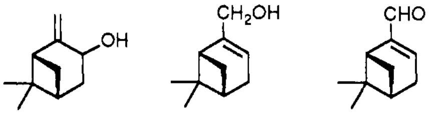
coupling to occur from the side opposite from the *gem*-dimethyl groups (that is, to give **11**), **11** would be formed with retention of configuration at the chiral center, and **13** and **14** would not be among the products.

Reaction is regioselective; cleavage of **8**$^{\bullet+}$ and **9**$^{\bullet+}$ gives the allylic radical-tertiary carbocation (**15** and **17**, respectively). Cleavage of radical cations occurs selectively to give the carbocation of the fragment radical with the lower oxidation potential.[7] The oxidation potential of the allylic radical is not known, but there is reason to believe that the oxidation potential of the tertiary radical is lower.[8] The fact that unreacted **8**, recovered from the reaction mixture, suffered no loss of rotation indicates that the radical cation cleavage is irreversible.

The results indicate that the reduction potentials of the allylic radicals **16** and **18** must be more negative than that of **1** (−1.66 V), otherwise **1**$^{\bullet-}$ would reduce the radical, which would then be protonated. The reduction potentials of allylic radicals of the type **16** and **18** are not known, but again the results are reasonable.[9]

These results have a bearing on the reported photosensitized (electron transfer) oxidation of **8** and **9**.[4c] Irradiation of an oxygen-saturated acetonitrile solution of **8** or **9** with 9,10-dicyanoanthracene present as photosensitizer gives good yields of oxygenated products (pinocarveol (**19**), myrtenol (**20**), and myrtenal (**21**)) *with the 3,1,1-bicyclic ring system intact*. In view of the facile cleavage of the radical cations **8**$^{\bullet+}$ and **9**$^{\bullet+}$ observed here it seems unlikely that these oxidation products involve the radical cation.



19 **20** **21**

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[7] Okamoto, A.; Snow, M. S.; Arnold, D. R. *Tetrahedron* **1986**, *42*, 6175.

[8] The oxidation potential of the tertiary butyl radical is 0.09 V (SCE), and the oxidation potential of the benzylic radical is 0.73 V. Even the cumyl radical has an oxidation potential (0.16 V) greater then that of the *tert*-butyl radical (Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132).

[9] The unsubstituted allyl radical is reduced at −1.6 V (SCE). Alkyl substitution at the terminal position will increase (make more negative) the reduction potential by ca. 0.2 V. (a) Jaun, B.; Schwarz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741. (b) Wayner, D. D. M.; Griller, D. In *From Atoms to Polymers: Isoelectronic Analogies*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers, Inc.: New York, 1989.

Synthesis and Characterization of the First Transition-Metal η^2-Disilene Complexes

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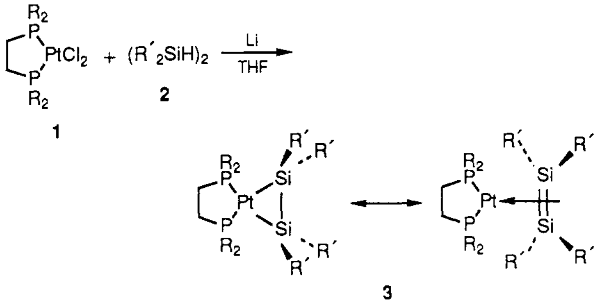
The isolation of disilenes (RR′Si=SiRR′) has historically depended on the use of sterically demanding substituents to impart protection and hence stability to the Si=Si double bond.[1] Disilenes with relatively smaller substituents have been observed at low temperatures[2] or inferred from trapping studies.[3] Alternatively, such reactive organosilicon species can be isolated in the coordination sphere of an unsaturated transition-metal fragment, as evidenced by the recent report of stable η^2-silene complexes of ruthenium.[4]

By analogy, bonding of reactive disilenes to transition-metal substrates may also be expected to stabilize them. Tessier-Youngs and Youngs have reported on the formation of Pt–Si dimers from the dehydrogenative coupling of monomeric silanes with platinum complexes.[5] To explain the unusually short cross-ring Si–Si interactions in these dimers, they proposed a bonding picture involving the coordination of a disilene with two metal moieties. However, disilene complexes in which the silicon–silicon double bond is formally bonded to a single metal center are still almost unknown.[6]

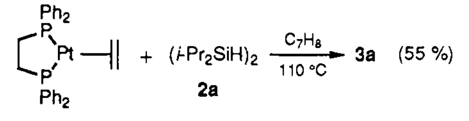
In this paper we describe the synthesis of the first η^2-disilene metal complexes, the platinum compounds **3ab**, by two different reactions. In the first synthesis, equivalent amounts of platinum complex **1**[7] and disilane **2**[8] were stirred overnight in THF in the presence of a slightly greater than 2-fold excess of lithium powder (2% Na content). The reaction mixture eventually turned orange-red with noticeable evolution of gas, presumably H_2. Solvent removal, followed by crystallization from warm toluene afforded yellow microcrystals of **3ab** (eq 1).



(1)

a, R = Ph; R′ = *i*-Pr (20%)
b, R = Cy; R′ = Ph (12%)

In the second route, the platinum–ethylene complex **4**[9] was heated under toluene reflux with an equimolar amount of **2a** to afford **3a** in much greater yield (eq 2).



(2)

4a

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[1] See, for example: (a) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343. (b) Watanabe, H.; Okawa, T.; Kato, M.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 781. (c) Masamune, S.; Tobita, H.; Murakami, S. *J. Am. Chem. Soc.* **1983**, *105*, 6524. (d) Schäfer, A.; Weidenbruch, M.; Pohl, S. *J. Organomet. Chem.* **1985**, *282*, 305. (e) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201.

[2] Michalczyk, M. J.; Fink, M. J.; De Young, D. J.; Carlson, C. W.; Welsh, K. M.; West, R.; Michl, J. *Silicon Germanium Tin Lead Compd.* **1986**, *9*, 75.

[3] For a review, see: Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

[4] Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 7558.

[5] (a) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 4068. (b) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1989**, 577.

[6] In 1986, evidence for complexes of tetramesityldisilene with $(Ph_3P)_2Pt$ and $(Et_3P)_2Pt$ was reported at a meeting: Pham, E. K.; West, R. *Abstracts of Papers*; 20th Organosilicon Symposium, Tarrytown, NY, April 18–19, 1986; p P2.3. Molybdenum and tungsten complexes of disilenes have recently been synthesized: Berry, D. H.; Chey, J.; Zipin, H. S.; Carroll, P. J. *J. Am. Chem. Soc.*, submitted. An unstable disilene–mercury complex which may have the η^2 structure is also known: Zybill, C.; West, R. *J. Chem. Soc., Chem. Commun.* **1986**, 857.

[7] **1a**: Appleton, T. G.; Bennett, M. A.; Tomkins, I. B. *J. Chem. Soc., Dalton Trans.* **1976**, 439. **1b**: Clark, H. C.; Kapoor, P. N.; McMahon, I. J. *J. Organomet. Chem.* **1984**, *265*, 107. **1a**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2) 45.5 ppm, $^1J_{Pt,P}$ = 3620 Hz (lit. 45.3 ppm, $^1J_{Pt,P}$ = 3618 Hz). **1b**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2) 65.4 ppm, $^1J_{Pt,P}$ = 3572 Hz (lit. 64.1 ppm, $^1J_{Pt,P}$ = 3577 Hz).

[8] **2a**: Weidenbruch, M.; Peter, W. *J. Organomet. Chem.* **1975**, *84*, 151. ^{29}Si NMR (C_6D_6) −14.07 ppm, $^1J_{SiH}$ = 174 Hz. **2b**: Gerval, P.; Frainnet, E.; Lain, G.; Moulines, F. *Bull. Soc. Chim. Fr.* **1974**, *7–8(2)*, 1548. ^{29}Si NMR (C_6D_6) −36.5 ppm, $^1J_{SiH}$ = 192 Hz.

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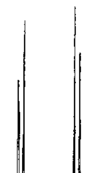
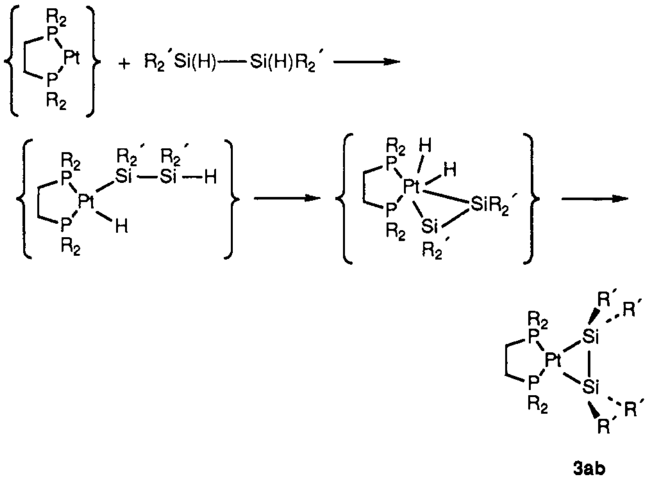


Figure 1. ^{29}Si[^{1}H] NMR spectrum for **3a**.

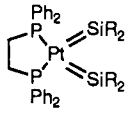
Scheme I. Proposed Mechanism for the Formation of **3ab**



The NMR, IR, and mass spectra of **3ab**[10] are consistent with their formulation as platinum–disilene complexes. In the fast atom bombardment MS of **3ab**, the highest mass (100%) peaks are those due to the parent ions, **3ab**$^+$. The IR spectra showed no indication of Si–H or Pt–H stretching frequencies, in the 1700–2500 cm^{-1} region. The ^{29}Si{^{1}H} NMR spectra, displayed for **3a** in Figure 1, show the expected pattern of a doublet of doublets from coupling to two different ^{31}P nuclei, along with satellites arising from coupling to ^{195}Pt. The ^{29}Si chemical shift values, 19.60 ppm for **3a** and −7.84 ppm for **3b**, are intermediate between those for typical disilenes (45–90 ppm) and those for other disilicon three-membered ring compounds (~ −60 ppm).[1e] The ^{31}P NMR spectra are singlets with satellites due to ^{195}Pt and ^{29}Si, the latter corroborating the values obtained from the ^{29}Si NMR spectrum.

We attribute the larger of the $^2J_{\mathrm{P,Si}}$ values, 138 Hz for **3a** and 148 Hz for **3b**, to trans coupling between silicon and phosphorus. The $^1J_{\mathrm{Pt,P}}$ coupling constants, 1344 Hz for **3a** and 1545 Hz for **3b**, are much smaller than those for **1ab** or for Pt–olefin complexes (ca. 3500 Hz).[11] This indicates that in **3ab** the Pt–P bond is made less covalent by a ligand of relatively high trans influence.[12] Silyl groups have been shown to reduce Pt–P coupling constants in trans bonds markedly.[13]

The proposed structure for **3ab** corresponds to the synergistic bonding of the Dewar–Chatt–Duncanson model, commonly used to describe bonding from alkenes to transition metals. Two other structures which might be considered for **3ab** are the bis-silylene structure **5** and the dimeric structure **6**. Although an oxygen-bridged bis-silylene complex of iron has recently been synthesized,[14] this structure seems unlikely in the absence of stabilization by bases and is inconsistent with the observation of an $i\mathrm{Pr}_2\mathrm{SiSi}i\mathrm{Pr}_2^+$ fragment in the mass spectrum of **3a**. Structure **6** can be ruled out because no long-range spin couplings, $^2J_{\mathrm{Pt,Si}}$ or $^3J_{\mathrm{P,Si}}$, were observed.



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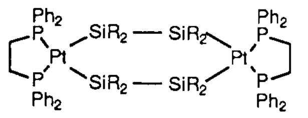

6

The formation of **3ab** may be rationalized via an oxidative addition–reductive elimination mechanism (Scheme I). First, the unsaturated Pt fragment, 1,2-bis(dialkyl/arylphosphino)ethaneplatinum, generated from LiCl elimination or loss of ethylene, adds oxidatively to the two Si–H bonds to yield the six-coordinate Pt intermediate which then eliminates dihydrogen, forming **3ab**. These results show that disilenes can be stabilized as platinum complexes, even without sterically hindering substituents on silicon. We are now investigating the reaction chemistry of **3ab**, and, while initial attempts have been unsuccessful, efforts to obtain single crystals of **3ab** suitable for X-ray diffraction are continuing.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research, Air Force Systems Command, USAF under contract No. F49620-86-C-0010 and the National Science Foundation, Grant No. CHE-8318810-02.

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(9) Head, R. A. *J. Chem. Soc., Dalton Trans.* **1982**, 1637. **4**: ^{31}P{^{1}H} (C_6D_6/CD_2Cl_2) 53.52 ppm, $^1J_{\mathrm{Pt,P}} = 3278$ Hz.

(10) **3a**: MS (FAB) *m/e* 822 (M$^+$, 100% rel intensity), 751 (M$^+$ − Si*i*-Pr, 20%), 708 (M$^+$ − Si*i*–Pr$_2$, 38%), 594 (M$^+$, Si$_2$*i*-Pr$_4$, 70%); ^{1}H NMR (CD_2Cl_2), 25 °C, 200 MHz) 7.61 (m, 8 H, *o*-PhH), 7.43 (m, 12 H, *m*- and *p*-PhH), 2.14 (dt, $^2J_{\mathrm{PH}} = 17.6$ Hz, $^3J_{\mathrm{HH}} = 6.3$ Hz), 2.05 (dt, $^2J_{\mathrm{PH}} = 17.6$ Hz, $^3J_{\mathrm{HH}} = 6.3$ Hz), 1.55 (m, 4 H, *i*-PrH), 0.85 (d, $^3J_{\mathrm{HH}} = 10.4$ Hz, 24 H, *i*-PrH); ^{31}P{^{1}H} NMR (C_7D_8, 27 °C, 202.5 MHz) 56.21 ppm (s, $^1J_{\mathrm{Pt,P}} = 1344$ Hz, $^2J_{\mathrm{P(cis),Si}} = 12.5$ Hz, $^2J_{\mathrm{P(trans),Si}} = 138$ Hz); ^{29}Si{^{1}H} NMR (C_7D_8, 27 °C, 99.4 MHz, INEPT) 19.60 ppm (dd, $^1J_{\mathrm{Pt,Si}} = 1128$ Hz, $^2J_{\mathrm{P(cis),Si}} = 12.5$ Hz, $^2J_{\mathrm{P(trans),Si}} = 138$ Hz). Anal. Calcd for $C_{38}H_{52}P_2Si_2Pt$: C, 55.52; H, 6.38. Found: C, 55.69; H, 6.36. **3b**: MS (FAB) *m/e* 982 (M$^+$, 100% rel intensity), 906 (M$^+$ − Ph, 77%), 877 (M$^+$ − SiPh, 46%), 800 (M$^+$ − SiPh$_2$, 52%); ^{1}H NMR (CD_2Cl_2, 25 °C, 200 MHz) 7.42 (m, 8 H, *o*-PhH), 7.1 (m, 12 H, *m*- and *p*-PhH), 2.3 (m, 4 H, PCH_2CH_2P), 1.7–1.4 (m, 44 H, CyH); ^{31}P{^{1}H} NMR (C_7D_8, 25 °C, 202.5 MHz) 73.47 ppm (s, $^1J_{\mathrm{Pt,P}} = 1545$ Hz, $^2J_{\mathrm{P(cis),Si}} = 13.5$ Hz, $^2J_{\mathrm{P(trans),Si}} = 148$ Hz); ^{29}Si{^{1}H} NMR (C_7D_8, 30 °C, 99.4 MHz, INEPT) −7.84 ppm (dd, $^2J_{\mathrm{P(cis),Si}} = 13.5$ Hz, $^2J_{\mathrm{P(trans),Si}} = 148$ Hz, $^1J_{\mathrm{Pt,Si}} = 1125$ Hz). Anal. Calcd for $C_{50}H_{68}P_2PtSi_2$: C, 61.1; H, 6.93. Found: C, 58.7; H, 6.94.

(11) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: Berlin, 1979; p 992.

(12) Pidcock, A.; Richards, R. E.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 1707.

(13) Heaton, B. T.; Pidcock, A. *J. Organomet. Chem.* **1968**, *14*, 235.

(14) Ueno, K.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1988**, *110*, 4092.

The Total Synthesis of (−)-Cryptosporin†

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(+)-Cryptosporin, a yellow fungal metabolite with weak activity against gram-positive bacteria, can be isolated from the fermentation broths of *Cryptosporium pinicola* LINDER.[1] Its original structural assignment was based on an analysis of NMR data and a comparison of a degradation product with a hydroxyjuglone, and the peri-hydroxyl was located at C-6. Later, the hydroxyl was relocated to C-9, as shown in **1** when a confusion in the original samples of hydroxyjuglone reference samples was

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† This paper is dedicated to William S. Johnson in the year of his 76th birthday and his Cope Medal award.

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