tionation of **1c**. This resembles the disproportionation of an SO_2 adduct of $Cp^*{}_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ to give an SO_3 adduct and S_8, the latter via SO.[7h] Such reactions are a feature of organic thiosulfinate ester chemistry;[2b,13a,b] however, the conditions required for **1c** to react are much more extreme than those required for organic systems. The initiating step in the complex decomposition process of the latter[2b,13b,20] is loss of a proton from the alkyl group attached to the sulfenyl sulfur (i.e., β-elimination[2b]). In **1a–c** this position is occupied by the ruthenium atom. Organic thiosulfinate esters are also readily deoxygenated by triphenylphosphine,[17b] but **1** did not react. Oxygen transfer has been postulated[21] to explain the apparent difficulty in stopping the oxidation of thiolato complexes at the sulfoxide stage (MS(O)R), sulfones ($MS(O)_2R$) being invariably obtained.[21-23]

The catenated polysulfur oxide ligands of **1a–c** and **2** juxtapose reduced and oxidized sulfur atoms and thus are of interest with respect to the Claus reaction, wherein H_2S and SO_2 combine to give sulfur and water, the mechanism of which is poorly understood.[24]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the Quebec Department of Education for financial support and for scholarships to P.-Y.P. Stephen von Loggerenberg of PGM Chemicals Ltd. is thanked for a generous gift of $RuCl_3 \cdot xH_2O$. Dr. Jim Britten is acknowledged for the crystal structure determinations.

Supplementary Material Available: Experimental procedures for the preparation of **1a–c** and **2**, tables of NMR data for **1a–c** and **2** and crystal data, atomic coordinates, thermal parameters, and bond lengths for angles for **1b** and **2** (25 pages); tables of final observed and calculated structure factors for **1b** and **2** (42 pages). Ordering information is given on any current masthead page.

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(20) Block, E.; Aslam, M. *Tetrahedron Lett.* **1985**, *26*, 2259.

(21) Weinmann, O. J.; Abrahamson, H. B. *Inorg. Chem.* **1987**, *26*, 3034.

(22) (a) Schrauzer, G. N.; Zhang, C.; Chadha, R. *Inorg. Chem.* **1990**, *29*, 4104. (b) Nicholson, T.; Zubieta, J.; *Inorg. Chem.* **1987**, *26*, 2094. (c) Lundeen, M.; Firor, R. L.; Seff, K. *Inorg. Chem.* **1978**, *17*, 701 and references therein.

(23) However, see: Sloan, C. P.; Krueger, J. H. *Inorg. Chem.* **1975**, *14*, 1481.

(24) (a) Datta, A.; Cavell, R. G. *J. Phys. Chem.* **1985**, *89*, 454. (b) Karge, H. G.; Lana, I. G. D. *J. Phys. Chem.* **1984**, *88*, 1538.

The First Stable Enethiolizable Thioaldehyde via a Zirconocene η^2-Thioacyl Complex

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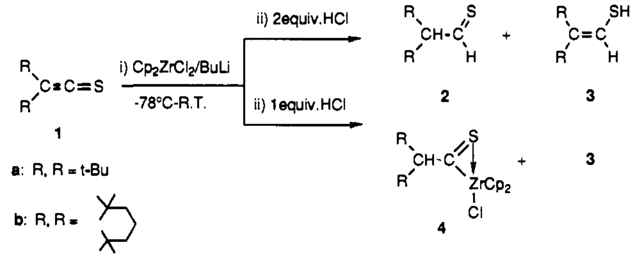
The group 4 metallocenes, i.e., Cp_2M (M = Ti, Zr),[1a,b] and their equivalents[1c-h] are well-known to exhibit high reactivity such as carbenoid like behavior and to add to a variety of unsaturated compounds to give Cp_2M complexes.[2,3] The high degree of π-back-bonding from the metal to the organic fragment makes the resulting complex behave more like metallacyclopropane,[3c] metallacyclopropene,[1c,3a-c] metallaoxirane,[3e-l] and metallathiirane,[1e,3d] respectively. These unique aspects of group 4 metallocenes have their parallels in the main-group chemistry of carbene and bivalent group 14 metals, e.g., the reactivity of silylene[4a-d] and germylene[4e,f] toward ketones, thioketones, and heterocumulenes. Summarizing our initial attempts in this area, we describe that the addition reactions of zirconocene to thioketenes (**1**) followed by acidolysis offer a novel route to stable thioaldehydes (**2**)[5] and their enethiol isomers (**3**) as well as η^2-thioacyl complexes of zirconium (**4**).[6] These represent not only the first enethiolizable thioaldehyde but also the first structurally characterized thioacyl complex of an early transition metal.[6d]

Scheme I



To a tetrahydrofuran (THF) solution of a "Cp_2Zr" equivalent [$Cp_2Zr(n\text{-}Bu)_2$] (1.1 mmol) prepared from Cp_2ZrCl_2 and BuLi[1f,g] was added a solution of thioketene (**1a** or **1b**) (1.1 mmol) in THF at −78 °C. The reaction mixture changed from purple to orange

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(1) For "Cp_2M" (M = Ti, Zr) in the free state: (a) Pez, G. P.; Armor, J. N. *Adv. Organomet. Chem.* **1981**, *19*, 1–50. (b) Bercaw, J. E. In *Fundamental Research in Homogeneous Catalysis*; Tsutui, M., Ugo, R., Eds.; Plenum: New York, 1977; Vol. 1, pp 129–146. For "Cp_2M" equivalent $Cp_2Ti(CO)_2$: (c) Fachinetti, G.; Floriani, C.; Marchetti, F.; Mellini, M. *J. Chem. Soc., Dalton Trans.* **1978**, 1398–1403. (d) Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1978**, *100*, 1921–1922; *Inorg. Chem.* **1978**, *11*, 2995–3001. (e) Seitz, K.; Behrens, U. *J. Organomet. Chem.* **1985**, *288*, C47–C50. For a review of thioketene complexes, see also: Schaumann, E. *Tetrahedron* **1988**, *44*, 1827–1871. $Cp_2Zr(n\text{-}Bu)_2$: (f) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 1829–2832. (g) Negishi, E.; Swanson, D. R.; Takahashi, T. *J. Chem. Soc., Chem. Commun.* **1990**, 1254–1255. $Cp_2M(PMe_3)_2$ (M = Ti, Zr): (h) Kool, L. B.; Raush, M. D.; Alt, H. G.; Herberhold, M.; Honold, B.; Thewalt, U. *J. Organomet. Chem.* **1987**, *320*, 37–45.

(2) Several synthetic methods for preparing Cp_2M complexes (M = Ti, Zr) have been reported. Among those, direct combination of a "Cp_2M" equivalent and an unsaturated organic fragment is limited to isolation of alkene,[1c,f-h] $\eta^2(C,O)$-ketene,[1d] and thioketene complexes.[1e] Recently the concerted methane and benzene elimination of methyl and phenylalkyl-zirconocene derivatives was utilized to prepare complexes of cycloalkenes,[3c] arynes,[3a-c] and η^2-thioaldehyde.[3d] η^2-Ketone and aldehyde complexes are generally prepared by migration of metal alkyl or hydride to a *cis*-acyl ligand.[3e-i] The deprotonation of an α-proton of an acyl complex affords an efficient route to $\eta^2(C,O)$-ketene complexes.[3j-l]

(3) (a) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189–202. (b) Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3659–3660. (c) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047–1058 and references therein. (d) Buchwald, S. L.; Nielsen, R. B.; Dewan, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 1590–1591. For an η^2-thioaldehyde titanium complex, see also: Park, J. W.; Henling, L. M.; Schaefer, W. P.; Grubbs, R. H. *Organometallics* **1990**, *9*, 1650–1656. (e) Rosenfeld, F.; Erker, G. *Tetrahedron Lett.* **1980**, *21*, 1637–1640; *J. Organomet. Chem.* **1982**, *224*, 29–42. (f) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103–109 and references therein. (g) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121–127. (h) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690–1691. (i) Waymouth, R. M.; Clauser, K. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6385–6387. (j) Bristow, G. S.; Hitchcock, P. B.; Lappert, F. *J. Chem. Soc., Chem. Commun.* **1982**, 462–464. (k) Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5499–5500. (l) Moore, E. J.; Straus, D. A.; Armantrout, J.; Santasriero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068–2070.

(4) For silylene with ketones and thioketones: (a) Ando, W.; Ikeno, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **1977**, *99*, 6447–6449. (b) Ando, W.; Ikeno, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **1978**, *100*, 3613–3615. (c) Ando, W.; Hamada, Y.; Sekiguchi, A.; Ueno, K. *Tetrahedron Lett.* **1983**, *24*, 4033–4036. (d) Ando, W.; Hagiwara, K.; Sekiguchi, A. *Organometallics* **1987**, *6*, 2270–2271. For germylene with thioketones and thioketenes: (e) Tsumuraya, T.; Sato, S.; Ando, W. *Organometallics* **1989**, *8*, 161–167. (f) Ando, W.; Tsumuraya, T. *Organometallics* **1989**, *8*, 1467–1472.

(5) For stable thioaldehyde: (a) Okazaki, R.; Ishii, A.; Fukuda, N.; Oyama, H.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1982**, 1187–1188. (b) Okazaki, R.; Ishii, A.; Inamoto, N. *J. Am. Chem. Soc.* **1987**, *109*, 279–280. (c) Vedejs, E.; Perry, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 1683–1684.

(6) For η^2-acyl and related complexes: (a) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059–1079. (b) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946–1950. (c) Fachinetti, G.; Floriani, C.; Stoeckli-Evans, H. *J. Chem. Soc., Dalton Trans.* **1977**, 2297–2302. (d) Clark, G. R.; Collins, T. J.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1978**, *157*, C23–C26; **1983**, *259*, 215–232. (e) Elsner, F. H.; Woo, H.-G.; Tilley, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 313–314. For the conversion of an η^2-acyl zirconium complex to aldehyde and related compounds, see also: Schwartz, J.; Labinger, J. A. *Angwew. Chem., Int. Ed. Engl.* **1976**, *15*, 333–340. (f) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440–4451.

0002-7863/91/1513-7782$02.50/0

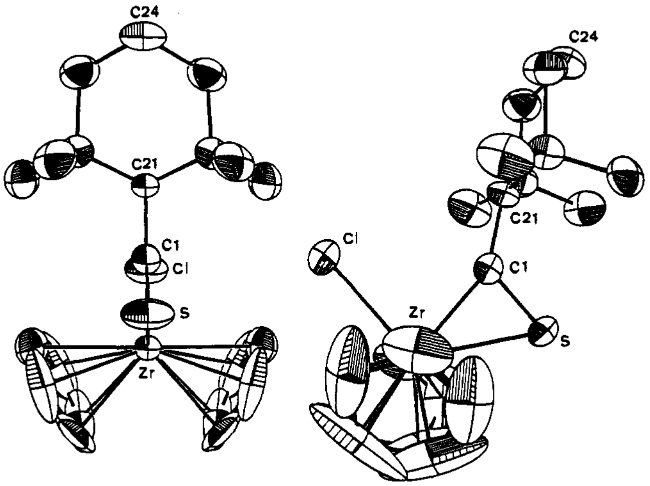
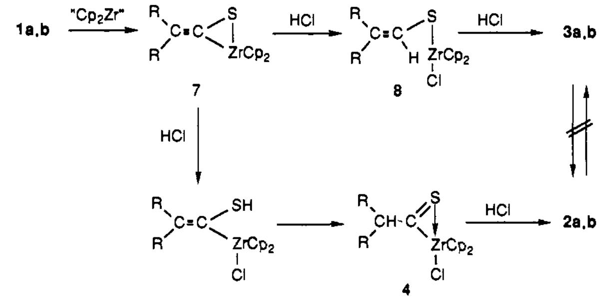


Figure 1. ORTEP drawing of **4b**. The projections perpendicular (left) and parallel (right) to a mirror plane. Selected bond lengths (Å) and angles (deg) are as follows: Zr–Cl, 2.554 (2); Zr–S, 2.615 (3); Zr–C(1), 2.298 (8); S–C(1), 1.623 (8); C(1)–C(21), 1.49 (1); Cl–Zr–C(1), 81.6 (2); S–Zr–C(1), 37.9 (2); Zr–C(1)–S, 81.7 (3); Zr–C(1)–C(21), 150.8 (6); S–C(1)–C(21), 127.6 (6).

during 2 h of stirring (−78 °C to room temperature) and was subjected to acidolysis with a varying HCl/**1** molar ratio. Typically the use of 2 equiv of HCl in acidolysis, after silica gel chromatography, gave rise to compound **2** (**2a**, 25% yield; **2b**, 10% yield) and compound **3** (**3a**, 37% yield; **3b**, 5% yield) as pink and colorless oils, respectively (Scheme I). The same molecular formulas of **2** and **3** require that the structures of these compounds are isomeric with each other. Analysis by ^{1}H and ^{13}C NMR and IR spectroscopy unequivocally confirmed the structures of **2** and **3** as ethanethials and ethenethiols (Scheme I).[7] Most characteristic in the ^{1}H NMR spectrum are the pairs of mutually coupled doublets for thioaldehyde and methine protons in **2** (**2a**, δ 11.58, 2.54, J = 10.5 Hz; **2b**, δ 11.65, 2.48, J = 10.4 Hz) and for vinylic and thiol protons in **3** (**3a**, δ 6.12, 2.85, J = 9.8 Hz; **3b**, δ 6.08, 2.76, J = 9.4 Hz). The low fields of ^{13}C NMR resonances (**2a**, δ 253.84; **2b**, δ 255.32) and IR and UV absorptions (**2a**, ν 1110 cm^{-1}, 536 nm; **2b** ν 1135 cm^{-1}, 529 nm) also indicate the presence of a thiocarbonyl group in **2a,b**, while IR absorptions at 2500 and 2248 cm^{-1} for **3a** and **3b** are assigned to S–H groups. Chemical evidence for ethanethials **2** is provided by treatment of **2a** with *m*-chloroperbenzoic acid, resulting in (*E*)- and (*Z*)-ethanethial *S*-oxides **5a-E** and **5a-Z** in 37% and 19% yields,[7] which are compatible with the published data of (*E*)- and (*Z*)-propanethial *S*-oxides.[8] Additional chemical proof for ethanethiol **3** is also afforded by LiAlH$_4$ reduction of **1a** to provide **3a** and subsequent oxidation with I$_2$ giving divinyl disulfide **6a**.[7] In recent years, remarkable progress has been made in the synthesis of stable thioaldehydes by means of sterically bulky groups.[5a,b] However, simple thioaldehydes bearing enethiolizable α-protons have not yet been reported, owing to the pronounced tendency of thiocarbonyl compounds to exist as the ethenethiol tautomer.[9] Therefore it is noteworthy that there is no tautomeric interconversion between **2a,b** and **3a,b** under our experimental conditions.[9]

Scheme II



In contrast to the above results, decreasing the amounts of HCl to 1 equiv led, after preparative HPLC, to the formation of zirconocene complexes **4** (**4a**, 26% yield; **4b**, 15% yield) as moisture-sensitive blue crystals along with **3** (**3a**, 14% yield; **3b**, 30% yield). The ^{13}C NMR spectrum[7] of **4a** exhibits an extremely low field single resonance at δ 379.33, diagnostic for the η^2-bonding of the thioacyl group.[6a] Instead, in **4b**, two resonances for thiocarbonyl carbons are observed at δ 369.91 and 380.75, which could be attributed to the existence of two isomers in solution, i.e., S-outside and S-inside conformers.[6a,f,10] Finally, an X-ray crystallographic study of **4b** confirmed the nature of the η^2-bonding picture of the thioacyl group (Figure 1).[11] The molecule lies in a crystallographic mirror plane, with Zr, S, C(1), C(21), and C(24) atoms in this plane. The mirror relates the two Cp rings and two halves of the cyclohexane ring. The marked deviation from the sp^2 bond angles around C(1), as well as the Zr–S bond distance, showed the thioacyl unit to be η^2-CS-bonded to zirconium in the S-outside configuration.[6a–d] The thioacyl group acts, in this case, as a bidentate three-electron donor.

With the structures of the products having been established, the most reasonable reaction pathways are shown in Scheme II: η^2(*C,S*)-thioketene complex **7** and metallathioenolate **8** as possible intermediates. Since the controlled acidification of **4a,b** furnished Cp$_2$ZrCl$_2$ and ethanethials **2a,b** in high yields, **4a,b** accounts for intermediates in the formation of **2a,b**. A similar route has been applied recently to synthesize the elusive formylsilane.[6e] Meanwhile, η^2(*C,S*)-thioketene complexes **7** are closely similar to the isoleptic titanium complex, which, however, was obtained from the "Cp$_2$Ti" precursor [Cp$_2$Ti(CO)$_2$] and thioketene **1b**.[1e] The oxygen-analogous pathway to η^2(*C,S*)-thioketene complex **7** giving thioacyl complex **4a,b** and/or metallathioenolate **8** under protic conditions finds precedents in the reactions of η^2(*C,O*)-titanium[1d,3k] and η^2(C,O)-vanadium ketene complexes.[12]

Thus, a zirconocene-mediated synthesis appears to be the only viable route for **2a,b**, and the η^2(*C,S*)-thioketene complex as an intermediate might exhibit enhanced reactivity arising from a metallathiirane character.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 03233101) and

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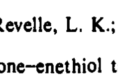
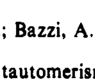
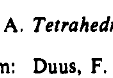
(7) Physical properties of all new compounds and their derivatives (**5a-E/Z** and **6a**) are provided in the supplementary material.



5a-E



5a-Z

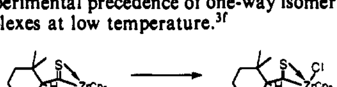


6a

(8) Block, E.; Revelle, L. K.; Bazzi, A. A. *Tetrahedron Lett.* **1980**, *21*, 1277–1280.

(9) For thioketone–enethiol tautomerism: Duus, F. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, D., Eds.; Pergamon: New York, 1977; Vol. 3, pp 373–487. In **3a**, the presence of 1 M HCl or Cp$_2$ZrCl$_2$ did not make **3a** isomerize to **2a**, while heating of **3a** in *o*-dichlorobenzene above 150 °C produced a trace amount of **2a** detected by ^{1}H NMR.

(10) In contrast to the equilibrium mixture of **4b** S-outside and **4b** S-inside, there has been experimental precedence of one-way isomerization for η^2-acyl zirconocene complexes at low temperature.[3f]



4b S-outside **4b** S-inside

(11) Crystal data for **4b**: C$_{21}$H$_{29}$ClSZr, M = 440.20, orthorhombic with a = 13.781 (5) Å, b = 7.839 (2) Å, c = 9.310 (3) Å, V = 1005.7 Å^3, space group $Pmn2_1$, Z = 2, μ(Mo Kα) = 7.7 cm^{-1}, ρ_{calcd} = 1.45 g/cm^3. The 1772 independent reflections [$2\theta \leq 50°$; $|F_o^2| > 3\sigma|F_o^2|$] were measured on an Enraf-Nonius CAD4 diffractometer using Mo Kα irradiation and ω-2θ scan. The structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically to R = 0.039 and R_w = 0.048.

(12) For the reactivity of η^2(*C,O*)-ketene complexes: (a) Bruno, J. W.; Fermin, M. C.; Halfon, S. E.; Schulte, G. K. *J. Am. Chem. Soc.* **1989**, *111*, 8738–8740. (b) Halfon, S. E.; Fermin, M. C.; Bruno, J. W. *J. Am. Chem. Soc.* **1989**, *111*, 5490–5491. (c) Galante, J. M.; Bruno, J. W.; Hatzin, P. N. *Organometallics* **1988**, *7*, 1066–1073. (d) Gambarotta, S.; Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 1173–1178. Also see ref 1d.

general scientific research from the Ministry of Education, Science and Culture, Japan.

Supplementary Material Available: Detailed information on the physical properties of all new compounds and X-ray crystal analysis of **4b** (15 pages); listing of observed and calculated structure factors for **4b** (5 pages). Ordering information is given on any current masthead page.

Free-Radical Cyclizations Promoted by Allylic *O*-Stannyl Ketyls: The Intramolecular Coupling of the β-Carbons of Activated Alkenes

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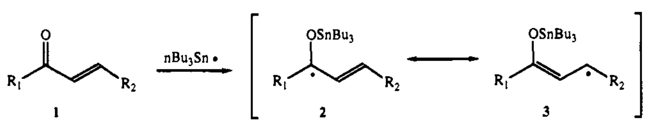
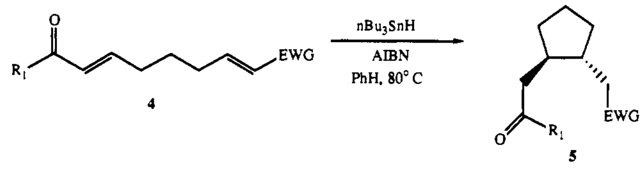
Received June 6, 1991

Free-radical-cyclization reactions have gained distinction in total synthesis and in new synthetic methodology and have been the focus of many recent important studies.[1] Much of this chemistry utilizes well-established precursors to carbon-centered radicals, such as halides, alkenes, alkynes, selenides, and sulfides, which are usually tethered to a suitable free-radical acceptor to produce cyclic derivatives when treated with tributyltin hydride. An α,β-unsaturated ketone or aldehyde is not generally considered to be a good precursor to a carbon-centered radical in these cyclizations; however, an allylic *O*-stannyl ketyl moiety[2,3] should be produced by the reaction of the enone functional group with a trialkyltin radical.[3] The *O*-stannyl ketyl radical would be resonance stabilized by the adjacent olefin moiety, which would provide interesting synthetic avenues to explore. It is also noteworthy that the stannyl enolate produced in this reaction can provide yet a second type of reactivity with these intermediates. If one can isolate the radical character from the nucleophilic character of the allylic *O*-stannyl ketyl by sequential reactions, an untapped reservoir of one- and two-electron reactions should result. This is important because the sequencing of one- and two-electron reactions is rapidly emerging as an important synthetic tool.[4] These observations are in direct contrast to how an α,β-unsaturated ketone is normally viewed in free-radical and nucleophilic reactions, where it often functions as an electron acceptor in 1,4-addition reactions at the β-carbon of the olefin with many one- and two-electron donors. Although the *O*-stannyl ketyl resonance contributors **2** and **3**, shown in Scheme I, should provide useful manifolds of concurrent two-electron reactions and one-electron cyclizations, they have not been used in this capacity prior to the studies outlined herein.

Scheme I



Scheme II[a]



[a] EWG = $COCH_3$, CN, CO_2CH_3.

Scheme III

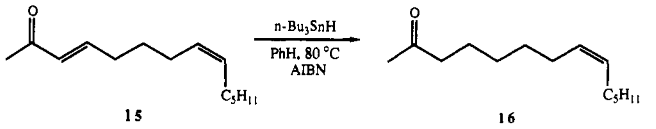
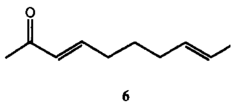
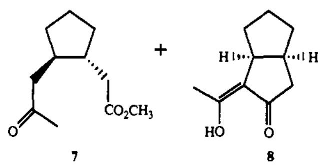
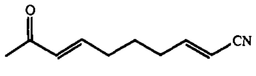
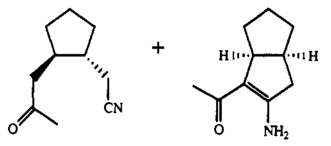
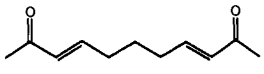
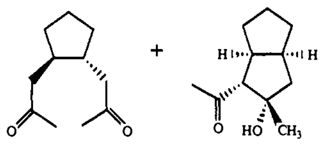


Table I. Cyclizations at the β-Carbons of Activated Alkenes

Starting Diene[a]	Products[b]
 6	 7 + 8 2.1 : 1 85%
 9	 10 + 11 3.0 : 1 94%
 12	 13 + 14 3.5 : 1 93%

[a] Starting dienes were prepared by standard methods.[10] [b] A general procedure is shown in footnote 11.

We now report in preliminary results that free-radical cyclizations with unsaturated ketone precursors, shown in Scheme II, afford substituted cyclopentane rings and bicyclo[3.3.0] ring systems. To our knowledge, the method outlined herein is a new *reagent-based* approach to the β-coupling[5] and cyclization of two activated alkenes and it compliments the only other currently available technique, electrochemical hydrodimerization.[6] The studies also show that a bifurcation in the reactivity pathways of the radical and anion of the *O*-stannyl ketyl can be achieved and these intermediates can be induced to react independently in the same molecule, providing examples of sequential one- and two-

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(5) There are only a few examples of a sodium-promoted *inter*molecular coupling of the β-carbons of activated alkenes. Most cases involve enones blocked on both ends (usually with *tert*-butyl groups): (a) Bowers, K. W.; Giese, R. W.; Grimshaw, J.; House, H. O.; Kolodny, N. H.; Kronberger, K.; Roe, D. K. *J. Am. Chem. Soc.* **1970**, *92*, 2783. (b) House, H. O.; Giese, R. W.; Kronberger, K.; Kaplan, J. P.; Simeone, J. F. *J. Am. Chem. Soc.* **1970**, *92*, 2800.

(6) For two excellent recent reviews on (non-reagent-based) electrochemical methods of β-coupling of activated olefins, see: (a) Fry, A. J. *Synthetic Organic Electrochemistry*; J. Wiley & Sons: New York, 1989; Chapter 7. (b) Little, R. D.; Baizer, M. M. In *The Chemistry of Enones*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 14.

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