13}C nmr provides a convenient method for monitoring the progress of the purification.
13. Utilizing dimesitylcobalt catalyst preparations which efficiently cyclize 2-butyne and diphenylacetylene in our hands, we have been able to trimerize 1 only in low (2-4%) yields.
14. A. J. Hubert and J. Dale, *J. Chem. Soc.*, 3160 (1965).