The variety of oxidizing agents that participate in reaction 2 indicates that the removal of two electrons from the bridging carbene complex 1 is all that is required for its conversion to the terminal carbene complex 2. The only other reported conversion of a bridging to a terminal carbene was communicated very recently;[12f] it involves the shift of the bridging carbene ligand in $Cp_2Mo_2(CO)_4(CR_2)$ upon reaction with R_2CN_2 ($R = p\text{-}MeC_6H_4$) to a terminal position in the product $Cp(CO)_3MoMo(CR_2)(N_2CR_2)Cp$. The type of bridging to terminal carbene conversion represented by the oxidation in eq 2 may be of more general applicability to a variety of bridging carbene complexes. Oxidation of other complexes with bridging carbenes containing heteroatoms (O, N, S, etc.) capable of stabilizing terminal carbene ligands are likely to yield isolable terminal carbene compounds as observed in reaction 2. On the other hand, oxidation of $\mu\text{-}CH_2$ and $\mu\text{-}CR_2$ complexes according to eq 2 would generate unstable terminal carbenes which would be converted rapidly to other products such as olefins, as in the decomposition of $Cp(CO)_2Fe{=}CH_2^+$.[17] In this way, oxidation may activate bridging carbenes to new types of reactivity.

Registry No. 1, 83043-22-5; 2, 69532-10-1; $\{CpFe(CO)(NCMe)[C(SMe)_2]\}PF_6$, 77781-29-4; $PPN[Co(CO)_4]$, 53433-12-8; $\{CpFe(CO)_2[C(SMe)_2]\}PF_6$, 69532-11-2; $ICo(CO)_2(PPh_3)_2$, 14767-53-4; Fe, 7439-89-6; Co, 7440-48-4.

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(17) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* 1977, *99*, 6099–6101.

Regiochemistry of Cycloaddition of (Trimethylenemethane)palladium Intermediates to Muconic Esters

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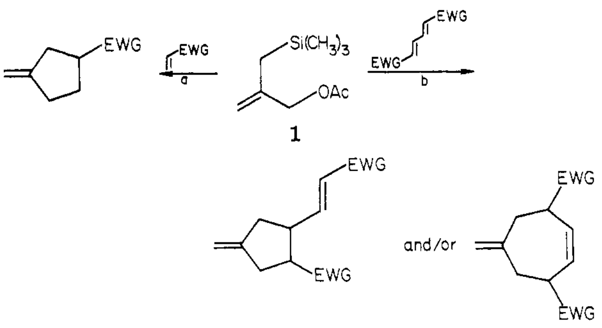
Summary: The palladium-catalyzed additions of 2-((trimethylsilyl)methyl)allyl acetate to muconic esters produces five- and seven-membered rings, whereas the phenyl-substituted derivative produces only five-membered-ring products.

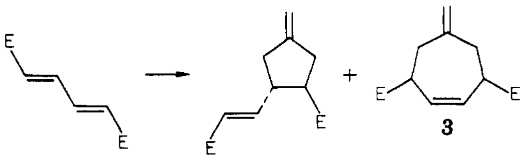
The palladium-catalyzed reaction of 2-((trimethylsilyl)methyl)allyl acetate (1) with electron-deficient olefins provides an exciting approach to methylenecyclopentanes (path a, eq 1).[1,2] Its utility ultimately depends upon its generality. A particularly intriguing problem derives from the use of a diene as an acceptor in which the competition between a seven- and a five-membered ring lurks (path b, eq 1). Exploration of this phenomenon within the context of muconic esters derives from the symmetry of the system and the utility of the resultant methylenecyclopentane for a synthesis of brefeldin A, an antitumor cyclopentanoid macrolide.[3]



(1)

EWG = electron-withdrawing group

Treatment of dimethyl (*E*,*E*)-muconate with 1 in the presence of Pd(0) catalysts leads to two products. Spectral analysis clearly assigns the structure of the major product as the methylenecyclopentane 2[4] and the minor product as the methylenecycloheptene 3.[4] The infrared spectrum of 2 showed conjugated and unconjugated ester carbonyl groups at 1735 and 1720 cm^{-1}; the NMR spectrum showed the conjugated double bond [^1H NMR δ 6.90 (dd, J = 15.8, 8.1 Hz) and 5.88 (dd, J = 15.8, 1.1 Hz) and ^{13}C NMR at δ 149.3 and 121.3] in addition to the exocyclic methylene group at δ 4.92. On the other hand, 3 only shows an unconjugated ester carbonyl group at 1748 cm^{-1} and an isolated symmetrical vicinal disubstituted double bond [^1H NMR δ 6.10 (d, J = 2.4 Hz); ^{13}C NMR δ 130.7] in addition to the exocyclic methylene group [^1H NMR δ 4.89; ^{13}C NMR δ 146.7 and 113.9]. The most notable effect on the ratio of the seven- to five-membered rings was temperature—with a higher temperature favoring five- over seven-membered-ring formation.



E = CO_2CH_3

$(Ph_3P)_4Pd$, dppe, THF	1.6	1	(47%[a])
$(Ph_3P)_4Pd$, dppe, dioxane	3.8	1	(98%[b])
$[(i\text{-}C_3H_7O)_3P]_4Pd$,[c] THF	1.1	1	(89%[b])

[a] Yield based on 1. Actual yield based upon recovered diene would be substantially higher. [b] Yield based upon recovered diene. [c] Catalyst formed in situ by reaction of $(i\text{-}C_3H_7O)_3P$ and $Pd(OAc)_2$.

The source of this competition can arise from two different pathways (eq 2). In the first (path A), initial attack occurs at a terminus of the diene unit which can lead to a cisoid (4) or transoid (5) dienolate intermediate in which the former can produce either five- or seven-membered rings but the latter is constrained to form the five-membered ring. If this mechanistic scheme is correct, the ratio of 2 to 3 would depend upon the partitioning of 4 or of 4 and 5. Alternatively, β attack on the diene system (path

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(1) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* 1979, *101*, 6429; 1981, *103*, 5972.

(2) For a related reaction of cooligomerization of alkylidenecyclopropanes and olefins catalyzed by Pd see: (a) Binger, P.; Bentz, P. *J. Organomet. Chem.* 1981, *221*, C33. (b) Binger, P.; Germer, A. *Chem. Ber.* 1981, *114*, 3325. (c) Binger, P.; Schuchardt, U. *Ibid.* 1981, *114*, 3313. (d) *Ibid.* 1980, *113*, 3334. (e) *Angew. Chem., Int. Ed. Engl.* 1977, *16*, 249. (f) Binger, P. *Synthesis* 1973, 427. For a cooligomerization catalyzed by Ni see: Noyori, R.; Yemakawa, M.; Takaya, H. *Tetrahedron Lett.* 1978, 4823 and earlier references therein.

(3) For some recent total syntheses see: Greene, A. E.; LeDrian, C.; Crabbe, P. *J. Am. Chem. Soc.* 1980, *102*, 7583. Koksal, Y.; Radditz, P.; Winterfeldt, E. W. *Angew. Chem. Int. Ed. Engl.* 1980, *19*, 472. Kitahara, T.; Mori, K.; Matsui, M. *Tetrahedron Lett.* 1979, 3021. Bartlett, P. A.; Green, F. R., III *J. Am. Chem. Soc.* 1978, *100*, 4858. Corey, E. J.; Wollenberg, R. H.; Williams, D. R. *Tetrahedron Lett.* 1977, 2243. Baudoriy, R.; Crabbe, P.; Greene, A. E.; LeDrian, C.; Orr, A. F. *Tetrahedron Lett.* 1977, 2973.

(4) This compound has been fully characterized spectrally and its elemental composition determined by high-resolution mass spectroscopy and/or combustion analysis.

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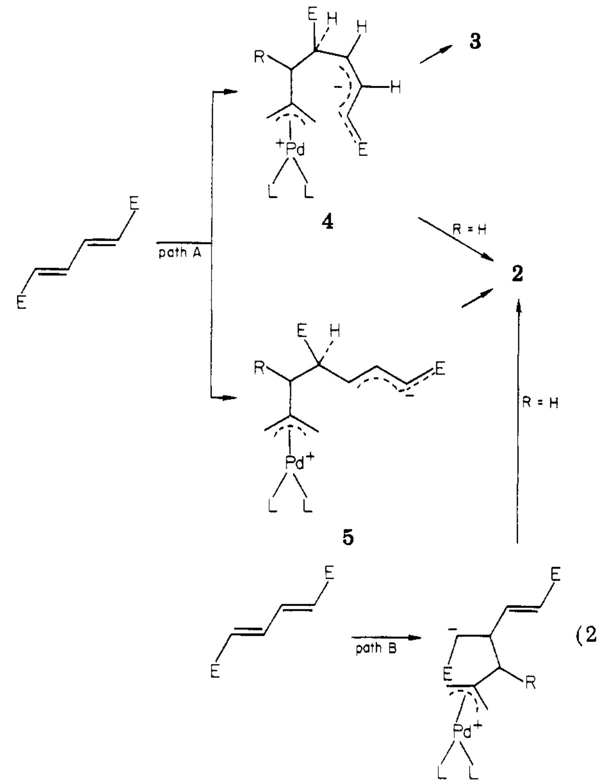
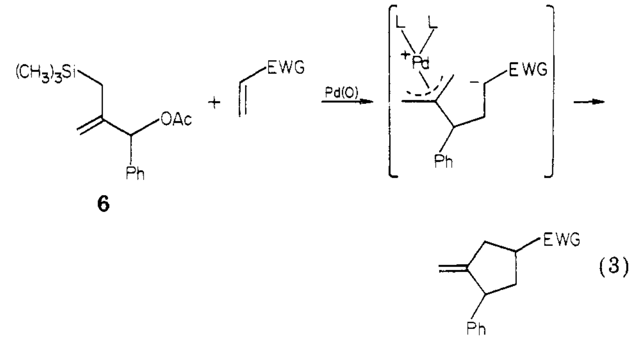


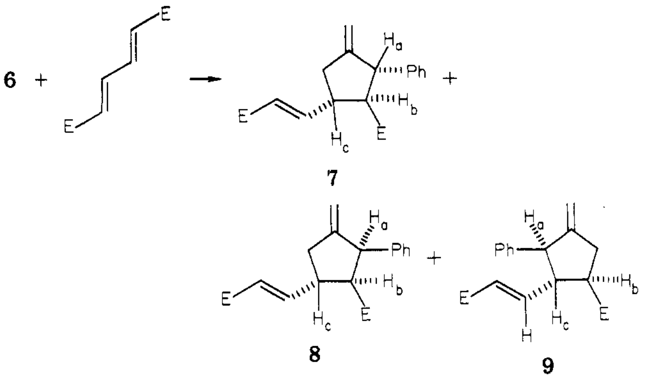
(2)

B) is constrained to form only five-membered-ring product. In this scenario, the ratio of 2 to 3 may derive from the competition between path B and path A. Of course, a blend of paths A and B may be responsible for the ratio of 2 to 3. In order to pursue these questions, we examined a substituted derivative of 1.

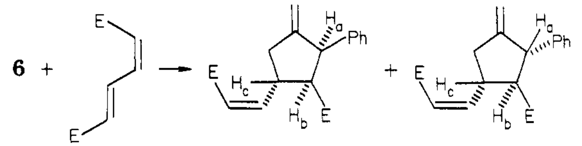
The phenyl-substituted derivative 6 has been shown to react exclusively by initial attack occurring at the carbon bearing the phenyl group (eq 3).[5,6] Reaction of 6 with dimethyl (*E*,*E*)-muconate catalyzed by $(Ph_3P)_4Pd$ or in situ formed $[(i\text{-}C_3H_7O)_3P]_4Pd$ led to four products in 74–87% yield based upon recovered muconate which were separated by HPLC. All four possessed an exocyclic methylene group as shown by two broad singlets between δ 4.5 and δ 5.2. The major products (70–75%) were assigned the trans,trans and cis,trans structures 7[4] and 8.[4] The regiochemistry is easily demonstrated by the fact that the H_A [7 δ 3.95 (dd, J = 11, 1.5 Hz); 8 δ 4.21 (d, J = 10 Hz)] couples to H_B [7 δ 2.82; 8 δ 3.13] and not H_C [7 δ 3.09; 8 δ 3.33]. Contrastingly, 9[4] shows H_A [δ 3.45 (d, J = 10 Hz)] coupled to H_C [δ 3.09] and not H_B [δ 2.9]—a fact which dictates the reverse regiochemistry as depicted. The fourth product was minor and could not be obtained pure. On the basis of the appearance of its NMR spectrum, it is tentatively identified as a stereoisomer. The stereochemistry depicted is based upon the comparison of the NMR spectral data to other methylenecyclopentanes and the known propensity for the cycloaddition to retain *E* olefin geometry.[1]



(3)

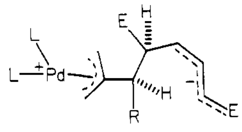


Reaction of dimethyl (*E*,*Z*)-muconate with 6 led to two addition products 10[4] and 11[4] in a 1:1 ratio in which reaction occurred only at the trans olefin! Spin-decoupling experiments establish that H_A [10 μ 4.16 (d, J = 8.8); 11 δ 4.04 (dd, J = 10, 1 Hz)] couples to H_B [10 δ 3.06; 11 δ 2.72] and not H_C [10 δ 4.39; 11 δ 4.13]. In this case, products derived only from initial terminal attack.



10 11

Thus, the preponderant mode of cycloaddition derives from path A of eq 1, but both paths do operate. The preference for terminal attack on a dienoate suggests that TMM–Pd is a relatively soft nucleophile for which delocalization of the developing negative charge in the acceptor is of considerable importance. It is striking that seven-membered-ring formation is limited to only the parent substrate 1. With the assumption of an extended conformation for 4 when R = H to minimize nonbonded interactions (i.e., 12, R = H), introduction of a bulky R group necessarily introduces unfavorable eclipsing interaction regardless of conformation. Thus, such a substituent disfavors 4 relative to 5 and thereby leads to enhanced cyclopentane formation. Equally striking is the dependence of terminal vs. β attack (path A vs. path B) on the geometry of the acceptor. Steric factors best account for this behavior too, since a bulky nucleophile must experience some nonbonded interactions with the cisoid ester as in 13 that is absent in 14. Thus, this cycloaddition reaction responds dramatically to steric perturbations—a fact that offers much promise to exercise high control over the reaction pathway. The preferential reaction of the *E*- over the *Z* olefin represents a puzzlement. Huisgen[7] has suggested the use of the faster rate of reaction of an *E* over



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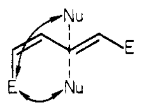
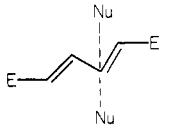


13



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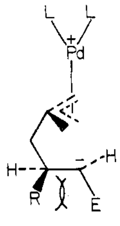
[5] Nanninga, T. N., unpublished work in these laboratories.

[6] This regiochemical result differs from the Pd-catalyzed co-oligomerization of a phenyl-substituted alkylidenecyclopropane with olefins. See ref 2c.

[7] Husigen states that "the ratio of the trans/cis rates offers an elegant and theoretically clear criterion for concerted additions leading to five- and six-membered rings". Husigen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 633.

a *Z* acceptor as a criterion of concertedness—a conclusion not in accordance with many of our other observations. On the other hand, the suggested source of this rate discrimination may indeed apply. For minimization of charge separation, a rigid cisoid (e.g., **15** or **16**) rather than a transoid geometry would likely prevail and thereby approach the geometrical constraints of a lopsided concerted process. Thus, rehybridization of the β-carbon would increase the nonbonded interactions with a *Z* acceptor as in **15** compared to an *E* acceptor.[8] A broadening of the interpretation of the *E*/*Z* rate factor to include nonconcerted reactions whose transition-state geometry approaches that of a concerted process may be necessitated.



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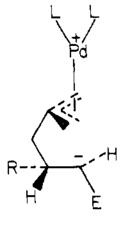

16

Acknowledgment. We thank the National Science Foundation for their generous support of our programs. We thank Johnson Matthey Ltd. and Englehardt Industries for generous supplies of palladium salts.

Registry No. 1, 72047-94-0; 2, 82823-81-2; 3, 82823-82-3; 6, 82823-83-4; 7, 82823-84-5; 8, 82863-89-6; 9, 82823-85-6; 10, 82863-90-9; 11, 82863-91-0; dimethyl (*E*,*E*)-muconate, 1119-43-3; dimethyl (*E*,-*E*)-muconate, 692-92-2; $(Ph_3P)_4Pd$, 14221-01-3; $[i\text{-}C_3H_7O)_3P]_4Pd$, 82838-61-7.

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[8] In a typical experiment, a solution of 1.4 equiv of dimethyl (*E*,*E*-muconate, 1.2 equiv of 1, 7.1 mol % of $(Ph_3P)_4Pd$, and 1.5 mol % of dppe in dioxane (0.2–0.25 M in substrate) was refluxed for 8 h. After the solution was cooled, the solvent was evaporated and the residue directly chromatographed to give pure products.

Thermal Extrusion of Sulfur Dioxide from (η^5-Cyclopentadienyl)cobalt η^4-Thiophene 1,1-Dioxides: A New Organometallic Reaction

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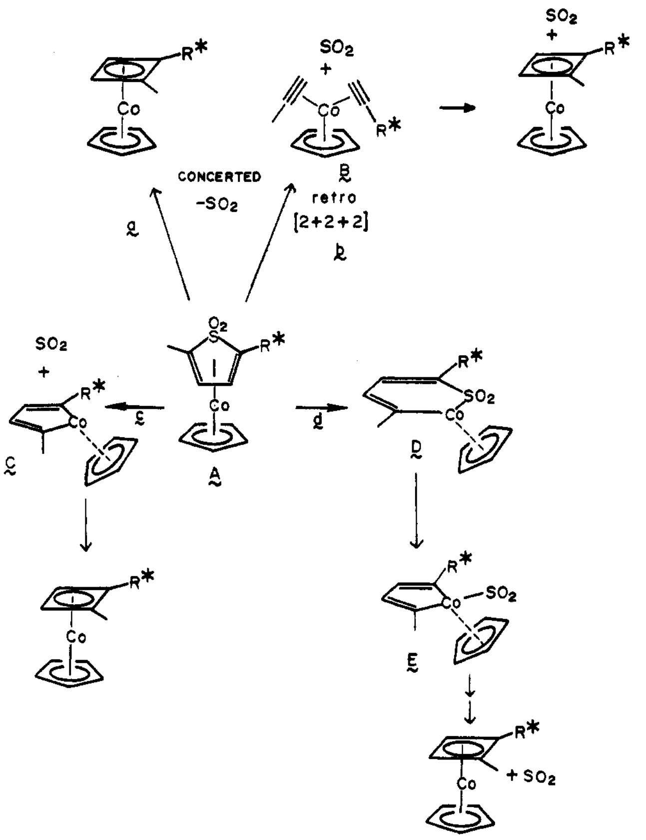
Received August 17, 1982

Summary: Flash vacuum pyrolysis of several (η^5-cyclopentadienyl)cobalt η^4-thiophene 1,1-dioxides leads to extrusion of SO_2 and the formation of (η^5-cyclopentadienyl)cobalt η^4-cyclobutadiene complexes. Stereochemical labeling experiments have been employed to pinpoint a likely pathway for this new transformation.

The prospect of increasing utilization of coal and coal-derived liquids as a source of fuel and chemical feed stocks has renewed interest in the development of chemical means by which sulfur may be removed from coal.[1] A large proportion of the organically bound sulfur in coal occurs in the form of thiophene and its derivatives. A potential way of eliminating its presence from such structures would be by an oxidation thermal desulfonation sequence. Thus, flash vacuum pyrolysis (FVP) of thiophene 1,1-dioxides derived from oxidation of the corresponding thiophenes leads to the predominant formation of furans by presumed loss of "SO".[2]

Scheme I



We have been interested in effecting transition-metal-mediated SO_2 extrusions from such systems in an effort to ultimately find catalytic organometallic pathways by which thiophene units may be converted into desulfurized chemicals. A previous thermal reactivity study[2a] of an iron tricarbonyl complexed thiophene dioxide was rendered inconclusive due to extensive decomposition and metal deposition, most likely a result of the relatively weak Fe–CO bond. We have previously established the utility of the remarkable thermal stability[3] of the CpCo unit (Cp = η^5-C_5H_5) in studies aimed at discovering novel ligand reorganizations.[4] It therefore appeared promising to extend this work to the thermal chemistry of (η^5-cyclopentadienyl)cobalt thiophene dioxides. This report details the first observation of the elusive[2a] SO_2 extrusion from such complexes and describes experiments, the outcome of which has considerably narrowed the number of alternatives by which this transformation occurs.

(η^5-Cyclopentadienyl)cobalt η^4-2,5-dimethylthiophene 1,1-dioxide (**1**) was prepared from $CpCo(CO)_2$ and the free heterocycle[5] by irradiation in boiling benzene (84%).[6] In

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[1] R. A. Meyers, "Coal Desulfurization", Marcel Dekker, New York, 1977.

[2] (a) W. J. M. van Tilborg and R. Plomp, *Recl. Trav. Chim. Pays-Bas*, **96**, 282 (1977); (b) E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, **88**, 2836 (1966); T. G. Squires, C. G. Venier, B. A. Hodgson, L. W. Chang, F. A. Davis, and T. W. Panunto, *J. Org. Chem.*, **46**, 2373 (1981).

[3] J. A. Connor, *Top. Curr. Chem.*, **71**, 71 (1976).

[4] (a) J. R. Fritch and K. P. C. Vollhardt, *Organometallics*, **1**, 590 (1982); (b) G. Ville, K. P. C. Vollhardt, and M. J. Winter, *J. Am. Chem. Soc.*, **103**, 5267 (1981); (c) J. R. Fritch and K. P. C. Vollhardt, *ibid.*, **100**, 3643 (1978); (d) *Angew. Chem.*, **91**, 439 (1979); *Angew. Chem., Int. Ed. Engl.* **18**, 409 (1979).