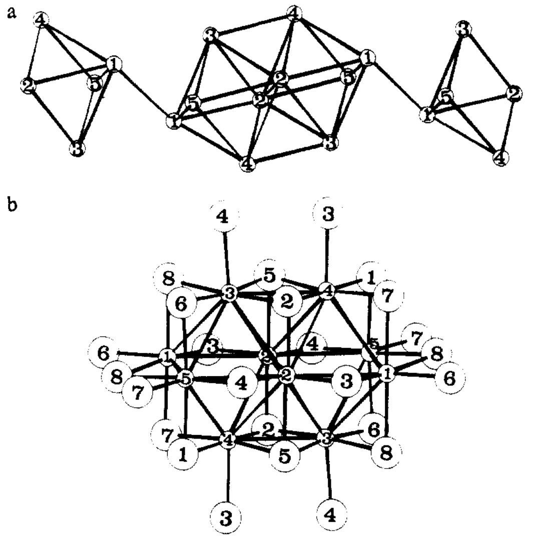

Figure 1. (a) The Mo_{10} cluster and its linkages to two identical units; (b) the $Mo_{10}O_{16}$ unit (Mo, small circles; O, large open circles).

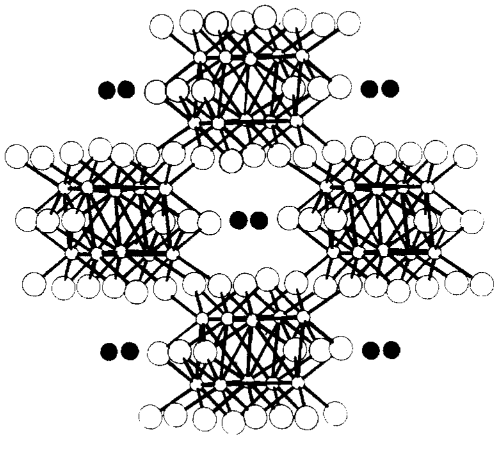

Figure 2. The $LaMo_5O_8$ structure viewed down z (La, solid circles; Mo, small circles; O, large open circles).

firmed by electron diffraction. The space group, $P2_1/a$, was determined from systematic absences in the X-ray and electron diffraction patterns. After removing impurity peaks due to molybdenum metal, the X-ray data were decomposed into 297 I_{hkl} values; the intensities of the overlapping reflections were broken up by considering electron diffraction patterns, of which 19 zones have been found. The heavy atoms were located by direct methods with negative quartets[16] and used as the starting model for Rietveld profile refinement.[17] Oxygen atoms were found from subsequent difference Fourier calculations, giving the composition $LaMo_5O_8$. Final details and atomic coordinates are given in Table I, which also contains the results of a Rietveld analysis of the neutron data (1237 reflections); the latter forms the basis of the discussion below. The La:Mo ratio of $LaMo_5O_8$ is slightly different from that used in the preparation (2:9), and a careful microanalytical examination of the sample has revealed a second new phase of approximate composition $La_5Mo_7O_{18}$. The presence of this minor impurity is presumably responsible for the rather high R-factors.

$LaMo_5O_8$ contains the first example of Mo_{10} clusters, consisting of two edge-shared octahedra, linked by two additional Mo–Mo bonds to form infinite chains (Figure 1). The chains are connected by bridging oxygens to define tunnels which contain lanthanum ions with 11-coordination (Figure 2). With the exception of Mo(2), which is shared by both octahedra, the molybdenum atoms are bonded to five oxygens in approximately square-pyramidal coordination. Mo–Mo distances within the cluster range from 2.676 to 2.836 Å. The shortest intercluster metal-metal bond is Mo(1)–Mo(1), 2.733 Å, but Mo(1) also forms weaker intercluster bonds to Mo(5), 2.921 Å, and Mo(3), 3.065 Å. Molybdenum–oxygen bonds fall in the range 1.984–2.163 Å. Calculation of Mo–O bond strengths[18] confirms Mo(2) as the Mo atom of lowest valency: 2.446. The valencies of the other Mo atoms are calculated as the following: Mo(1), 2.720; (Mo(3), 2.785; Mo(4), 2.895; and Mo(5), 3.087. The relative values for waist (shared edge) and apex molybdenums are comparable to those found for infinite edge-shared Mo_6 clusters found in $NaMo_4O_6$ and related compounds.

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Palladium-Catalyzed Arylation of Siloxycyclopropanes with Aryl Triflates. Carbon Chain Elongation via Catalytic Carbon–Carbon Bond Cleavage

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Activation of a carbon–carbon bond by homogeneous transition-metal complexes has been a challenge for chemists.[1] Although the preparation of stable complexes[2] and the rearrangement of highly strained molecules initiated by C–C bond cleavage have been extensively studied,[3] little is known about the utility of C–C bond activation for carbon chain elongation, not to mention its catalytic use.[4,5] The purpose of this communication is to disclose the first example of a *catalytic reaction of general synthetic utility*, in which a C–C bond is cleaved by an organopalladium complex to create a new C–C bond. Namely, the present reaction demonstrates the general synthetic utility of homoenolate[6] A as the inverse-polarity synthon[7] of a Michael acceptor B (see below),

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(1) Cf. Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.
(2) (a) Tipper, C. F. H. *J. Chem. Soc.* **1955**, 2043. (b) Kang, J. W.; Moseley, R.; Maitlis, D. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970. (c) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324. (d) DePuy, C. H.; McGirk, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 1121. DePuy, C. H. *Top. Curr. Chem.* **1973**, *70*, 73. (e) Eilbracht, P. *Chem. Ber.* **1976**, *109*, 1429. (f) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 1300. (f) Hoberg, H.; Herrea, A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 877. (g) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6470. (h) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1984**, *106*, 3054. (i) Donaldson, W. A.; Hughes, R. P. *J. Am. Chem. Soc.* **1982**, *104*, 4846. (j) Crabtree, R. H.; Dion, R. P. *J. Chem. Soc., Chem. Commun.* **1984**, 1260. (k) Flood, T. C.; Statler, J. A. *Organometallics*, **1984**, *3*, 1795.
(3) Bishop, K. C., III. *Chem. Rev.* **1976**, *76*, 461.
(4) Insersion of carbon monoxide to a strained C–C bond: Cf. (a) Casser, L.; Halpern, J. *J. Chem. Soc. D* **1971**, 1082. (b) Moriarty, R. M.; Chen, K.-N.; Curchill, M. R.; Chang, S. W.-R. *J. Am. Chem. Soc.* **1974**, *96*, 3661.
(5) Insersion of ethylene derivatives: Cf. Noyori, R.; Kumagai, Y.; Takaya, H. *J. Am. Chem. Soc.* **1970**, *96*, 634. Noyori, R. Odagi, T.; Takaya, H. *J. Am. Chem. Soc.* **1970**, *92*, 5780.
(6) Review: Werstiuk, N. H. *Tetrahedron* **1983**, *39*, 205. Ryu, I.; Sonoda, N. *J. Synth. Org. Chem., Jpn.* **1985**, *43*, 112. Hoppe, D. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 932. Stowell, J. C. *Chem. Rev.* **1984**, *84*, 409.
(7) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239. Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147. Groebel, B. T.; Seebach, D. *Synthesis* **1977**, 357.

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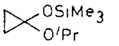
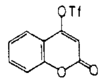
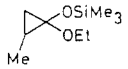
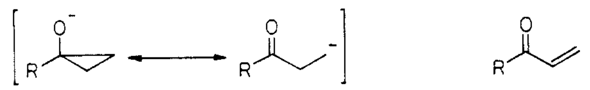
Table I. Arylation of Ester Homoenolate[a]

entry	siloxy-cyclopropane	ArOTf	3-aryl-propionate
1		C_6H_5OTf	50
2		o-FC_6H_4OTf	71
3		p-$CH_3C(O)C_6H_4OTf$	59
4		o-$CH_3C(O)OC_6H_4OTf$	49
5		m-$CH_3OC_6H_4OTf$	50
6		p-$CH_3OC_6H_4OTf$	0
7		1-$C_{10}H_7OTf$[b]	89
8			90[c]
9		1-$C_{10}H_7OTf$	87[d]

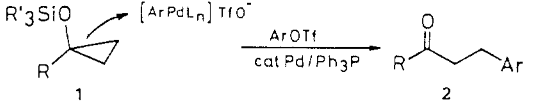
[a] Performed with a 1:1–1.1 ratio of the reactants in benzene at 90–100 °C as described in footnote 11. [b] Slight excess (1.1 equiv) of the triflate was used. [c] Excess (1.5 equiv) cyclopropane was used. [d] The product was methyl 2-methyl-3-(1-naphthyl)propionate.

which can generate ketone and aldehyde homoenolates as well as an ester homoenolate.[8,9]



(A) (B)

Donation of electrons from a C–C bond to the vacant orbital of a metal complex is the dominant contributor in the organometallic bonding to C–C σ bonds.[2,3] Consequently, a C–C bond with maximum electron-releasing capability should have the best opportunity for metal/C–C bond interaction. Siloxycyclopropanes **1** ideally meet this criteria of the donor molecule, since their HOMO energy is not only higher than that of cyclopropane but even slightly higher than that of ethylene.[10] We have found that they strongly interact with a cationic arylpalladium complex catalytically generated from the aryl trifluoromethanesulfonate (triflate). The net result shown in eq 1 represents a novel synthetic procedure for direct arylation of siloxycyclopropanes by the aryl triflate.

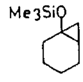
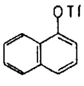
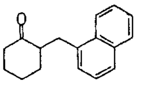
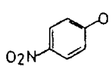
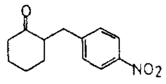
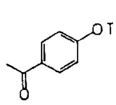
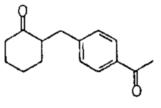
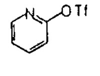
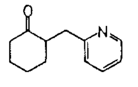
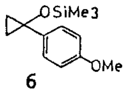
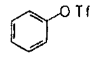
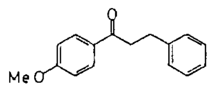
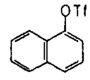
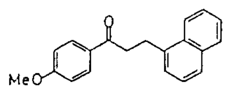
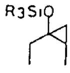
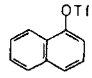
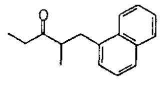
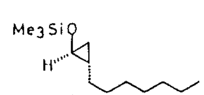
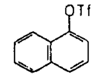
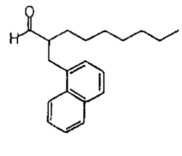
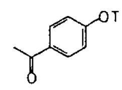
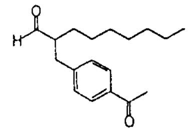


(1)

1 2

$R'_3Si = Me_3Si$, t-$BuMe_2Si$
a; R = alkoxy, **b**; R = alkyl, **c**; R = hydrogen

Table II. Arylation of Ketone and Aldehyde Homoenolates[a]

siloxycyclopropane	ArOTf	product	yield (%)
 5			68, 84[b]
			68[b]
			70[b]
			50[b]
 6			65[b]
			69
 7 R3 = Me3 8 R3 = ^tBuMe2			46 56
 9			58[b]
			65[b]

[a] Carried out as described in footnote 11 except that the reaction was performed for ca. 12 h in HMPA, and $[PdCl(C_3H_5)]_2$ (5 mol%) and Ph_3P (20 mol%) were used as a catalyst. [b] Excess siloxycyclopropane (1.5 equiv) was used.

The reaction can be illustrated by the formation of isopropyl 3-phenylpropionate (**2a**, R = i-PrO, 50%) in the reaction of 1-isopropoxy-1-trimethylsiloxycyclopropane (**1a**)[8] with phenyl triflate (1 equiv, 100 °C, benzene or butyronitrile) in the presence of 5–10 mol % of a palladium catalyst.[11a] Interestingly, palladium-catalyzed arylation of **1a** with PhN_2BF_4, which is known to generate in situ a cationic arylpalladium species upon reaction with a palladium catalyst,[12] takes place even *at room temperature*

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(8) (a) Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1977**, *99*, 7360. (b) Nakamura, E.; Oshino, H.; Kuwajima, I. *J. Am. Chem. Soc.* **1986**, *108*, 3745. (c) Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1984**, *106*, 3368. (d) Oshino, H.; Nakamura, E.; Kuwajima, I. *J. Org. Chem.* **1985**, *50*, 2802. (e) Nakamura, E.; Kuwajima, I. *Tetrahedron Lett.* **1986**, *27*, 83. (f) Nakamura, E.; Shimada, J.; Kuwajima, I. *Organometallics* **1985**, *4*, 641.

(9) For contribution by other groups, after our report on the first example of the synthetic use of ester homoenolate (ref 8a), see: (a) Ryu, I.; Matsumoto, K.; Ando, M.; Murai, S.; Sonoda, N. *Synth. Commun.* **1984**, *14*, 1175. Ryu, I.; Ando, M.; Ogawa, A.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1983**, *105*, 7192. Murai, S.; Ryu, I.; Sonoda, N. *J. Organomet. Chem.* **1983**, *250*, 121. (b) Caine, D.; Frobese, A. S. *Tetrahedron Lett.* **1978**, 883. (c) Goswami, R.; Corcorn, D. E. *Tetrahedron Lett.* **1982**, *23*, 1463. Goswami, R. *J. Am. Chem. Soc.* **1980**, *102*, 5973. (d) Giese, B.; Horler, H.; Zwick, W. *Tetrahedron Lett.* **1982**, *23*, 931. (e) Tamaru, Y.; Ochiai, H.; Nakamura, T.; Tsubaki, K.; Yoshida, Z. *Tetrahedron Lett.* **1985**, *26*, 5559. (f) Tamaru, Y.; Ochiai, H.; Nakamura, T.; Yoshida, Z. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1157.

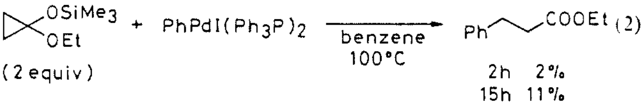
(10) (a) The HOMO of 1,1-dihydroxycyclopropane (C_{2v} symmetry) is 1.6 eV higher than that of cyclopropane itself and 0.4 eV higher than that of ethylene, and the orbital of the C–C σ bond dominantly contributes to the HOMO (by MNDO: Dewer, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. Provision of the program from Professor E. Osawa is deeply acknowledged.). (b) In the stoichiometric reaction of **1a** with metal halides, we have obtained solid evidence for the direct C–C bond cleavage by the metal halides.

(11) (a) Typically a 1:4 molar mixture of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and PPh_3 was used as a catalyst. In the reactions of ketone and aldehyde homoenolates that were performed in HMPA, $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$ has also been used successfully for some runs. Although the nature of the reactive species presently remains speculative, a tetracoordinated aryl palladium(II) complex (shown in eq 1) similar to the platinum complex recently reported (ref 14) is most probable. (b) Typical experimental procedure: A solution of the cyclopropane **3** (0.315 mL, 1.5 mmol), 1-naphthyl triflate (0.290 mL, 1.5 mmol), $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (1.83 mg, 0.05 mmol), and PPh_3 (52.4 mg, 0.20 mmol) in 5.0 mL of benzene was degassed, sealed in vacuo, and heated at 100 °C for 6 h to give 287 mg (79%) of isopropyl 3-(1-naphthyl)propionate (5% ethyl acetate in hexane, R_f = 0.15). Use of 10% excess of the triflate improved the yield to 89%. Procedure for ketone and aldehyde homoenolates is described in the supplementary Material. (c) The reaction of vinyl triflates thus far becomes complex partly due to isomerization of the initial product.

(12) Ikenaga et al. suggested the formation of a cationic aryl palladium complex, $ArPd^+BF_4^-$, in the reaction of $ArN_2^+BF_4^-$ and Pd(dibenzylideneacetone)$_2$. Ikenaga, K.; Kikukawa, K.; Matsuda, T. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1959.

(25% in THF, 37% in PhCl at 50 °C), indicating that the cleavage of the C–C bond by an electron-demanding cationic complex is a remarkably facile process.

Halobenzenes (PhX) failed to react with **1a**, due to the inability of the $PhPdXL_n$ complex generated in situ to activate the C–C bond. In fact, **1a** was phenylated in very poor yield even by a stoichiometric amount of $PhPdI(Ph_3P)$[13] (eq 2). In addition, the presence of either LiCl (3 equiv) or Bu_4NBr (1 equiv), which converts a tetracoordinated platinum triflate complex to the halide complex,[14] almost completely inhibited the reaction of **1a** with the aryl triflate. These observations indicate that the high electron-demanding nature of the intermediary arylpalladium complex[11] (cf. eq 1) is essential for the desired C–C bond cleavage.



(2)

In addition to the siloxycyclopropanes **3** and **4** that generate ester homoenolates, the siloxycyclopropanes **5**–**9** that produce ketone and aldehyde homoenolates also cleanly reacted with various aryl triflates.[15] Tables I and II show the examples, which demonstrate the utility of the reaction for the functionalization of various aromatic nuclei including coumarin and pyridine. The high functional group selectivity (e.g., aldehyde, ketone, ester, and nitro groups remaining intact) of this reaction stands in contrast to the limited selectivity of the standard, classical Umpolung-counterpart[7] such as the conjugate addition of aryl cuprates to unsaturated carbonyl compounds.[16] Substituted siloxycyclopropanes **4**, **5**, **7**, **8**, and **9** underwent exclusive cleavage of the less substituted C–C bond connected to the siloxy group. *tert*-Butyldimethylsiloxycyclopropane **8** also gave the arylation product in good yield.

It should be noted that *p*-methoxyphenyl triflate (Table I, entry 6) fails to arylate the cyclopropane **3**, which makes sharp contrast to the result with the *m*-methoxy derivative (entry 5). The deactivating effect of the *p*-methoxy group gives strong supporting evidence for the presumed importance of the electron-demanding nature of the metal in this reaction (vide supra).[17]

In summary, it is demonstrated that *the combination of an electron-rich C–C bond and an electron-demanding metal complex provides a viable protocol for catalytic C–C bond cleavage for organic synthesis.* In addition, the successful use of the highly labile, nucleophilic homoenolates of ketone and aldehyde provides a significant addition to the repertory of homoenolate chemistry.[18]

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Registry No. **2** (R = O-*i*-Pr; Ar = C_6H_5), 22767-95-9; **2** (R = O-*i*-Pr; Ar = *o*-FC_6H_4), 113777-12-1; **2** (R = O-*i*-Pr; Ar = *p*-$CH_3C({=}O)C_6H_4$), 113777-13-2; **2** (R = O-*i*-Pr; Ar = *o*-$CH_3C({=}O)OC_6H_4$), 113777-14-3; **2** (R = O-*i*-Pr; Ar = *m*-$CH_3OC_6H_4$), 113777-15-4; **2** (R = O-*i*-Pr; Ar = 1-$C_{10}H_7$), 113777-16-5; **2** (R = O-*i*-Pr; Ar = 4-coumarinyl), 113777-17-6; **3**, 84098-44-2; **4**, 113777-08-5; **5**, 38858-74-1; **6**, 60068-19-1; **7**, 113777-09-6; **8**, 113777-10-9; **9**, 113777-11-0; $[PdCl(\eta^3\text{-}C_3H_5)]_2$, 12012-95-2; PPh_3, 603-35-0; C_6H_5OTf, 17763-67-6; *o*-FC_6H_4OTf, 113777-27-8; *p*-$CH_3C({=}O)C_6H_4OTf$, 109613-00-5; *o*-$CH_3C({=}O)OC_6H_4OTf$, 113777-28-9; *m*-$CH_3OC_6H_4OTf$, 66107-33-3; *p*-$CH_3OC_6H_4OTf$, 66107-29-7; 1-$C_{10}H_7OTf$, 99747-74-7; ethyl 2-methyl-3-(1-naphthyl)propionate, 113777-18-7; 2-(1-naphthylmethyl)cyclohexanone, 113777-19-8; 2-(4-nitrophenylmethyl)cyclohexanone, 113777-20-1; 2-(4-acetylphenylmethyl)cyclohexanone, 113777-21-2; 2-(2-pyridylmethyl)cyclohexanone, 113777-22-3; 1-(4-methoxyphenyl)-3-phenyl-1-propanone, 5739-38-8; 1-(4-methoxyphenyl)-3-(1-naphthyl)-1-propanone, 113777-23-4; 2-(1-naphthylmethyl)-3-pentanone, 113777-24-5; 2-(1-naphthylmethyl)nonanone, 113777-25-6; 2-(4-acetylphenylmethyl)nonanal, 113777-26-7; 4-coumarinyl triflate, 113777-29-0; 4-nitrophenyl triflate, 17763-80-3; 4-acetylphenyl triflate, 109613-00-5; 2-pyridyl triflate, 65007-00-3.

Supplementary Material Available: A typical procedure of arylation of ketone and aldehyde homoenolates and physical properties of new compounds (5 pages). Ordering information is given on any current masthead page.

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A Solution to the *in,out*-Bicyclo[4.4.1]undecan-7-one Problem Inherent in Ingenane Total Synthesis

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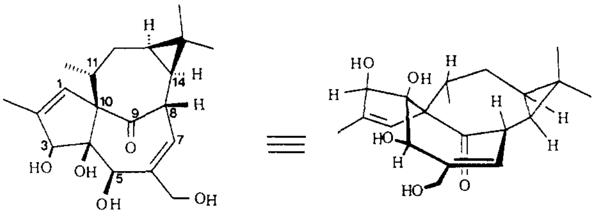
In 1968 Hecker reported the isolation and chemical characterization of a new irritant and cocarcinogenic substance, ingenol 3-hexadecanoate, from the latex of *Euphorbia ingens* and from the seed oil of *Euphorbia lathyris*.[2] It is now known that ingenol 3-hexadecanoate is one member of a structurally diverse group of compounds which are believed to promote tumor formation by activating protein kinase C.[3] Moreover, this natural product embodies a rare example of in,out-bridged bicyclic topological isomerism.[4] In most of the previously reported routes to ingenol, including one of our own, a solution to the in,out-stereochemical



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