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The Photochemical Nucleophile–Olefin Combination, Aromatic Substitution Reaction: Methanol–α- and β-Pinene–1,4-Dicyanobenzene. The Photo-NOCAS Reaction. 3[1]

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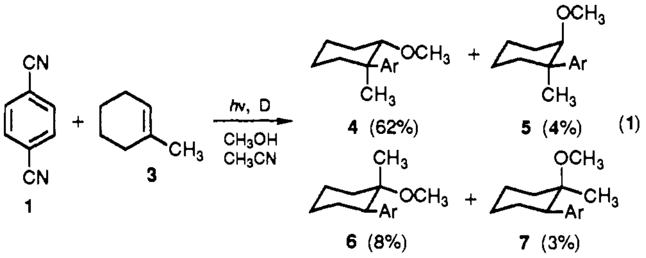
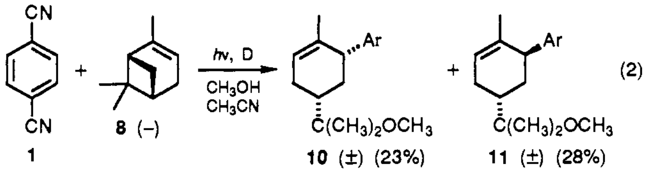
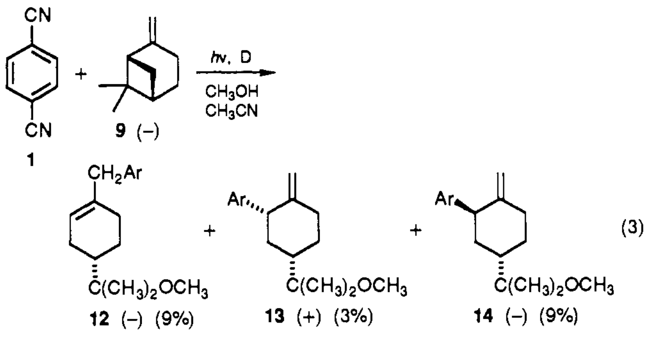
When a solution of 1,4-dicyanobenzene (**1**), and 1-methylcyclohexene (**3**) in acetonitrile–methanol (3:1) is irradiated, the 1:1:1 (alcohol/olefin/aromatic) adducts **4–7** are obtained. Reaction is more efficient and the yield is greater when biphenyl (**2**) (an electron-donating sensitizer) has been added (reaction 1).[1a]



The mechanism originally proposed for this reaction can account for most of the results; however, some important features require further clarification. As an example, a more thorough understanding of the sequence of events occurring during the addition may lead to greater control of the regio- and stereochemistry. In particular, it has been observed that the sensitizer has an affect on the product ratio. This has been explained in terms of a variation of the extent of reaction occurring, while the olefin radical cation and the dicyanobenzene radical anion ($1^{\bullet -}$) are still in the geminate radical ion pair, relative to reaction involving the solvated olefin radical cation (or a complex formed between the olefin radical cation and the sensitizer) free from the influence of the radical anion.[1a] Results of this study using α-pinene (**8**) and β-pinene (**9**) as the olefin provide additional evidence regarding the mechanism and further illustrate the synthetic utility of the reaction.

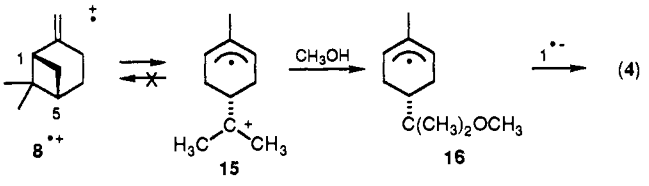
The results of the irradiation of **8** and **9** under these conditions are shown in reactions 2 and 3.[2,3] Both **10** and **11** are formed as the racemic mixtures. The configuration of **9** (5*S*) is retained in **12–14**. There was no loss of rotation in unreacted **8** or **9** recovered after >90% conversion of **1**. Formation of the trans adducts **11** and **14** is only slightly favored over formation of the cis isomers **10** and **13**. Both reactions 2 and 3 are less efficient when the irradiation is carried out in the absence of added **2**; the ratio of products remains essentially the same.

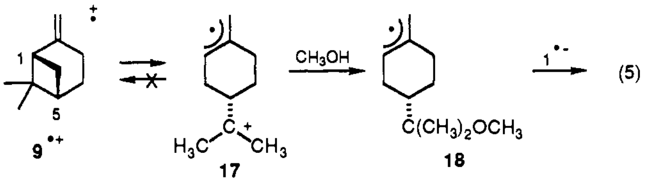




Ar = 4-cyanophenyl D = biphenyl (**2**)

Initial excitation may involve either **1** or **2**. The singlet energy of **2** is slightly less than that of **1**; however, the extinction coefficient at long wavelength and the concentration of **1** are greater than that of **2**.[4] Sensitization by **2** has been attributed to a particularly efficient solvent separation of the radical ions from the geminate radical ion pair and to complex formation involving **2**.[5] The free energy for electron transfer from **8** or **9** to the excited singlet state of **1**, or from the excited singlet state of **2** to **1**, calculated by using the Weller equation, is negative.[4,6] Electron transfer from **8** or **9** to the biphenyl radical cation ($2^{\bullet +}$) is also favorable.





These results indicate that the four-membered ring of $8^{\bullet +}$ and $9^{\bullet +}$ cleaves before reaction with methanol or with $1^{\bullet -}$. Reaction of the distonic radical cations **15** and **17** with methanol would be rapid, leading to the allylic radicals **16** and **18**, which couple with $1^{\bullet -}$ at both ambident ends and from both sides of the ring. Coupling on the pseudo-axial side trans to the side chain should be favored and would account for the slight preference for formation of **11** and **14**. If coupling of the radical cation and the radical anion occurred before ring opening or while the radical ion pair was still oriented, there would be a strong preference for

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[1] Preceding publications in this series are as follows: (a) Arnold, D. R.; Snow, M. S. *Can. J. Chem.* **1988**, *66*, 3012. (b) Borg, R. M.; Arnold, D. R.; Cameron, T. S. *Can. J. Chem.* **1984**, *62*, 1785.

[2] A solution of 1,4-dicyanobenzene (**1**) (0.05 M), biphenyl (**2**) (0.015–0.025 M), and α- or β-pinene (**8** or **9**) (0.10 M) in acetonitrile–methanol (3:1) was irradiated at 10 °C through a Pyrex filter with a medium-pressure mercury vapor lamp. Progress of the reaction was followed by capillary column gas chromatography with a mass selective detector. After >95% consumption of **1**, the photo-NOCAS products were isolated by medium-pressure column chromatography on silica gel. The specific rotation of the unreacted olefins was essentially the same as that of the starting material ($[\alpha]_D^{20^\circ C}$ ($CHCl_3$) **8**, −50.1; **9**, −15.5).

[3] The structural assignments are in accord with the ^1H and ^{13}C NMR and mass spectra. The ^1H NMR spectrum of the isomer assigned the cis configuration (**10**) had a signal with an integrated intensity of one at 3.36 ppm which was coupled by 9.25 Hz. This signal was assigned to the benzylic proton, coupled by axial–axial proton interaction. The signal (3.42 ppm) assigned to the benzylic proton in the other isomer (**11**) was relatively sharp. The distinction between **13** and **14** was made on the same basis. In this case the isomer which was assigned the cis configuration (**13**) had a signal (3.29 ppm) due to the benzylic proton coupled by 10.25 Hz. The spectrum of the major isomer-assigned structure (**14**) had a sharp signal at 3.77 ppm which was attributed to the equatorial benzylic proton. The signal due to one of the vinyl protons in the spectrum of **13** is shifted significantly to higher field (3.77 relative to 4.90 ppm) by the adjacent equatorial aryl group. The observed (minimum) specific rotations ($[\alpha]_D^{20^\circ C}$ ($CHCl_3$)) of **12**, **13**, and **14** were −51.9, +6.7, and −138.6.

[4] Singlet energy (kcal/mol): **1**, 97.6;[4a] **2**, 95.9.[4b] Oxidation potentials (V, SCE): **2** 1.82;[4b] **8**, 1.63;[4c] **9**, 1.82.[4c] Reduction potential (V, SCE) **1**, −1.66.[4a] (a) Arnold, D. R.; Maroulis, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 5931. (b) Loutfy, R. O.; Loutfy, R. O. *Can. J. Chem.* **1976**, *54*, 1454. (c) Zhang, B.-w.; Ming, Y.-f.; Cao, Y. *Photochem. Photobiol.* **1984**, *40*, 581.

[5] (a) Schaap, A. P.; Lopez, L.; Gahnon, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 663. (b) Majima, T.; Pac, C.; Nakasone, A.; Sakurai, H. *J. Am. Chem. Soc.* **1981**, *103*, 4499. (c) Mattes, S.; Farid, S. *Org. Photochem.* **1983**, *6*, 233.

[6] Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

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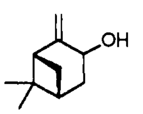
coupling to occur from the side opposite from the *gem*-dimethyl groups (that is, to give **11**), **11** would be formed with retention of configuration at the chiral center, and **13** and **14** would not be among the products.

Reaction is regioselective; cleavage of $\mathbf{8}^{\bullet+}$ and $\mathbf{9}^{\bullet+}$ 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 $\mathbf{1}^{\bullet-}$ 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 $\mathbf{8}^{\bullet+}$ and $\mathbf{9}^{\bullet+}$ observed here it seems unlikely that these oxidation products involve the radical cation.



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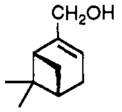

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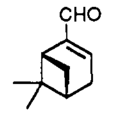

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[7] Okamoto, A.; Snow, M. S.; Arnold, D. R. *Tetrahedron* **1986**, *42*, 6175.

[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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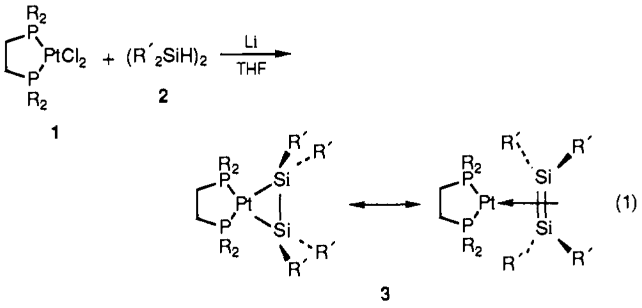
The isolation of disilenes (RR′Si=SiRR′) has historically depended on the use of sterically demanding substituents to impart protection and hence stability to the Si=Si double bond.[1] Disilenes with relatively smaller substituents have been observed at low temperatures[2] or inferred from trapping studies.[3] 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]

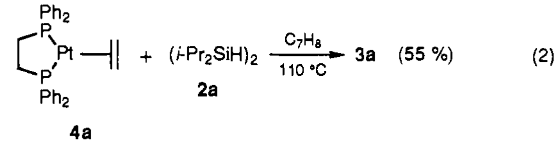
By analogy, bonding of reactive disilenes to transition-metal substrates may also be expected to stabilize them. Tessier-Youngs and Youngs have reported on the formation of Pt–Si dimers from the dehydrogenative coupling of monomeric silanes with platinum complexes.[5] To explain the unusually short cross-ring 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).



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).



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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.

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[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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