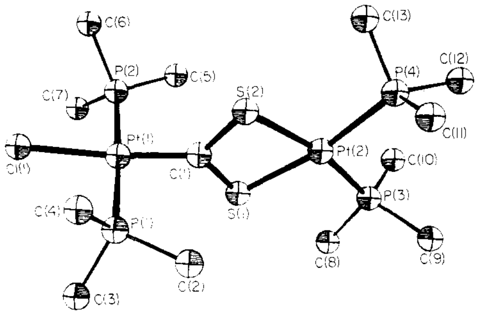

Figure 1. A computer generated perspective drawing of $[Cl(Ph_3P)_2Pt(CS_2)Pt(PPh_3)_2]BF_4 \cdot 0.2CH_2Cl_2$. The phenyl carbons of the PPh_3 groups have been omitted for clarity.

and $c = 27.190$ (2) Å and $\beta = 95.061$ (7)°. A total of 5351 reflections were judged observed after correction for Lorentz, polarization, and background effects. All 90 nonhydrogen atoms were located using heavy atom methods. Full-matrix least-squares refinement[7] varying positional and anisotropic thermal parameters for the atoms of the complex and positional and occupancy parameters for the solvent converged to the present discrepancy index of 0.07.

The computer generated drawing (Figure 1) of the dimeric cation shows a square-planar geometry about each of the platinum atoms with the two planes being perpendicular (89.97°) to each other. Donor groups to Pt(2) involve P(3) and P(4) of the two Ph_3P ligands and two sulfur atoms of the metallodithiocarboxylate ligand, $(Ph_3P)_2(Cl)Pt(CS_2^-)$. Structurally this ligand is similar to the familiar dithio acid $(R\text{-}CS_2^-)$, xanthate $(RO\text{-}CS_2^-)$, and dithiocarbamate $(R_2N\text{-}CS_2^-)$ ligands.[8,9] The Pt(2)-S(1), 2.353 (5) Å, and Pt(2)-S(2), 2.361 (5) Å, bond distances are similar to an average value of 2.32 Å reported for the Pt-S bond distances in the dithiocarbamate complex, $(Et_2NCS_2)_2Pt$.[10] The S(1)-Pt(2)-S(2) bond angle is 72.4 (2)° as compared to 75.5° for the analogous angle in the above-mentioned dithiocarbamate complex. The C(1)-S(1), 1.709 (21) Å, and C(1)-S(2), 1.692 (20) Å, bond distances and the S(1)-C(1)-S(2) bond angle (109.9 (9)°) are very similar to related parameters reported[8,9] for a variety of dithiocarbamate and xanthate complexes. The Pt(1)-C(1) bond distance (1.950 (15)Å) is among the shortest Pt-C(sp^2) distances known. In the Pt-carbene complexes where this bond might be expected to be shortened due to multiple bonding, the values[11-13] range from 1.98 to 2.13 Å. For the complex *cis*-$PtCl_2(PEt_3)[C(OMe)(NHPh)]$ where the bond distance[14] is 1.98 (2) Å, Cotton and Lukehart[13] have estimated a Pt-C(sp^2) bond order of 1.2 suggesting the presence of some Pt to C π-bonding. The shortness (1.95 Å) of the Pt(1)-C(1) bond in the metallodithiocarboxylate ligand suggests Pt to C π-bonding occurs here as well. Further structural details can be found in Tables I-III (supplementary material).

While we have not been able to definitively establish the path which leads from the impure $[(Ph_3P)_2Pt(Cl)(CS)]BF_4$ to the metallodithiocarboxylate complex, a possible route is one which involves initial slow hydrolysis (eq 2) of the reactive thiocarbonyl complex by small amounts of atmospheric moisture. This could be followed by attack of H_2S produced in reaction 1 on unreacted thiocarbonyl complex (eq 3). The resulting metallodithiocarboxylate ligand could then react (eq 4) with the carbonyl complex generated in reaction 1 to give the dimeric product. Support for reaction 3 derives from the mechanism postulated for the reaction of $(R_3P)_2Pt(Cl)(CO)^+$ with H_2O to form CO_2 and $(R_3P)_22Pt(Cl)H$. It involves H_2O attack at the carbonyl carbon atom.[15] In the formation of the metallodithiocarboxylate complex, the concentration of H_2O is important. At high concentrations, only the carbonyl complex is produced as noted above (eq 2). Very low concentrations presumably allow reactions 3 and 4 to occur, resulting in the formation of the dimeric product.

$$(Ph_3P)_2Pt(Cl)(CS)^+ + H_2S \longrightarrow (Ph_3P)_2Pt(Cl)(CS_2^-) + 2H^+ \qquad (3)$$

$$(Ph_3P)_2Pt(Cl)(CS_2^-) + (Ph_3P)_2Pt(Cl)(CO)^+ \longrightarrow [(Ph_3P)_2(Cl)Pt(CS_2)Pt(PPh_3)_2]^+ + Cl^- + CO \qquad (4)$$

The unusually high stability of this metallodithiocarboxylate complex suggests that it will be possible to synthesize other complexes bearing this general type of ligand.

Supplementary Material Available. The fractional coordinates (Table I), bond distances (Table II), and important bond angles (Table III) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-75-656.

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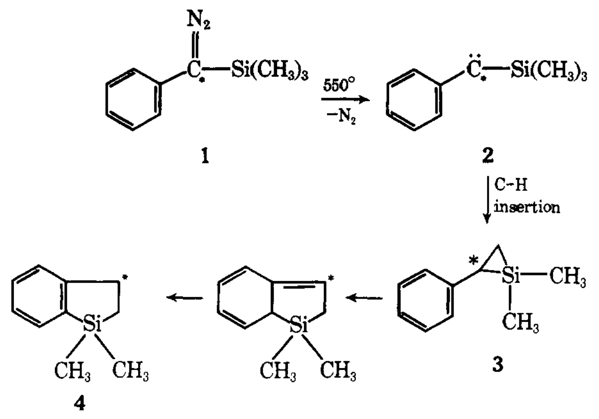
On the Alleged Intermediacy of a Silacyclopropane in the Pyrolysis of Phenyltrimethylsilyldiazomethane

Sir:

The synthesis, isolation, and characterization of the long elusive silacyclopropane ring system by Seyferth[1] can be expected to remove inhibitions from the proposal of such compounds as reactive intermediates. Earlier this year Ando

Scheme I

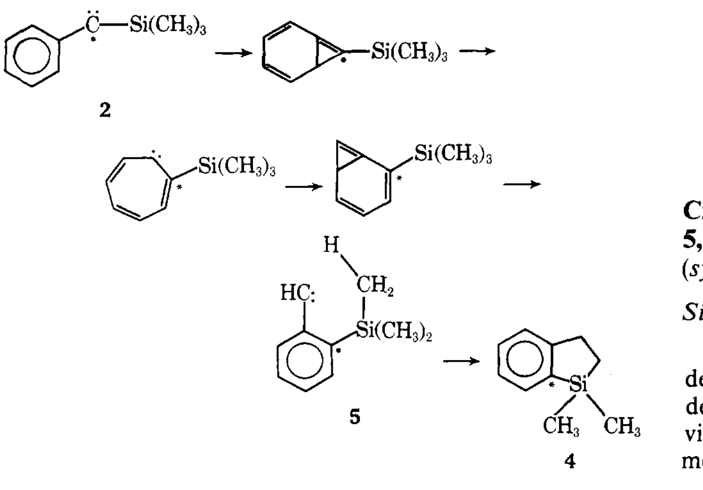


and coworkers[2] reported that the gas-phase pyrolysis (550°, N_2 flow) of phenyltrimethylsilyldiazomethane (**1**) afforded benzosilacyclopentene (**4**) and that this product was evidence for the intermediacy of silacyclopropane (**3**), which resulted from the intramolecular insertion of carbene **2** into a C–H bond of a methyl group (Scheme I).

We had previously observed the formation of **4**, and rationalized it in terms of quite a different mechanism. We considered the precursor to **4** to be the carbene **5**, itself formed by a well-precedented sequence of steps involving carbene-to-carbene rearrangements[3] (Scheme II). Carbene **5** can lead to **4** by a straightforward insertion into a carbon-hydrogen bond.

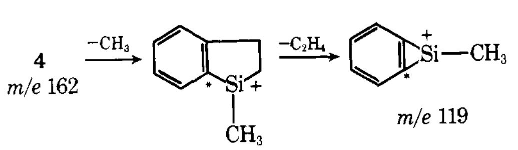
A method of distinguishing between these two mechanistic pathways is obvious once it is noted that the benzylic carbon of **1** remains aliphatic in the Ando mechanism (Scheme I) but becomes the aromatic carbon bonded to silicon in the carbene-interconversion mechanism (Scheme II). Phenylmagnesium bromide was converted to ^{13}C labeled benzoic acid with labeled CO_2 and then to labeled **1** by the procedure of Brook and Jones.[4] Mass spectrometric analysis of the intermediate tosylhydrazone indicated a 24.3% ^{13}C content. Thermal decomposition of labeled **1**, carried out in the inlet port of the preparative gas chromatograph at 300°, afforded **4**. Comparison of the ^{13}C nmr spectra of labeled and unlabeled **4** revealed *no* enhancement of the three aliphatic carbon absorptions (31.81, 11.47, and −1.59 ppm from TMS) and hence no incorporation of ^{13}C into the saturated carbons of the five-membered ring. The absorption of only one aromatic carbon (139.86 ppm from TMS) was enhanced by an average factor of 19.7 over the other aromatic carbon absorptions.

Scheme II



A second sample of **4** was prepared independently by the flash pyrolysis (420° (0.5 mm)) of the lithium salt of the tosylhydrazone of phenyltrimethylsilyl ketone. The ketone was prepared from ^{13}C labeled methyl benzoate (12.8%) by the method of Picard, *et al.*[5] In this case an average enhancement of 13-fold was observed for the same aromatic absorption as was found previously in the decomposition of the diazo compound.

The conclusion that the labeled carbon is now in the aromatic ring is further confirmed by a comparison of the mass spectra of the labeled and unlabeled benzosilacyclopentenes (**4**). The fragmentation of **4** proceeds through loss of a methyl group and then the loss of C_2H_4 (there is no metastable peak for the C_2H_4 loss, so the concertedness of the process is unknown) to yield an ion of the composition C_7H_7Si (*m/e* 119.03185 ± 0.0006, calcd 119.0317). Comparison of the m/e 162/163 and 119/120 intensity ratios indicated a ^{13}C content of 24.8% in the parent ion with 23.6% in the fragment ion. Thus, within reasonable experimental error limits, all of the extra ^{13}C remained with the aromatic fragment.



In summary, the thermal conversion of **1** to **4** does not involve a silacyclopropane but rather provides a further example of the phenylcarbene–cycloheptatrienylidene interconversion.

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Crystal Structure of 5,6,11,12-Tetradehydrodibenzo[*a,e*]cyclooctene (*sym*-Dibenzo-1,5-cyclooctadiene-3,7-diyne)

Sir:

We report the results of a single-crystal X-ray structure determination on the recently described[1] 5,6,11,12-tetradehydrodibenzo[*a,e*]cyclooctene (**1**). The only other previously known compound with two triple bonds in the eight-membered system is 1,5-cyclooctadiyne (**2**), for which only