state for insertion.[20] Included in this mechanistic picture is possible complexation between the divalent silicon and the tetravalent silicon atom of the hydride prior to insertion.[21] This possibility has been investigated by NMR analysis of the products from insertion into the Si–H(D) bonds of di-*tert*-butyldeuteriosilane. The product isotope effect, 1.25, obtained from the H/D ratio on the mesityl-labeled silicon atom is similar to that reported for insertion of diphenylsilylene into the Si–H and Si–D bonds of triethylsilane.[22]
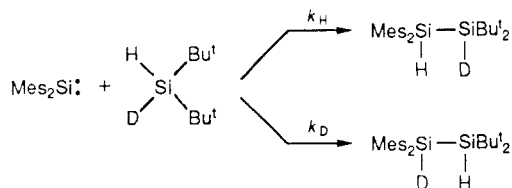
Cycloaddition of divalent silicon to organic π-electrons has provided an efficient synthesis of a variety of substituted siliranes. The rate constant for the dimesitylsilylene reaction with cyclohexene,[23] $k_r = 2.8 \times 10^6$ M^{-1} s^{-1}, is less, as might be anticipated from product studies, than that observed for addition to the conjugated 2,3-dimethylbutadiene, 8.8×10^6 M^{-1} s^{-1}. A more revealing comparison is between the rates of insertion into a silicon–hydrogen σ bond of a trialkylsilane and of addition to the π system of a diene. Triethylsilane is 9 times more reactive than the 2,3-disubstituted diene, in quite reasonable agreement with a factor of 6 reported by Walsh and co-workers[24,25] for kinetic studies of gas-phase reactions of dimethylsilylene.

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(23) The measurement of the rate constant with cyclohexene proved difficult. An initial value of 1.4×10^8 M^{-1} s^{-1} was obtained from a sample dried over sodium and freshly distilled. Further purification, by passing of the cyclohexene through an alumina column and treating with molecular sieves, led to the value in Table I. Naturally, given the large difference, one may wonder if the second treatment provided sufficient purification or if the true rate constant is even lower. In this sense the error limits quoted for cyclohexene may be open to question.
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(25) Baggot, J. E.; Blitz, M. A.; Frey, H. M.; Lightfoot, P. D.; Walsh, R. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 515.
(26) Reaction products were characterized by NMR spectroscopy (^{1}H, ^{13}C, and ^{29}Si), but the assignments must be regarded as tentative until full characterization.

Synthesis and Characterization of the First Example of Insertion by Platinum(II) into a Tetrasubstituted Cyclopropane

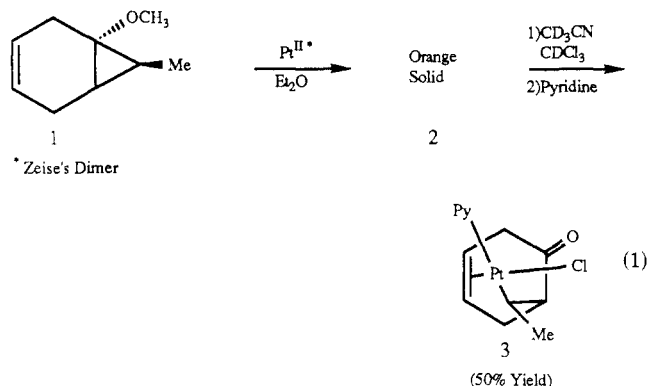**John O. Hoberg, Raymond D. Larsen, and P. W. Jennings***

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Summary: Methodology for the preparation and characterization of insertion of Pt^{II} into a tetrasubstituted cyclopropane is established. In this case, the insertion of Pt^{II} was accomplished with use of 7-methyl-1-methoxybicyclo[4.1.0]hept-3-ene. A unique rearrangement involving a platinacyclobutane as an intermediate is suggested.

Metallacyclobutanes may be involved as intermediates in various processes such as isomerization of alkenes, alkene metathesis, polymerization, and also strained-ring rearrangements.[1-5] Platinacyclobutanes were the first such compounds to be prepared and studied.[6] Formation of platinacyclobutanes is often accomplished by the insertion (oxidative addition) of platinum into a cyclopropane. To date, mono-, di-, and trisubstituted cyclopropanes[1,7] have shown insertion of platinum(II) while tetrasubstituted examples have failed to react.[8]

Earlier work has shown that the bicyclo[4.1.0] system reacts with Pt(II) to form platinacyclobutanes.[9] It has also been observed that electron-releasing groups facilitate the reaction.[10,11] Reaction of a cyclopropane[12] encompassing both of these principles resulted in the first example of insertion of Pt(II) into a tetrasubstituted cyclopropane (eq 1).

(1)

(50% Yield)

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(2) Johnson, T. H.; Chenq, S. S. *Synth. Commun.* **1980**, *10*, 381.
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(12) 1 was synthesized by reaction of 1-methoxy-1,4-cyclohexadiene (Aldrich) with 1,1-diiodoethane and Zn–Cu couple (60%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 5.4 (m, 2 H), 3.3 (s, 3 H), 2.6–2.1 (m, 4 H), 1.25 (m, 1 H), 1.2 (d, 3 H), 0.8 (dq, 1 H), J_{HH} = 6.0 Hz). ^{13}C NMR (125 MHz, CDCl$_3$): δ 123.5 (d), 124.1 (d), 63.3 (s), 54.2 (q), 27.3 (t), 25.5 (t), 23.9 (q), 19.8 (d), 11.8 (d).
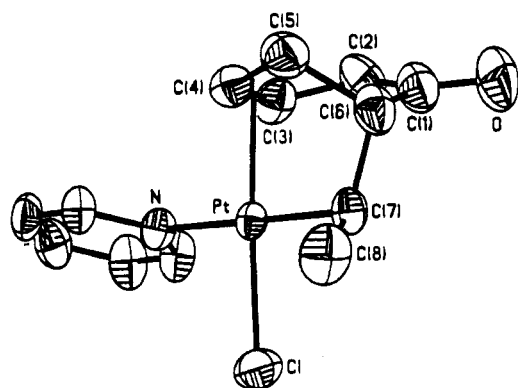
Figure 1. Thermal ellipsoid drawing of structure 3 with labeling scheme.

Table I. Selected Bond Angles (deg) and Distances (Å) for 3

Angles			
C(7)-Pt-Cl	91.3 (3)	C(7)-Pt-N	178.8 (4)
Cl-Pt-N	89.1 (2)	C(2)-C(1)-C(6)	117 (1)
C(2)-C(1)-O	120 (2)	C(6)-C(1)-O	122 (1)
C(1)-C(2)-C(3)	115 (1)	C(2)-C(3)-C(4)	119 (1)
C(3)-C(4)-C(5)	119 (1)	C(4)-C(5)-C(6)	107 (1)
C(1)-C(6)-C(5)	111 (1)	C(1)-C(6)-C(7)	107 (1)
C(5)-C(6)-C(7)	107 (1)	Pt-C(7)-C(6)	109 (1)
Pt-C(7)-C(8)	113 (1)	C(6)-C(7)-C(8)	110 (1)

Distances			
Pt-C(3)	2.12 (1)	Pt-C(4)	2.14 (1)
Pt-C(7)	2.04 (1)	Pt-Cl	2.314 (3)
Pt-N	2.16 (1)	C(1)-C(2)	1.48 (2)
C(1)-C(6)	1.47 (2)	C(1)-O	1.23 (2)
C(2)-C(3)	1.47 (2)	C(3)-C(4)	1.41 (2)
C(4)-C(5)	1.50 (2)	C(5)-C(6)	1.53 (2)
C(6)-C(7)	1.55 (1)	C(7)-C(8)	1.54 (2)

NMR spectra of complex 3 showed several significant features corroborating its structure: (a) a ^{13}C resonance at 25.7 ppm with 723-Hz coupling to ^{195}Pt, which is assigned to the CH σ-bonded to Pt, (b) carbon resonances at 81.0 and 75.1 ppm coupled to ^{195}Pt by 271 and 277 Hz, respectively, assigned to the olefinic moiety, (c) in addition, a resonance appearing at 211 ppm, attributed to the carbonyl, (d) finally, the proton NMR spectrum showing the olefinic protons resonating at 4.8 and 5.5 ppm with ^{195}Pt coupling of 66 and 67 Hz. Complete NMR data for complex 3 is listed below.[13] Even though the NMR spectral data were consistent with the organic portion of 3, the inorganic portion was still in doubt. Thus, an X-ray crystal structure was sought to elaborate the detailed structure. Results of the analysis are shown in Figure 1,[14] which unambiguously establishes 3 as a Pt(II) complex with square-planar geometry. Selected bond angles and distances are given in Table I.

A few points should be made about the reaction shown as eq 1. First, the methoxy group enhances the insertion of platinum into the cyclopropane, as the reaction of bicyclo[4.1.0]hept-3-ene with Zeise's dimer merely results in complexation of the platinum to the olefin.[15] Second, from this result and our previous studies, it is reasonable to suggest the pathway shown as eq 2. Isolation of the
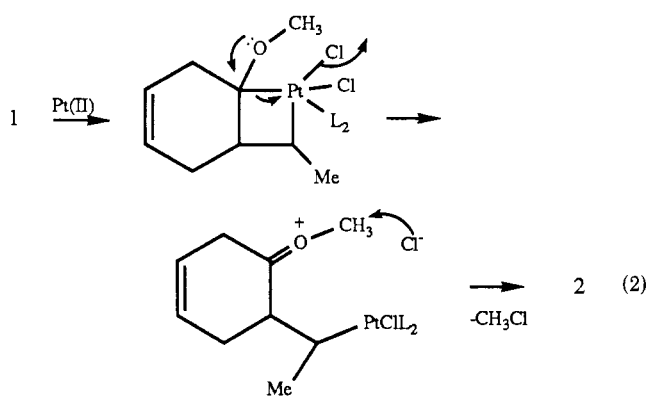
platinacycle is virtually precluded by the fact that platinacycles from bicyclo[4.1.0]heptanes are very unstable except under unique conditions such as in neat pyridine, which would inhibit this reaction.[8,9,17] In addition, the alkoxy moiety will stabilize an incipient cation. Further, evidence for the platinacyclobutane intermediate is the fact

that only one diastereomer is formed as indicated. Ionic cleavage of the cyclopropyl moiety would have certainly produced a mixture of diastereomers as well as other products. The second intermediate proposed in this sequence best describes both the release of the methyl moiety and the reduction to Pt(II).[18]

Finally, ^{13}C CP/MAS experiments on solid 2 exhibit downfield resonances at 75 and 200 ppm, further suggesting that formation of the carbonyl complex occurs in the first stage of eq 1 and not upon addition of the ligand. Further studies are underway to characterize complex 2.

Supplementary Material Available: Listings of atomic coordinates and thermal parameters (2 pages). Ordering information is given on any current masthead page.

(13) IR: 1715 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 4.8 (m, 1 H, J_{PtH} = 66 Hz), 5.5 (m, 1 H, J_{PtH} = 67 Hz), 2.4–3.0 (m, 4 H), 2.0 (m, 1 H), 1.6 (brd, 1 H), 0.6 (d, 3 H). ^{13}C NMR (125 MHz, CD$_3$CN): δ 211 (s), 81.0 (d, J_{PtC} = 271 Hz), 75.1 (d, J_{PtC} = 277 Hz), 60.8 (d, J_{PtC} = 28 Hz), 39.2 (t, J_{PtC} = 26 Hz), 31.0 (t), 25.7 (d, J_{PtC} = 723 Hz), 22.9 (q, J_{PtC} = 37 Hz).

(14) X-ray structure determination of 3: Crystals suitable for crystallographic data collection were grown by slow evaporation from a chloroform solution. A pale yellow crystal (approximately 0.31 × 0.40 × 0.52 mm) was mounted on a glass fiber for data collection on a Nicolet R3mE automated diffractometer at 25 °C with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). The unit cell was triclinic with dimensions of a = 7.165 (1) Å, b = 9.734 (2) Å, c = 10.538 (3) Å, α = 114.08 (2)°, β = 98.00 (2)°, and γ = 96.14 (2)°, obtained by least-squares refinement with 25 centered reflections for which 20° < 2θ < 30°. ω scans were used to collect intensity data for 6877 unique reflections in the range 4° < 2θ < 75°. Data reduction, including corrections for Lorentz and polarization effects, gave 3809 reflections with I > 3σ(I), which were used for structure solution and refinement. On the basis of the cell volume (653.4 (3) Å^3), the centric space group P$\bar{1}$ was assumed and subsequently confirmed by successful structure solution and refinement. The platinum position was determined from a Patterson synthesis, and a difference map revealed the remaining non-hydrogen positions. Absorption corrections were calculated by Gaussian integration using crystal dimensions and indices for crystal faces, μ = 110.4 cm^{-1}; the transmission factor range was 0.034–0.111. The calculated density for C$_{13}$H$_{16}$NOClPt, Z = 2, is 2.20 g/cm^3 (F(000) = 408). All atoms were refined with anisotropic thermal parameters, except hydrogens, which were assigned to idealized positions with a common refined isotropic thermal parameter. The orientation of the methyl group was taken from a difference map. Statistical weighting was used in the least-squares refinement of 155 parameters, and no corrections for extinction were needed. The final R value for structure refinement was 0.0578 (R$_w$ = 0.0589). All calculations were performed on a Data General Eclipse computer with the SHELXTL program package by G. M. Sheldrick, Nicolet Instrument Corp., Madison, WI.

(15) Under identical conditions, as well as elevated temperatures, no insertion of platinum into the cyclopropane moiety was observed.

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(18) This intermediate was suggested by one of the reviewers.