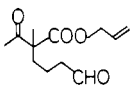

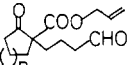

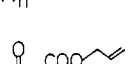

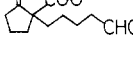

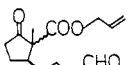

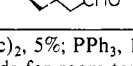

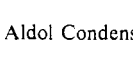

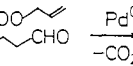

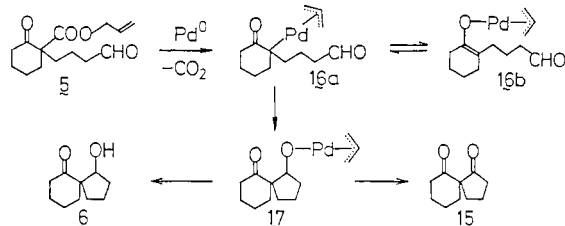


Table I. Pd-Catalyzed Intramolecular Aldol Reaction^a

aldehyde		reaction		product ^b		
		temp (°C)	time (h)			yield (%)
	1	rt ^d	29		2	82 (1/5)
	3 n = 1	40	4		4	90 (1/1)
	5 n = 2	rt ^d	40		6	69 ^c (1/1)
	7 n = 4	rt ^d	30		8	77 (1/2)
	9 n = 8	65	40		10	85 (1/1)
	11	rt ^d	5		12	93 (1/1)
	13a trans	rt ^d	10		14	70 (1/4)
	13b cis	rt ^d	34		14	96 (1/4)

^a Pd(OAc)₂, 5%; PPh₃, 10%; in acetonitrile. ^b The erythro/threo ratios are shown in parentheses. ^c The diketone **15** was obtained in 9% yield from **5**. ^d rt stands for room temperature.

Scheme I. Aldol Condensation via Pd Enolate



as shown in Table I. The reaction is highly chemoselective and almost no competitive reactions such as allylation, dehydrogenation, or hydrolysis was observed. For example, treatment of the allyl acetoacetate derivative **1** having the butanal side chain at the α -carbon with palladium complex (5 mol % of Pd(OAc)₂ and 10 mol % of triphenylphosphine) at room temperature in acetonitrile for 4 h gave a diastereomeric mixture of the cyclopentanol derivative **2** (erythro **2a**/threo **2b** = 1/5) in 82% yield. Similarly, other five- and six-membered spiro-aldol compounds **4**, **6**, **8**, **10**, and **12** were obtained in good yields. When the butanal side chain was introduced at the β -carbon of α -methyl- α -(allyloxy)carbonylcyclopentanone, 9-methylbicyclo[4.3.0]nonan-8-on-1-ols **14a,b** were obtained as expected. Both stereoisomers of the β -keto esters **13a** and **13b** were cyclized to form the cis ring junction exclusively.¹² The diastereomeric ratio of **14a**(erythro)/**14b**(threo) was almost 20/80 in both cases. The palladium enolate is insensitive to water, and similar results were obtained by the reactions of **1** and **11** carried out in dry and wet (10% H₂O) acetonitrile or THF.

As shown in Scheme I, the formation of the palladium enolates (**16a** or **16b**) is responsible for the aldol reaction. But there remains ambiguity particularly about how the catalytic species of Pd is regenerated from the palladium alkoxide **17** formed by the aldol reaction at the last step of the catalytic cycle. We expected the formation of the diketone **15** by the elimination of β -hydrogen as a reasonable reaction path.¹³ Actually in one case we obtained spiro[4.5]decane-1,6-dione (**15**) from **5**, but it was a minor product (9%).

The attempted intermolecular aldol reaction was competitive with the allylation reaction. The reaction of allyl 2-methylacetoacetate (1 mmol) with hexanol (3 mmol) gave the aldol product (54%) and the allylated ketone (23%).

In summary, we could, for the first time, demonstrate the aldol reaction as a convincing enolate reaction of palladium. The

characteristic features of this reaction are as follows. 1. It is possible to generate regioselectivity the palladium enolate of unsymmetrical ketones by the decarboxylation of β -keto esters. 2. The reaction proceeds under completely neutral conditions by using the palladium-phosphine complex only in a catalytic amount. 3. The reaction is particularly suitable for the intramolecular reaction.

Acknowledgment. We thank the Analysis Center of our university for ¹H and ¹³C NMR and HRMS measurements.

Supplementary Material Available: Experimental data for compounds **2**, **4**, **6**, **8**, **10**, and **12** consisting of ¹H NMR, ¹³C NMR, IR, HRMS(EI), and *R_f* (6 pages). Ordering information is given on any current masthead page.

 γ -Silicon Effects on 2-Norbornyl Cations

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The effects of trimethylsilyl groups on carbocations have been studied extensively over the past decade. α -Silyl substitution at a positively charged carbon is destabilizing relative to methyl but stabilizing relative to hydrogen.¹ A β -silyl group strongly accelerates solvolysis, particularly if oriented antiperiplanar to the leaving group.² Recently evidence was adduced that γ -Me₃Si groups stabilize carbocations and the transition states for their formation through the "W" conformation.^{3,4} With very few exceptions,^{5,6} Me₃Si probes have not been applied to the notorious

(1) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1985**, *107*, 2806, and references cited therein.

(2) Lambert, J. B.; Wang, G.-t.; Finzel, R. B.; Tamura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838, and references cited therein.

(3) (a) Shiner, V. J., Jr.; Ensinger, M. W.; Kriz, G. S. *J. Am. Chem. Soc.* **1986**, *108*, 842. (b) Davidson, E. R.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 3135. (c) Shiner, V. J., Jr.; Ensinger, M. W.; Rutkowske, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 804.

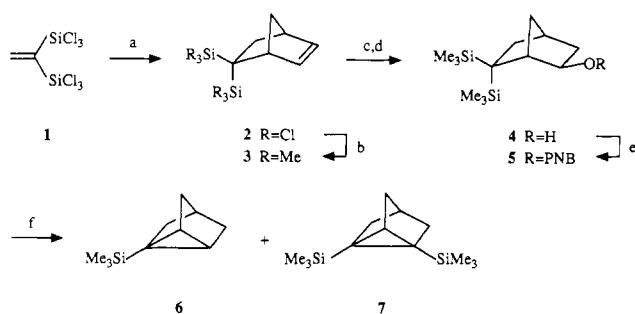
(4) (a) Grob, C. A.; Sawlewicz, P. *Tetrahedron Lett.* **1987**, *28*, 951. (b) Grob, C. A.; Gründel, M.; Sawlewicz, P. *Helv. Chim. Acta* **1988**, *71*, 1502.

(5) For electrophilic additions to 7-trimethylsilyl-2-norbornenes, see: Fleming, I.; Michael, J. P. *J. Chem. Soc., Chem. Commun.* **1978**, 245.

(6) For the oxidative decarboxylation of 3-(trimethylsilyl)norbornane-2-carboxylic acid, see: Hermeling, D.; Schaefer, H. J. *Angew. Chem.* **1984**, *96*, 238; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 233.

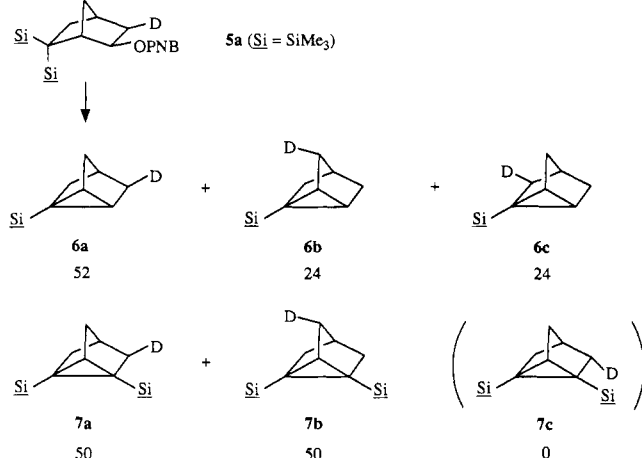
(12) NOEs between the angular methyl and proton in both **14a** and **14b** were observed (4.3% and 3.2%) indicating that the both rings are cis fused.

(13) Ketones were obtained from similar intermediates in the Pd-catalyzed oxidation of alcohols via allyl carbonates. Tsuji, J.; Minami, I.; Shimizu, I. *Tetrahedron Lett.* **1984**, *25*, 2791-2792.

Scheme I^a

^a Reagents: (a) cyclopentadiene (1 equiv), 60–70 °C, 3 h, quantitative; (b) MeMgI (11 equiv), Et₂O, 40 °C, 35 days, 80%; (c) B₂H₆ (1.1 equiv), THF, 0 °C, 2 h; then 5 M KOH (1.5 equiv), 37% H₂O₂ (1.4 equiv), 20 °C, 2 h, 98%; (d) chromatography, SiO₂, Et₂O–hexane (1:1), 28%; (e) 4-O₂N-C₆H₄COCl (1.03 equiv), Py, 0 °C, 10 min, then 40 °C, 25 min and 20 °C, 12 h, 68%; (f) 97% TFE, 2,6-lutidine (2.8 equiv), 75 °C, 16 h, 86%, 6:7 = 62:38.

Scheme II

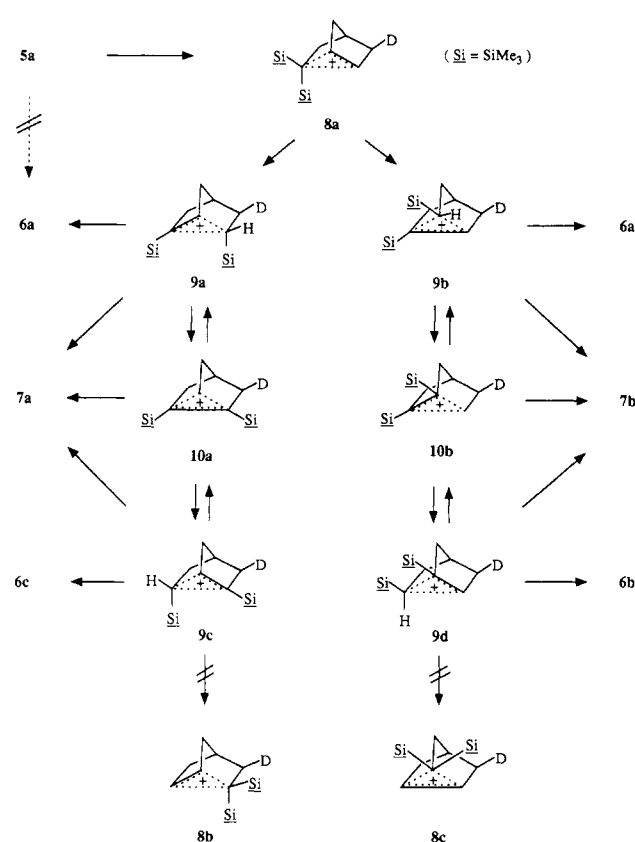


2-norbornyl cation. We report here that the 6,6-bis(trimethylsilyl)-2-norbornyl cation **8** undergoes unprecedented 6,2 (6,1)-silyl shifts prior to desilylation and deprotonation.

Preparation of the *p*-nitrobenzoate **5** was accomplished as outlined in Scheme I. The Diels–Alder reaction of 1,1-bis(trichlorosilyl)ethene (**1**)⁷ with cyclopentadiene proceeded smoothly, but exchange of all chlorines for methyl in the adduct **2** required prolonged heating with excess methylmagnesium iodide. Hydroboration of **3** gave a mixture of the 2,5- and 2,6-isomers (64:36) from which **4** was isolated by chromatography. Sulfonates of **4** proved to be too reactive for isolation, whereas the *p*-nitrobenzoate **5** (mp 113 °C) was readily obtained. Solvolysis of **5** in buffered TFE at 75 °C afforded the norbornyl cations **6** and **7** in a 62:38 ratio;⁸ products of nucleophilic substitution were not observed.

The formation of **7** clearly involves a silyl shift. For further insight into the reaction paths leading to **6** and **7**, the deuterated *p*-nitrobenzoate **5a** was prepared according to Scheme I, using B₂D₆. The solvolysis products of **5a** were separated and analyzed for the distribution of deuterium by means of ¹H and ¹³C NMR. Within experimental error ($\pm 3\%$), D-**6** was a 2:1:1 mixture of **6a**, **6b**, and **6c**. The isotopomers **7a** and **7b** were formed in a 1:1 ratio, **7c** being conspicuously absent (Scheme II). The observed distribution of deuterium is reasonably derived from a rapidly equilibrating mixture of the carbocations **9a–9d** (Scheme III).

Scheme III



(The bridged structures are drawn for analogy with the parent 2-norbornyl cation. In a formal sense, Wagner–Meerwein pairs of rapidly equilibrating open ions would also accommodate our data.) The interconversion of **9a** with **9c**, and of **9b** with **9d**, is thought to proceed by 6,2-hydride shifts, involving **10a** and **10b**, respectively, as intermediates. The ions **10** may eventually contribute to the formation of **7**.

Several implications of our data are worthy of note: (a) Although the solvolysis of **5** is strongly accelerated (by a factor of 3×10^4 relative to 2-norbornyl *p*-nitrobenzoate in TFE at 100 °C),⁹ concerted ionization and desilylation¹⁰ is insignificant. A contribution of the concerted process would lead to more than 50% of **6a**. (b) The exo- and endo-6-Me₃Si groups become equivalent prior to the silyl shift, as visualized by the bridged structure **8a** of the first intermediate. Otherwise the yields of **6b** and **6c** would not be equal. (c) The silyl shifts **8a** \rightarrow **9a,b** are rapid as compared to desilylation of **8a**, otherwise the fraction of **6a** (in **6**) should exceed 50%. (d) The silyl shifts **8a** \rightarrow **9a,b** are irreversible under solvolytic conditions. The reversal of these shifts is equivalent to the transformation of **9c** into **8b** and of **9d** into **8c**. The intervention of **8b,c** is excluded since subsequent silyl and hydride shifts would lead to **7c**, and to a 1:1:1 ratio of **6a–c**.

Our results establish the relative energies of bis-silylated 2-norbornyl cations as **8** > **10** \geq **9**, although structures **9** and **10** place a (partial) positive charge α to silicon. The relative instability of **8** may, in part, be due to steric compression of the geminal Me₃Si groups.¹¹ A study of monosilylated (necessarily unsymmetrical) norbornyl cations is in progress to resolve this issue. The facile 1,3-migration of silyl groups observed here is without

(7) Petrov, A. D.; Mironov, V. F.; Mashantsker, D. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1956, 550.

(8) When subjected to solvolysis conditions (TFE, 1 equiv of *p*-nitrobenzoic acid, 2.8 equiv of lutidine, 75 °C, 16 h), **7** was recovered almost quantitatively ($\leq 2\%$ of **6** was observed). In the absence of lutidine, both **6** and **7** underwent acidolysis to give 2-norbornyl trifluoroethyl ether.

(9) Bentley, T. W., manuscript in preparation.

(10) Evidence for concerted 1,3-deoxystannylation reactions has been reported: (a) Davis, D. D.; Black, R. H. *J. Organomet. Chem.* 1974, 82, C-30. (b) McWilliam, D. C.; Balasubramanian, T. R.; Kuivila, H. G. *J. Am. Chem. Soc.* 1978, 100, 6407.

(11) For further support of steric compression, see: Kirmse, W.; Söllenböhmer, F. *J. Chem. Soc., Chem. Commun.*, accepted for publication.

precedent in acyclic and monocyclic systems.³ We are tempted to associate this novel reactivity with the bridged structure of 2-norbornyl cations.¹² The well-known 6,2-shifts of hydrogen are paralleled by silyl groups, behaving as "super protons".

(12) For recent reviews, see: (a) Lenoir, D.; Apeloig, Y.; Arad, D.; Schleyer, P. v. R. *J. Org. Chem.* **1988**, *53*, 661. (b) Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley: New York, 1987. (c) Vogel, P. *Carbocation Chemistry*; Elsevier: Amsterdam, 1985. (d) Shubin, V. G. *Top. Curr. Chem.* **1984**, *116*, 267. (e) Brown, H. C. *The Nonclassical Ion Problem* (with comments by Schleyer, P. v. R.); Plenum: New York, 1977.

Oxidative Coupling of *cis*-Carbene Ligands: Synthesis, Structure, and Reactivity of an Iridium(III) Bis(oxacyclopentylidene) Complex

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The propensity of carbene ligands to engage in useful coupling reactions¹ has stimulated interest in the preparation, structure, and reactivity of mononuclear bis(alkoxycarbene) complexes.²⁻⁴ Herein we report the application of alkynol cyclization methodology to the preparation of an iridium bis(carbene) complex, structural characterization of this complex and unprecedented base-induced carbene ligand coupling chemistry.

Previously we reported the reaction of 3-butyne-1-ol and Ir-(CR=CR=CR)(PPh₃)₂(CO)(NCCH₃)⁺BF₄⁻ (R = CO₂CH₃) to generate the carbene complex Ir-(CR=CR=CR)(PPh₃)₂(CO)(=C(CH₂)₃O)⁺BF₄⁻.⁵ We have now utilized an iridium(III) precursor, **1**, containing two labile *cis*-acetonitrile ligands in reaction with excess 3-butyne-1-ol to generate the first bis(alkoxycarbene) complex of iridium, Ir-(CR=CR=CR)(PPh₃)₂(=C(CH₂)₃O)₂⁺BF₄⁻, **2** (R = CO₂CH₃). Bis(carbene) **2** undergoes a remarkable base-induced ligand coupling reaction to give an iridium hydride complex **3** and 2-(2(5*H*)-furanlydene)tetrahydrofuran, **4**, as a single stereoisomer.

When a chloroform solution of 3-butyne-1-ol (230 μL, 3.0 mmol) and bis(acetonitrile) complex **1** (630 mg, 0.54 mmol, 0.02 M)⁶ is heated at 50 °C (3.5 h), conversion to bis(carbene) **2** occurs in 87% isolated yield.⁷ The ¹H NMR spectrum of **2** in CD₃CN

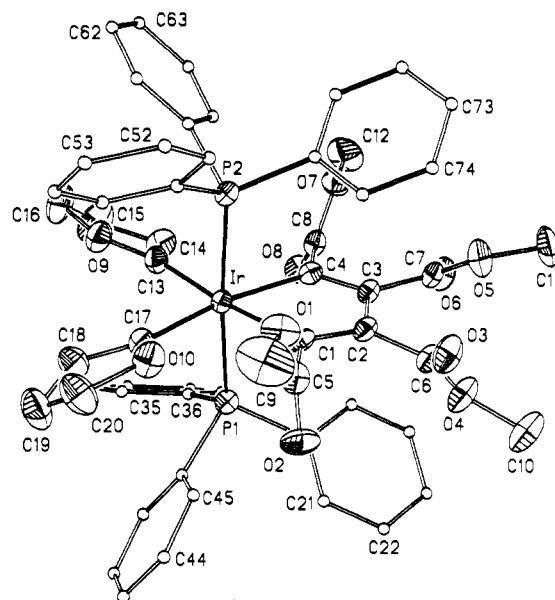
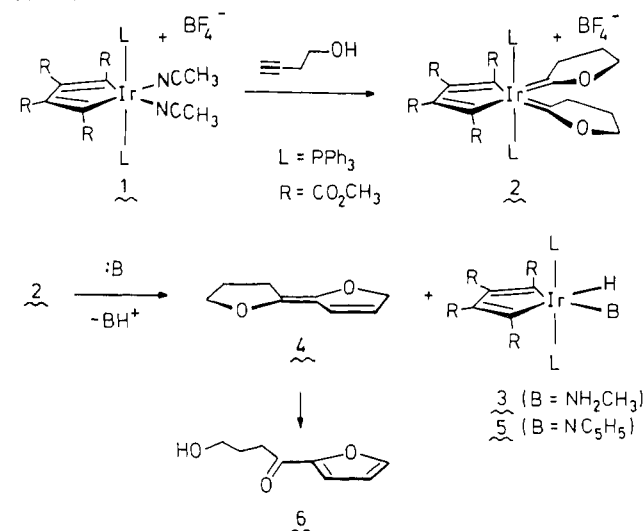
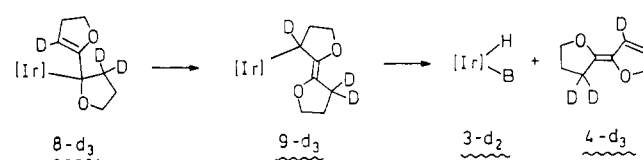


Figure 1. Molecular structure and labeling scheme for **2**: Ir-C(1), 2.146 (7); Ir-C(4), 2.122 (6); Ir-C(13), 2.033 (8); Ir-C(17), 2.059 (7); C-(1)-Ir-C(4), 77.4 (3); C(1)-Ir-C(13), 174.9 (3); C(4)-Ir-C(13), 98.4 (3); C(1)-Ir-C(17), 94.0 (3); C(4)-Ir-C(17), 170.6 (3); C(13)-Ir-C(17), 90.4 (3).

Scheme I



Scheme II



(1) (a) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI: Greenwich, CT, 1987; Vol. 1. Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984.

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(5) (a) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 7578. (b) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *Organometallics* **1988**, *7*, 2060.

(6) Compound **1** is prepared by AgBF₄ abstraction of halide from Ir-(CR=CR=CR)(PPh₃)₂Cl in CH₃CN solution.

consists of one set of resonances for the hydrogens of the 2-oxacyclopentylidene ligands, indicative of either a symmetrical static structure or rapid rotation about the iridium carbene bonds on the NMR time scale. In the solid state, the 2-oxacyclopentylidene ligands in **2** are skewed such that the plane of the metallacycle bisects the plane of one carbene ring (C(13)-C(16), O(9)) at an angle of 29.4° and the second carbene ring at an angle of 31.5° (Figure 1).⁸

(7) Characterization data for **1-6** is provided as Supplementary Material.