A Novel Solid-state Molecular Complex of Diphenylacetylene and 1,1-Dimethyl-2,5-diphenyl-1-silacyclopentadiene†

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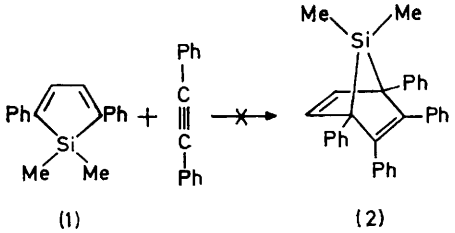
Summary Diphenylacetylene and 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene crystallize from solution as a 1:1 crystal complex, not as the Diels-Alder adduct; the structure of this complex was determined by *X*-ray diffraction.

MARUCA[1] has recently reported that 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (**1**) and diphenylacetylene (tolan) form a stable 1:1 adduct for which he suggested the 7-silanorbornadiene (**2**) as a possible structure. We had previously observed that activated acetylenes [*e.g.* dimethoxycarbonyl- or bis(trifluoromethyl)-acetylene] are required for a Diels–Alder reaction to occur with (**1**). The lack of activation of tolan, the steric crowding in the transition state, and the ease of formation (no heating required) all militated against structure (**2**). Maruca suggested that adduct (**2**) underwent a ready retro-Diels–Alder reaction, but the well established pathway for decomposition of 7-silanorbornadiene through silylene extrusion[2] made this suggestion very unlikely. We report here the results of an *X*-ray diffraction study on this adduct.



(1) (2)

The complex crystallized as long needles. *Crystal data:* $C_{14}H_{10}$–$C_{18}H_{18}Si$, Monoclinic, $a = 6{\cdot}96(2)$, $b = 25{\cdot}47(1)$, $c = 7{\cdot}31(1)$ Å, $\beta = 93{\cdot}07(3)°$; space group $P2_1/m$; Zr-filtered Mo-K_α radiation (0·7107 Å). Using a fully automated Hilger–Watts four-circle diffractometer, all reflections in the *hkl* and $\bar{h}kl$ octants with $2\theta \leqslant 60°$ were measured. No absorption corrections were made. A sharpened three-dimensional Patterson synthesis clearly showed the Si atom and strongly indicated that the correct space group was $P2_1/m$.[3] A three-dimensional electron density synthesis showed all 17 unique carbon atoms.[4] Full-matrix least-squares refinement smoothly converged to the present *R* value of 10·8% for the observed reflections.

The Figure is a computer-generated drawing of the unit cell. The individual bond distances and angles show no significant perturbations over those found in the monomer structure.[5] The most important aspect of the structure is that it is clearly not the Diels–Alder adduct. Each tolan molecule is surrounded by four silole molecules but the

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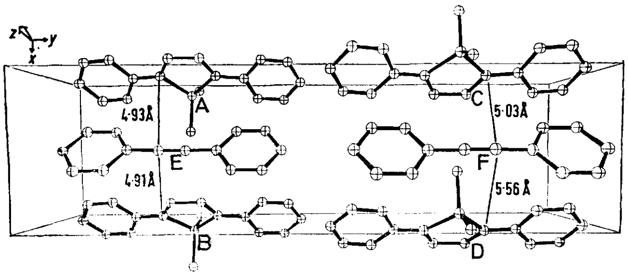
† For preceding paper in the series: 'Heterocyclopentadienes', see: T. J. Barton, J. L. Witiak, and C. L. McIntosh, *J. Amer. Chem. Soc.*, submitted for publication.



FIGURE

average distance of the potential Diels–Alder bonds is 5·11 Å.

The exact nature and cause of this crystal complex remain a puzzle. Although the solid-state u.v. spectrum (KBr disks) does show long wavelength bands (*ca.* 4400 Å) which are not present in the solution spectra of the starting reagents [(**1**): $\lambda_{\max}$ (EtOH) 3740 Å], these bands are also present in the solid-state spectrum of (**1**). There is therefore no evidence for formation of a charge-transfer complex between (**1**) and tolan. To date we have not observed this phenomenon to occur between (**1**) and any other acetylene. There is clear evidence that the tolan may be sublimed under reduced pressure from the complex to leave crystalline (**1**).

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[1] R. Maruca, *J. Org. Chem.*, 1971, **36**, 1626.

[2] For a recent, general review on divalent silicon intermediates (silyenes) see W. H. Atwell and D. R. Weyenberg, *Angew. Chem. Internat. Edn.*, 1969, **9**, 469. The Diels–Alder adduct of (**1**) and perfluorobut-2-yne does *not* decompose by this route in a neat pyrolysis: T. J. Barton, J. L. Witiak, and C. L. McIntosh, submitted to *J. Amer. Chem. Soc.*

[3] J. Rodgers and R. A. Jacobson, "ALF: A General Fourier Program in PL 1 for Triclinic, Monoclinic, and Orthorhombic Space Groups", U.S.A.E.C. Report IS-2155, Iowa State University, Ames, Iowa 50010.

[4] W. R. Busing, K. O. Martin, and H. A. Levy, 'ORFLS, A Fortran Crystallographic Least-Squares Program.' ORNL-TM-305, The Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1962.

[5] Tolan parameters from: J. M. Robertson and I. Woodward, *Proc. Roy. Soc.*, 1938, **164**, *A*, 436; silole parameters from: J. C. Clardy and L. K. Read, unpublished results.