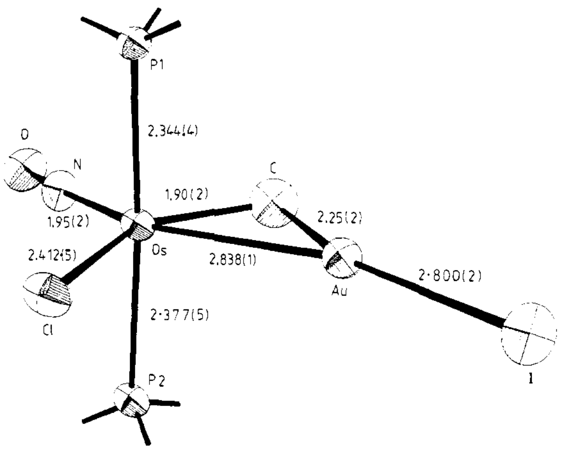

Figure 2. Inner coordination sphere of $\overline{\mathrm{Os(CH_2Au}}\mathrm{I)Cl(NO)(PPh_3)_2}$. Interatomic angles: P1–Os–P2, 173.9 (2)°; C–Os–Au, 52.4 (5)°; C–Os–N, 104.5 (7)°; N–Os–Cl, 121.0 (5)°; Cl–Os–Au, 82.1 (1)°; Au–C–Os, 85.8 (6)°; C–Au–Os, 41.8 (4)°; Os–Au–I, 156.6 (1)°; C–Au–I, 161.6 (4)°.

gives $\mathrm{Os({=}CH_2)Cl(NO)(PPh_3)_2}$, I. I forms orange crystals, mp 209–210 °C, with good air stability. No interaction of I with triphenylphosphine or nitrogen bases such as pyridine is detectable. The structure of I[14] is shown in Figure 1 and its reactions in Scheme I.[11]

The geometry of I is very similar to $\mathrm{Os(C\text{-}\mathit{p}\text{-}tolyl)Cl(CO)(PPh_3)_2}$.[15] Both molecules have large C–Os–Cl angles (126.6 (4)° in I, 133° in the carbyne complex). The metal–carbon distance, 1.92 (1) Å, is comparable with that found in the osmium vinylidene complex.[16] The methylene hydrogens lie perpendicular to the equatorial plane as expected.[17]

I reacts readily with a number of electrophilic reagents as detailed in Scheme I. In the rearrangement of IV to VI it is attractive to postulate the cationic methylene complex $\mathrm{[Os({=}CH_2)Cl_2(NO)(PPh_3)_2]^+}$ as the reactive intermediate. This species, by analogy with $\mathrm{[OsCl_2(NO)(CO)(PPh_3)_2]^+}$,[12] can be thought of as osmium(II) and hence, in this higher oxidation state complex, the electrophilic propety of the carbene ligand returns, and phosphine is coordinated to form VI.

Reactions of I with sulfur, selenium, and tellurium are slow, giving examples of coordinated thioformaldehyde, selenoformaldehyde, and telluroformaldehyde (VIII).[18] These reactions parallel those with the osmium–carbyne system[14] and represent a new route to these little-studied ligands.

Likewise, $\mathrm{PPh_3AuCl}$[19] reacts with I but adduct formation is readily reversible. However, the AuI (IX) and $\mathrm{[AuPPh_3]^+}$ (X) adducts are stable compounds.

Figure 2 shows the structure of IX.[14] The gold iodide fragment is indeed bridging the double bond but the interaction is weak. Remarkably little structural reorganization accompanies this adduct formation. The osmium–carbon bond length is 1.90 (2) Å, which does not differ significantly from the bond length in I, and the C–Os–Cl angle is increased by only 8° upon adduct formation.

We conclude that the reactivity of the linkage $\mathrm{L}_n\mathrm{M{=}CH_2}$ is strongly dependent on the oxidation state of the metal. Providing the metal center is sufficiently electron rich, even in 18-electron complexes of group 8 metals the carbene center may be nucleophilic.

The methylene ligand in I undergoes coupling reactions with carbon monoxide and isocyanides, and the nature of these products is under investigation.

Acknowledgment. We thank the N.Z. Universities Grants Committee for the award of a Postgraduate Scholorship to A.H.W. and for grants toward equipment and Johnson Matthey Ltd. for a generous loan of osmium tetroxide.

Registry No. I, 86645-81-0; II, 86645-82-1; III, 86645-83-2; IV, 86645-84-3; V, 86645-85-4; VI, 86668-00-0; VII, 86645-86-5; VIIIa, 86645-87-6; VIIIb, 86645-88-7; VIIIc, 86645-89-8; IX, 86668-01-1; X, 86668-02-2; XI, 86645-90-1; $\mathrm{OsCl(NO)(CO)(PPh_3)_2}$, 22186-54-5; $\mathrm{OsCl(CO_3)(NO)(PPh_3)_2}$, 86645-91-2; $\mathrm{HgCl_2}$, 7487-94-7; HCl, 7647-01-0; $\mathrm{Et_4NAuI_2}$, 50481-02-2; $\mathrm{PPh_3AuCl}$, 14243-64-2; $\mathrm{CH_2N_2}$, 334-88-3; S, 7704-34-9; Se, 7782-49-2; Te, 13494-80-9.

Supplementary Material Available: Listings of atomic coordinates and thermal parameters for I and IX (32 pages). Ordering information is given on any current masthead page.

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(11) All complexes analyze satisfactorily for C, H, N. Geometries are assigned by X-ray for I and IX and by IR and NMR data. Spectral data for I–XI are as follows: ν(NO) cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$, 25 °C) δ, J(H–P) Hz. I: 1628; 13.8 t, 19.2. II: 1805; 1.39 t, 5. III: 1815; 2.30 t, 5.6. IV: 1780; 3.88 t, 10.1. V: 1845; 4.90 t, 5. VI: 1815; 3.86 dd, 13, 7. VII: 1760; 4.72 dt, 8. VIIIa: 1728, 3.60 t, 1.5. VIIIb: 1735; 4.03 t, 2. VIIIc: 1740; 4.88 t, 3. IX: 1757; 8.87 t, 11. X: 1745; 10.45 dt, 12, 5. XI: 1630.

(12) Wilson, R. D.; Ibers, J. A. *Inorg. Chem.* **1979**, *18*, 336. Laing, K. R.; Roper, W. R. *Chem. Commun.* **1968**, 1556.

(13) de Boer, Th. J.; Backer, H. J. "Organic Syntheses; Wiley: New York, 1963; Collect. Vol. IV, p 250.

(14) Crystal data and refinement results for $\mathrm{Os({=}CH_2)Cl(NO)(PPh_3)_2}$: Orthorhombic; $a = 16.874$ (5), $b = 17.956$ (1), $c = 21.979$ (2) Å; space group P_{cab}; $Z = 8$. For $\overline{\mathrm{Os(CH_2Au}}\mathrm{I)Cl(NO)(PPh_3)_2}$ ($\mathrm{C_6H_6}$ solvate): triclinic; $a = 10.032$ (2), $b = 12.936$ (1), $c = 17.545$ (1) Å; $\alpha = 103.480$ (6)°, $\beta = 96.73$ (1)°, $\gamma = 82.45$ (1)°; space group $P_{\bar{1}}$; $z = 2$. Intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with monochromated Mo Kα radiation. The structures were solved by conventional methods. Full-matrix least-squares refinement, with anisotropic thermal parameters assigned to all non-hydrogen atoms, has given $R = 0.032$ for 3255 observed reflections for I and a present R of 0.065 for 5640 observed reflections for IX. Details of the structure determinations will be published elsewhere.

(15) Clark, G. R.; Marsden, K.; Roper, W. R.; Wright, L. J. *J. Am. Chem. Soc.* **1980**, *102*, 6570.

(16) Roper, W. R.; Waters, J. M.; Wright, L. J.; van Meurs, F. *J. Organomet. Chem.* **1980**, *201*, C27.

(17) Albright, T. A. Tetrahedron **1982**, *38*, 1339.

(18) A related series of chalcoformaldehyde complexes, $\mathrm{Os(\eta^2\text{-}CH_2X)(CO)_2(PPh_3)_2}$ (X = O, S, Se, Te), has recently been reported. Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1983**, *244*, C53.

(19) Clark, G. R.; Cochrane, C. M.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1980**, *199*, C35.

Macrolide Formation via an Isomerization Reaction. An Unusual Dependence on Nucleophile

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Received March 15, 1983

One of the major problems associated with the formation of macrolides has been the requirement of relatively high dilutions.[1,2] We envisioned resolving this problem by use of an isomerization of vinyl epoxides[3-5] such as **1** using polymerically bound transition-metal catalysts.[4,6] Since neither the nucleophilic nor electrophilic centers are unmasked until the substrate encounters an active site on the polymer, this cyclization should be independent

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(1) Galli, C.; Mandolini, L. J. *Chem. Soc., Chem. Commun.* **1982**, 251. Nicolaou, K. C. *Tetrahedron* **1977**, *33*, 683. Masamune, S.; Bates, G. S.; Corcoran, J. W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 585. Back, T. G. *Tetrahedron* **1977**, *33*, 3041. Newkome, G. R.; Sauer, J. D.; Roper, J. M.; Hager, D. C. *Chem. Rev.* **1977**, *77*, 513.

(2) Also see: Regen, S. L.; Kumura, Y. *J. Am. Chem. Soc.* **1982**, *104*, 2064. These authors report substrate concentrations of <0.003 M.

(3) For neutral alkylations with vinyl epoxides see: Trost, B. M.; Molander, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 5969. Tsuji, J.; Kataoka, H.; Kobayashi, Y. *Tetrahedron Lett.* **1981**, *22*, 2575.

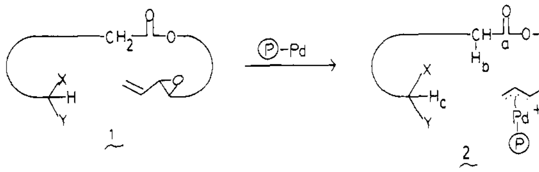
(4) Trost, B. M.; Warner, R. W. *J. Am. Chem. Soc.* **1982**, *104*, 6112.

(5) Takahashi, T.; Kataoka, H.; Tsuji, J. *J. Am. Chem. Soc.* **1983**, *105*, 147.

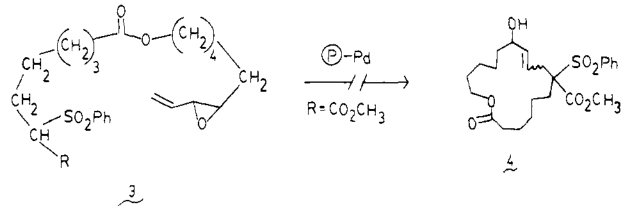
(6) For polystyrene-supported palladium catalysts see: Trost, B. M.; Keinan, E. *J. Am. Chem. Soc.* **1978**, *100*, 7779. Pittman, C. U., Jr.; Ng, Q. *J. Organomet. Chem.* **1978**, *153*, 85. Terasawa, M.; Kaneda, K.: Imanaka, T.; Teranishi, S. *Ibid.* **1978**, *162*, 403.

0002-7863/83/1505-5940$01.50/0

of the solution concentration of **1**.[4] However, the success of this approach depends upon the chemoselectivity of the intermediate **2** in which three sites of reaction (a, b, and c) can be identified.

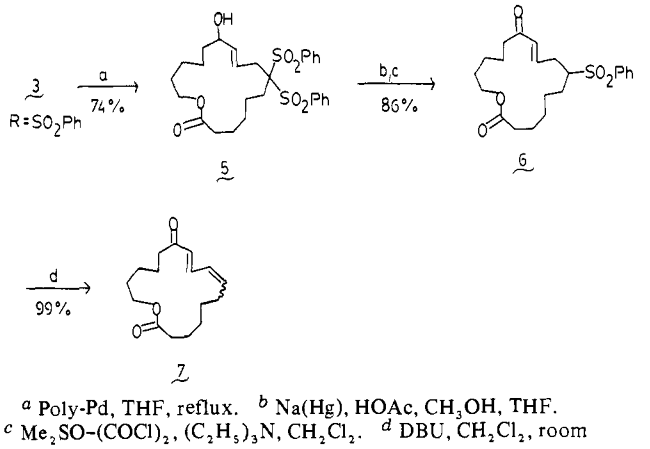


We were therefore not surprised by the failure of **3** ($R = CO_2CH_3$)[7] to lead to any macrolactone **4**.[8] In attempting to determine the source of this failure, we discovered an unusual dependence of the cyclization reaction on the nature of the nucleophile that now permits formation of macrolides in 70–87% yields at 0.1–0.5 M concentrations.



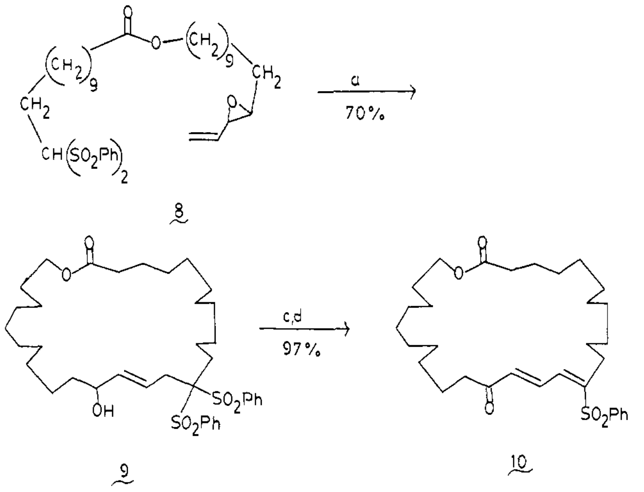
To avoid introduction of a chiral center, we chose a bis(benzenesulfonyl)alkane as our pro-nucleophile. Subjecting a 0.2 M solution of **3** ($R = PhSO_2$)[7] to approximately 5 mol% of a polymer-bound palladium catalyst[9] (THF, reflux, 3 h) led regio- and stereoselectively to a single macrolide **5**[10,11] in 74 % yield, averaged over 10 runs. The *E* stereochemistry derives from the 16-Hz coupling of the vinyl protons (δ 5.83 and 5.6). Its monocyclic nature was confirmed by both ^{13}C NMR spectroscopy of **5** and high-resolution mass spectroscopy of the further transformation products **6**[11-13] [*m/e* 406.1972 (calcd 406.1812)] and **7**[11] [*m/e* 264.1725 (calcd 264.1724)] (Scheme I). These transformations also illustrate the flexibility of the benzenesulfonyl group for further structural manipulation.

Scheme I



^{a} Poly-Pd, THF, reflux. ^{b} Na(Hg), HOAc, CH_3OH, THF. ^{c} $Me_2SO-(COCl)_2$, $(C_2H_5)_3N$, CH_2Cl_2. ^{d} DBU, CH_2Cl_2, room temperature.

Subjecting **8**[7] to the same conditions led to a 70% isolated yield of a single 27-membered ring macrolide **9**[10,11] in a completely regio- and stereoselective fashion. The monomeric nature is clearly established by both FAB (*m/e* ($M + H^+$) 689) and laser desorption (*m/e* (M + Na) 711 and (M + K) 727) mass spectroscopy and further confirmed by the conventional mass spectrum of the further transformation product **10**[11] [*m/e* 544.3224 (calcd 544.3222)]. The *E* stereochemistry derives from the ^1H NMR spectrum which exhibits a 16.2 Hz coupling between the vinyl protons (δ 5.84 and 5.60). A modified Moffatt oxidation[12a] and elimination generates the interesting α-sulfonyl α, β, γ, δ-dienone, illustrating another dimension of the flexibility of the bis(benzenesulfonyl) unit.



The failure of **3** ($R = CO_2CH_3$) compared to **3** ($R = PhSO_2$) and **8** cannot be attributed to thermodynamic pK_a differences[14] (cf. **11** and **12**). To further demonstrate this point, the bis(methanesulfonyl) derivative **14**[7] was subjected to the typical

	$(PhSO_2)_2CH_2$	$PhSO_2CH_2CO_2CH_3$	$(CH_3SO_2)_2CH_2$
	11	**12**	**13**
Pk_A	12.2	12-13	15

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(7) The syntheses of the cyclization subtrates are described in the supplementary material, which appears in the microfilm edition of the journal.

(8) A successful cyclization of a sulfone ester to a favorable six-membered ring with homogeneous catalysts has just been reported, ref 5.

(9) A Rohm and Haas Amberlite XE-305A resin was brominated and phosphinylated (Schwartz, R. H.; San Filippo, J., Jr., *J. Org. Chem.* **1979**, *44*, 2705) and loaded by exchanging with $(Ph_3)P)_4Pd$ in PhH. Anal. P, 5.75; Pd, 3.76.

(10) **5**: ^1H NMR ($CdCl_3$) δ 8.00 (m, 4 H), 7.66 (m, 2 H), 7.56 (m, 4 H), 5.83 (m, 1 H), 5.6 (dt, *J* = 16.0, 6.9 Hz, 1 H), 4.18 (m, 1 H), 4.04 (m, 2 H), 3.00 (m, 2 H), 2.26–1.35 (m, 19 H); ^{13}C NMR ($CDCl_3$) δ 173.1, 139.5, 137.0, 134.4, 131.1, 129.4, 129.0, 91.3, 72.1, 64.1, 37.3, 34.5, 33.8, 32.0, 29.4, 28.5, 26.6, 25.4, 24.9, 24.5; IR ($CHCl_3$) 1735, 1325, 1140 cm^{-1}. Anal. ($C_{28}H_{36}O_7S_2$): C, H. 9: ^1H NMR ($CDCl_3$) δ 7.99 (m, 4 H), 7.63 (m, 2 H), 7.51 (m, 4 H), 5.84 (m, 1 H), 5.60 (dt, *J* = 16.2, 6.6 Hz, 1 H), 4.06 (m, 3 H), 3.00 (m, 2 H), 2.26 (m, 2 H), 1.2–2.0 (m, 37 H); ^{13}C NMR ($CDCl_3$) δ 173.7, 139.5, 136.9, 134.3, 131.8, 131.1, 128.4, 122.3, 91.6, 72.2, 63.9, 37.2, 34.6, 31.4, 30.4, 29.7, 29.5, 29.4, 29.2, 28.9, 28.8, 28.4, 25.8, 25.2, 23.2, 22.5; IR ($CHCl_3$) 1715, 1340, 1140 cm^{-1}; MS (laser desorption), *m/e* 727 ($M^+ + K$), 711 ($M^+ + Na$), 569 ($M^+ + Na - PhSO_2H$), 427 ($M^+ + Na - 2PhSO_2H$). Anal. ($C_{38}H_{56}O_7S_2$): C, H. **15**: ^1H NMR ($CDCl_3$) δ 5.70 (m, 2 H), 4.16 (m, 3 H), 3.16 (s, 6 H), 2.97 (m, 2 H), 1.3–2.5 (m, 19 H); partial ^1H NMR (C_6D_6) δ 5.80 (m, 1 H), 5.43 (dd, *J* = 15.07, 6.25 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 172.9, 139.8, 121.5, 86.9, 77.2, 71.6, 64.1, 39.2, 37.1, 34.4, 29.3, 28.7, 28.3, 26.5, 25.9, 24.8, 22.6; IR ($CHCl_3$) 1725, 1330, 1305, 1140 cm^{-1}. Calcd for $C_{18}H_{32}O_7S_2$: 424.1587. Found: 424.1591. **16**: ^1H NMR ($CDCl_3$) δ 7.77 (m, 2 H), 7.65 (m, 1 H), 7.53 (m, 2 H), 6.88 (dt, *J* = 15.4, 7.4 Hz, 1 H), 6.19 (d, *J* = 15.4 Hz, 1 H), 4.10 (dt, *J* = 11, 6.2 Hz, 1 H), 3.95 (dt, *J* = 11, 5.9 Hz, 1 H), 3.62 (s, 3 H), 3.15 (dd, *J* = 15.4, 5.9 Hz, 1 H), 2.96 (dd, *J* = 15.4, 5.9 Hz, 1 H), 2.71 (m, 1 H), 2.38 (m, 1 H), 1.1–2.3 (m, 16 H); ^{13}C NMR ($CDCl_3$) δ 200.5, 172.8, 167.4, 140.5, 135.3, 134.2, 130.0, 128.7, 74.7, 63.9, 52.9, 39.1, 34.4, 32.7, 30.0, 28.7, 28.2, 25.6, 25.0, 24.6, 23.1; IR ($CHCl_3$) 1730, 1670, 1630, 1320, 1310, 1145 cm^{-1}. Anal. ($C_{24}H_{32}O_7S$): C, H.

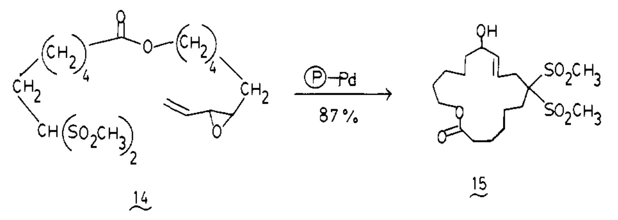
(11) (a) This compound has been fully characterized by spectral data. (b) The elemental composition has been established by high-resolution mass spectroscopy and/or combustion analysis.

(12) (a) Mancuso, A. J.; Brownfain, D. S.; Swern, D. *J. Org. Chem.* **1979**, *44*, 4148. (b) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3477.

(13) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4743.

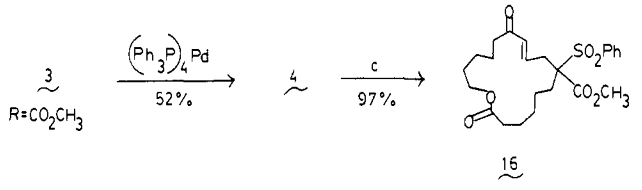
(14) Bordwell, F. G.; Van Der Puy, M.; Vanier, N. R. *J. Org. Chem.* **1976**, *41*, 1883. Bordwell, F. G. Drucker, G. E.; McCollum, G. J. *Ibid.* **1982**, *47*, 2504. The data for **12** are extrapolated from $PhSO_2CH_2CN$ whose pK_a = 12. The data recorded for **13** comes from Bordwell. Cf.: Pearson, R. G.; Dillon, R. L. *J. Am. Chem. Soc.* **1953**, *75*, 2439. It should be noted that the pK_a's were determined in Me_2SO, whereas, our experiments were performed in THF. While the magnitude of the pK_a's will likely be solvent dependent, their relative ordering is less likely to change.

cyclization conditions. Interestingly, this cyclization to **15**[10,11] was

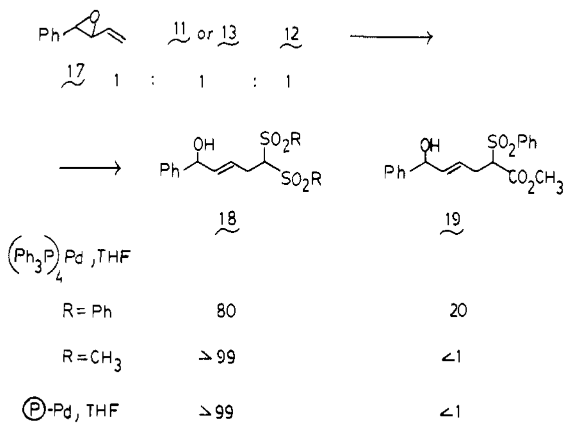


the fastest (15 min vs. 3 h for **3** R = $PhSO_2$) even though **14** must be less acidic than either **3** (R = CO_2CH_3) or **3** (R = $PhSO_2$) by comparing the pK_a's of **11** → **13**.

That the failure of **3** (R = CO_2CH_3) stemmed from the nature of the "active site" of the catalyst and not the thermodynamic pK_a was conclusively demonstrated by subjecting **3** (R = CO_2CH_3) to a homogeneous catalyst [5 mol % $(Ph_3P)_4Pd$, 10 mol % dppe][13] at 0.001 M (THF, reflux), which now indeed did cause it to cyclize. Due to the diastereomeric nature of **4** it was best characterized after oxidation[12a] to the homogeneous enone **16**.[10,11]



The dramatic sensitivity of the cyclization to the nature of the nucleophile appears to stem from the facility of absorption of the substrate on the polymer and a favorable competition for proton transfer and alkylation compared to alternative pathways of reaction for the initially ionized intermediate. To test the relative reactivity of **11**, **12**, and **13** with vinyl epoxides, **11** and **12** as well as **12** and **13** were allowed to compete for a limited amount of vinyl epoxide **17**. In the **11** vs. **12** competition with a homogeneous catalyst, a 4:1 ratio favoring alkylation of **11** was obtained. With the polymeric catalyst, exclusive alkylation of **11** occurred. Similarly, the **12** vs. **13** competition favored alkylation of the bis(sulfone) **13**. Thus, the bis(sulfone) system intrinsically is more reactive—a reactivity advantage that is enhanced by the polymer. The high reactivity of the bis(sulfonylalkane) unit toward the vinyl epoxides then accounts for its ability to competitively swamp any undesired reactions.[15] The delicate balance that must exist is highlighted by the total failure of the polymer-based reaction by simply substituting an ester for one sulfonyl group. While the range of pro-nucleophiles that can be used in this cyclization by isomerization remains to be elucidated, the excellent success of the bis(sulfone) combined with its tremendous versatility makes the current method a very useful one. The possible implications of the relative reactivity of the bis(sulfone) unit in other types of cyclizations would be interesting to explore.[16]



Acknowledgment. We thank the National Institutes of Health, General Medical Sciences, and the National Science Foundation for their generous support of our programs. Appreciation of Johnson Matthey Inc. and Englehardt Industries for generous supplies of palladium salts is heartily noted. Robert W. Warner would like to thank Artie G. Romero for his helpful insight and enthusiastic contributions in this work.

Registry No. 3 (R = $PhSO_2$), 86471-67-2; **3** (R = CO_2CH_3), 86471-68-3; **4**, 86471-69-4; **5**, 86471-70-7; **6**, 86471-71-8; **7**, 86471-72-9; **8**, 86471-73-0; 9, 86471-74-1; **10**, 86471-75-2; **11**, 3406-02-8; **12**, 34097-60-4; **13**, 1750-62-5; **14**, 86471-76-3; **15**, 86471-77-4; **16**, 86471-78-5; **17**, 20248-57-1; **18** (R = Ph), 86471-79-6; **18** (R = CH_3), 86471-80-9; **19**, 86471-81-0.

Supplementary Material Available: Schemes of the preparation of **3** (R = CO_2CH_3, $PhSO_2$), **14**, and **8** and spectra data of these compounds (3 pages). Ordering information is given on any current masthead page.

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[15] This result contrasts with our earlier observation on the stereochemistry of the Pd-catalyzed intermolecular alkylation (Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730) of allylic acetates. In the vinyl epoxide reaction, two stages determine the alkylation (1) rate of proton transfer and (2) rates of formation of the carbon–carbon bond. Since the allylic acetate reactions only depend upon the rate of carbon–carbon bond formation, the kinetic preference for **11** may relate to its rate of proton transfer. The fact that the thermodynamic pK_a's of **11** and **12** are virtually identical suggests that scrambling of anions after initial proton transfer does not occur.

[16] For reviews on sulfone chemistry see: Magnus, P. D. *Tetrahedron* **1977**, 33, 2019. Durst, T. *Compr. Org. Chem.* **1979**, *2*, 171.

α-Elimination of α-Acetoxysilanes Induced by Palladium: Evidence for the Intermediacy of a Vinylcarbene–Palladium Complex

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Modifying the behavior of reactive intermediates by complexing them to transition metals may offer the potential of adjusting their reactivity pattern. An interesting example is trimethylenemethane, whose complexation to transition metals permits variations running from selective cycloadditions to electron-deficient olefins[1-3] to forming stable unreactive complexes.[4] Use of palladium as the transition metal apparently alters its structure such that it behaves as a zwitterion rather than a diradical.[2] In order to probe the ability of palladium to impose polar properties on or to reverse such properties of reactive intermediates, we considered the case of vinylcarbenes.[5,6] If one considers a potential dipolar form for

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[1] Noyori, R.; Odagi, T.; Takaya, H. *J. Am. Chem. Soc.* **1970**, *92*, 5780. Noyori, R.; Ishigami, I.; Hayashi, N.; Takaya, H. *Ibid.* **1973**, *95*, 1674. Noyori, R.; Yamakawa, M.; Takaya, H. *Tetrahedron Lett.* **1978**, 4823.

[2] Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1979**, *101*, 6429, 6432; **1980**, *102*, 6359; **1981**, *103*, 5972; **1982**, *104*, 3733. Gordon, D. J.; Fenske, R. F.; Nanninga, T. N.; Trost, B. M. *Ibid.* **1981**, *103*, 5974. Trost, B. M.; Nanninga, T. N.; Chan, D. M. T. *Organometallics* **1982**, *1*, 1543. Albright, T. A. *J. Organomet. Chem.* **1980**, *198*, 159.

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