

# Communications

## Substituent Effects for the Olefination of Aldehydes by Zirconium "Metalloazines"

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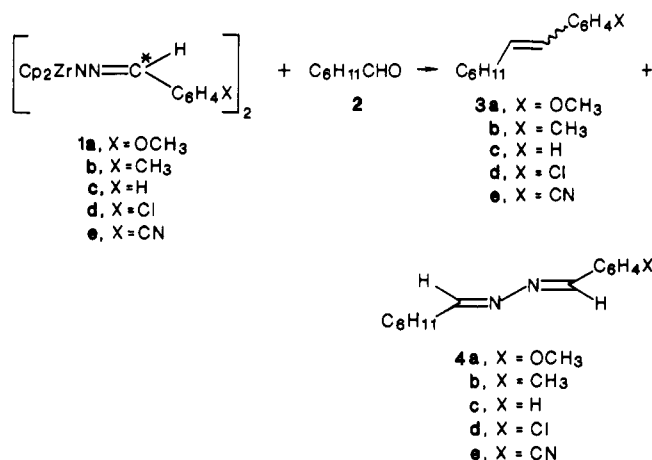
Received August 26, 1986

**Summary:** The reaction between Zr(IV) "metalloazines" and aldehydes affords unsymmetrical olefins and azines. Relative rates for formation of these species (and corresponding yields) were found to depend on the electron-donating ability of the metalloazine and on the electron-accepting ability of the aldehyde. Second-order rate constants were determined, and a reaction mechanism for olefin synthesis is proposed based on observed electronic effects.

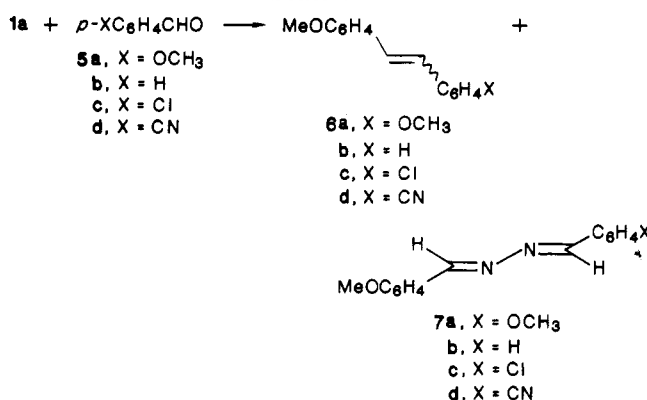
Zr(IV) "metalloazines" prepared<sup>1</sup> from  $\text{Cp}_2\text{Zr}^{\text{IV}}\text{XY}$  and hydrazone derivatives of aldehydes or ketones are susceptible to electrophilic attack at either the hydrazone group carbonyl-derived carbon  $\text{C}^*$  or at Zr-N, as shown by their reaction with organic carbonyl compounds (Schemes I and II). The olefination reaction is most interesting since it is an "umpolung" activation of a hydrazone by coordination to a metallic center. We have studied this process as a function of the substituents both on the metal complex and on the organic substrate, and we find that the rate of olefin synthesis correlates with the electron-donor ability of groups on  $\text{C}^*$  and with the electron-acceptor properties of groups on the organic carbonyl compound, but not necessarily with the one-electron reduction potentials of the organic substrates.

Reactions between various aldehydes and 1 were carried out under  $\text{N}_2$  and were studied by NMR (in a screw-cap tube with a Teflon septum through which the aldehyde was added). In a typical procedure, 5.00  $\mu\text{L}$  of benzaldehyde (distilled from  $\text{CaH}_2$ ) was syringed into an NMR tube containing 0.750 mL of a 0.0570 M solution of 1a (0.0430 mmol) in dry  $\text{C}_6\text{D}_6$  (with dioxane, 0.00671 M, added as an internal standard) at 10 °C. The growth of signals at 3.60 ( $-\text{OCH}_3$ , 6b) and 8.63 ppm ( $-\text{N}=\text{C}(\text{H})\text{R}$ , 7b) was followed for 6 h (vs. dioxane internal standard). Second-order rate constants were determined by noting product increases over 90 min. Each Zr "metalloazine" contains 2 equiv of reactive groups which are likely transferred sequentially to each of 2 equiv of aldehyde substrate (Scheme III). In order to best isolate the study of reactions of 1 from those of the intermediate 8, rate data were measured only for the initial phase of reactions between each substrate and aliquots of 1. Product ratios (olefins/azine) in the early stages of these reactions accurately reflect ratios of rate constants measured during this time (ratios of azine to olefin measured after consumption of *both* equivalents of side chain of the starting dimer can be different from these initial ratios since the

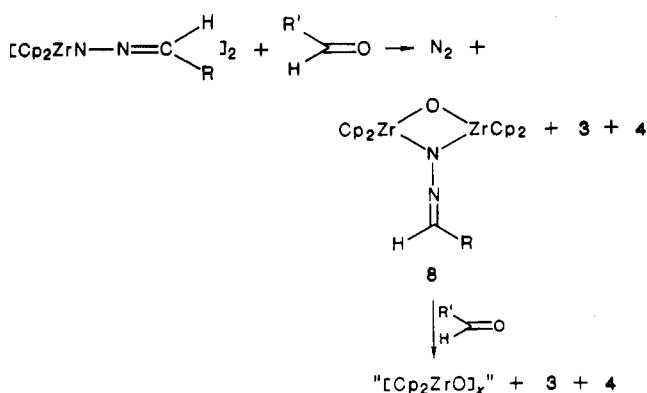
Scheme I



Scheme II



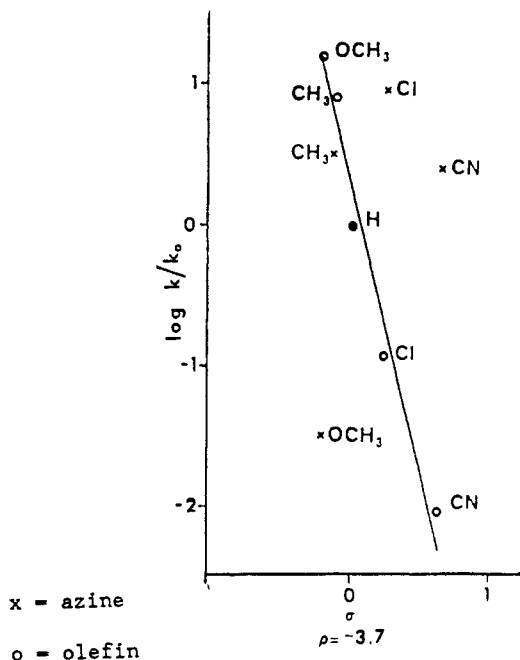
Scheme III



aldehyde need not partition equivalently between olefin and azine on reaction with either 1 or 8). The effect of para substitution of the arylazine unit on second-order rate constants is shown in Figure 1. A linear Hammett correlation<sup>2</sup> was obtained for olefination and shows that electron-donating groups enhance the rate for olefin for-

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(2) Jaffé, H. H. *Chem. Rev.* 1953, 53, 191.



	azine formation		olefin formation		Hammett $\sigma$
	$k$ , M min <sup>-1</sup>	log $k/k_0$	$k$ , M min <sup>-1</sup>	log $k/k_0$	
1a	$5.0 \times 10^{-3}$	-1.5	$9.1 \times 10^{-2}$	1.2	-0.27
1b	$3.7 \times 10^{-2}$	0.51	$6.6 \times 10^{-2}$	0.89	-0.17
1c	$2.2 \times 10^{-2}$	0	$2.7 \times 10^{-2}$	0	0
1d	$5.6 \times 10^{-2}$	0.92	$1.1 \times 10^{-2}$	-0.92	0.23
1e	$3.3 \times 10^{-2}$	0.40	$3.5 \times 10^{-3}$	-2.0	0.63

**Figure 1.** Reactions between para-substituted Zr complexes and  $C_6H_{11}CHO$ .

**Table I. Final Yields for Reactions of Metalloazines and Aldehydes**

	olefin, <sup>a</sup> %	azine, <sup>a</sup> %
1a + 2	58	13
1b + 2	43	25
1c + 2	36	40
1d + 2	29	60
1e + 2	17	68
1a + 5a	44	29
1a + 5b	48	29
1a + 5c	54	22
1a + 5d	77	0

<sup>a</sup> Determined by GC with internal standard.

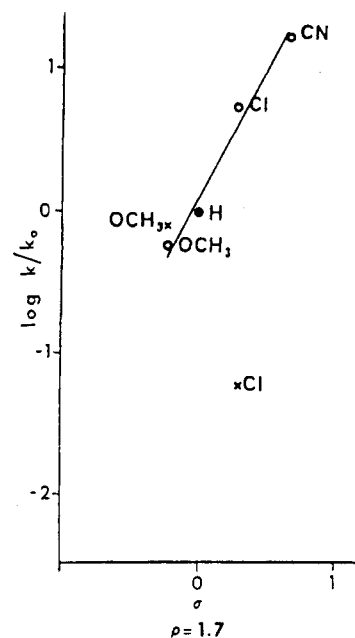
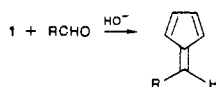
mation;<sup>3</sup> no such trend exists for formation of the unsymmetrical azine.<sup>5</sup>

In a complementary study, rate constants for reaction of a series of para-substituted benzaldehydes with complex 1a were obtained. These also follow a linear Hammett correlation. In this case, second-order rate constants for olefin formation increase with the electron-withdrawing ability of the substituent as shown in Figure 2. Interestingly, the rate of azine formation here increases with

(3) We find that the electronegativity of the metal center also is related to olefin formation. The analogous Ti complex [CpTi(Cl)-NNCHPh]<sub>2</sub><sup>4</sup> prepared from CpTiCl<sub>3</sub> and H<sub>2</sub>NNCHPh reacts with cyclohexanone to give only the unsymmetrical azine.

(4) Gambrotta, S.; Floriani, C.; Chiesi-Villa, A.; Guantini, C. *J. Chem. Soc., Chem. Commun.* 1982, 1015-1017.

(5) Transfer of a cyclopentadienyl ligand to unreacted carbonyl compound was found to occur on alkaline workup of the reaction



X	azine formation		olefin formation		Hammett $\sigma$
	$k$ , M min <sup>-1</sup>	log $k/k_0$	$k$ , M min <sup>-1</sup>	log $k/k_0$	
5a	$5.8 \times 10^{-3}$	-0.11	$3.7 \times 10^{-2}$	-0.25	-0.27
5b	$6.5 \times 10^{-3}$	0	$4.8 \times 10^{-2}$	0	0
5c	$2.0 \times 10^{-3}$	-1.2	$9.8 \times 10^{-2}$	0.71	0.23
5d	a		$1.6 \times 10^{-1}$	1.2	0.63

<sup>a</sup> Yield azine = 0.

**Figure 2.** Reactions between 1a and para-substituted benzaldehydes.

the electron-donating ability of the benzaldehyde substituent, suggesting that strong interaction of the carbonyl group oxygen with a zirconium center is important in the transition state leading to the formation of azine<sup>6</sup> (but not necessarily in the one leading to olefin).

Benzaldehyde and less easily reduced cyclohexanecarboxaldehyde ( $E_{1/2} = -1.15$  V vs.  $-1.85$  V vs. SCE for the analogue pentanal<sup>7</sup>) react with 1a at comparable rates ( $k_2 = 1.73 \times 10^{-2}$  vs.  $4.81 \times 10^{-2}$  M min<sup>-1</sup>), and, therefore, a mechanism of electron transfer from the complex to the aldehyde seems unlikely. We suggest that olefin formation occurs by a process of electrophilic attack by the carbonyl group containing substrate upon the azine carbon center of the organometallic in which C-C bond formation is the rate-limiting step; an electron-donating substituent on the arylazine unit should increase the nucleophilicity of C\* and an electron-withdrawing substituent on the aldehyde should increase the electrophilicity of the carbonyl group.<sup>8</sup> Control of product distributions of olefins and azines is now undergoing study in order to make zirconium "metalloazines" useful as reagents for organic synthesis.

**Acknowledgment.** We acknowledge support for this work given by the National Science Foundation and the National Institutes of Health.

(6) (a) We thank a reviewer for bringing this to our attention. (b) Note the correlation with  $\nu_{CO}$  for the substituted benzaldehydes (0.25 M in CCl<sub>4</sub>): 5a, 1701 cm<sup>-1</sup>; 5b, 1708 cm<sup>-1</sup>; 5c, 1712 cm<sup>-1</sup>; 5d, 1717 cm<sup>-1</sup>.

(7) Meites, L. *CRC Handbook of Series in Organic Electrochemistry*, CRC Press: Cleveland, OH, 1976.

(8) These trends correspond to a negative  $\rho$  value for Scheme I and a positive  $\rho$  value for Scheme II, analogous to the reaction<sup>9</sup> of X-C<sub>6</sub>H<sub>4</sub>COCl and X-C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> in which attack by N on the carbonyl carbon is rate-determining.

(9) (a) Williams, E. G.; Hinshelwood, C. N. *J. Chem. Soc.* 1934, 1079. (b) Stubbs, F. J.; Hinshelwood, C. N. *J. Chem. Soc.* 1949, S71.

Registry No. 1a, 105336-81-0; 1b, 105336-82-1; 1c, 105336-83-2; 1d, 105336-84-3; 1e, 105336-85-4; 2a, 105371-89-9; 2b, 105371-90-2; 2c, 5700-45-8; 2d, 105371-91-3; 2e, 105371-92-4; 3a, 105371-93-5; 3b, 105371-94-6; 3c, 105371-95-7; 3d, 105371-96-8; 3e, 105371-97-9; 4a, 4705-34-4; 4b, 1142-15-0; 4c, 5043-91-4; 4d, 52364-50-8; 5a, 41097-47-6; 5b, 41097-54-5; 5c, 105399-71-1; C<sub>6</sub>H<sub>11</sub>CH<sub>3</sub>, 2043-61-0; P-(OCH<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COH, 123-11-5; PhCHO, 100-52-7; p-ClC<sub>6</sub>H<sub>4</sub>CHO, 104-88-1; p-(CN)C<sub>6</sub>H<sub>4</sub>CHO, 105-07-7.

## A Novel Synthesis of 2-Siloxazolidines by 1,5-Elimination from 1-(Trimethylsiloxy)-2-(N-substituted-N-(methoxydimethylsilyl)amino)ethanes

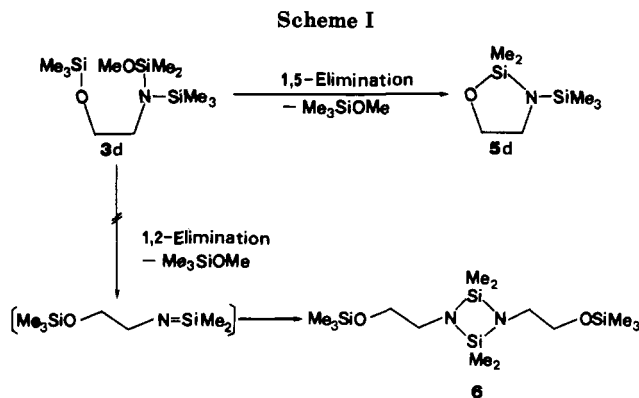
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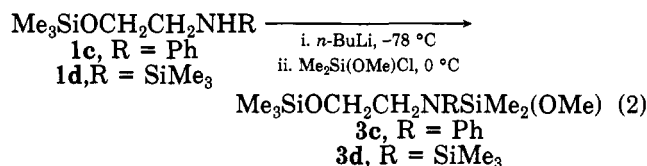
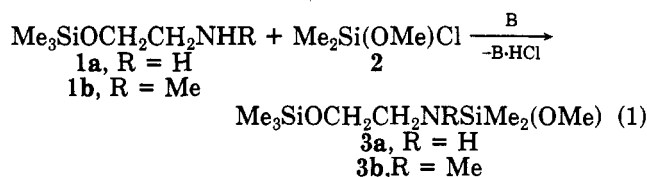
Received August 21, 1986

**Summary:** The vacuum sealed tube thermolyses of Me<sub>3</sub>SiOCH<sub>2</sub>CH<sub>2</sub>NRSiMe<sub>2</sub>(OMe) (R = Me, Ph, SiMe<sub>3</sub>) gave new heterocyclic compounds, 2,2,3-trimethyl-2-siloxazolidine, 2,2-dimethyl-3-phenyl-2-siloxazolidine, and 2,2-dimethyl-3-(trimethylsilyl)-2-siloxazolidine, through the 1,5-elimination of trimethylmethoxysilane, respectively. These 2-siloxazolidine derivatives reacted easily with methanol to give ring-cleavage products.

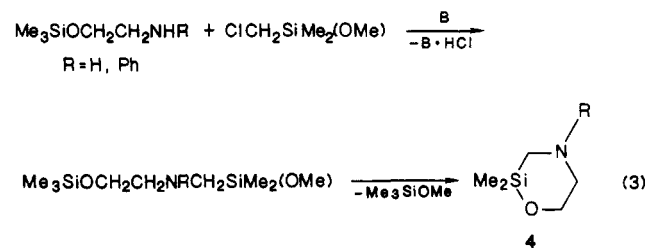
It has been anticipated that 5-membered heterocyclic compounds containing a N-Si-O moiety would be readily synthesized via reactions of bifunctional silanes with ethanolamine derivatives. However, all attempts to synthesize the 2-siloxazolidines have been unsuccessful to date,<sup>1</sup> although 2-siloxazolidones<sup>2</sup> and 2,2-dimethyl-3-oxa-2-silaindolines<sup>3</sup> were prepared from the reaction of bifunctional silanes with amino acid derivatives and o-aminophenol, respectively. We have recently become interested in synthesizing 2-siloxazolidines having a N-Si-O bond and their thermal and chemical properties. In this communication we wish to report the preparation and properties of these new heterocyclic compounds, 2-siloxazolidines. Considering that the 2-siloxazolidines can be formed from a ring-closure reaction through an intramolecular transalkoxylation,<sup>4</sup> 1-(trimethylsiloxy)-2-(N-substituted-N-(meth-



oxydimethylsilyl)amino)ethanes (3a-d) were prepared. The reactions of dimethylmethoxychlorosilane (2) with (2-(N-substituted amino)ethoxy)trimethylsilanes (1a and 1b) gave compounds 3a<sup>5</sup> and 3b<sup>6</sup> in 48 and 49% yields, respectively (eq 1). Compounds 3c<sup>7</sup> and 3d<sup>8</sup> were obtained in 45 and 66% yields, respectively, after the aminoethoxytrimethylsilanes (1c and 1d) were lithiated with *n*-butyllithium at -78 °C and 2 was subsequently added at 0 °C (eq 2).



It is of interest to note that each of the products 3a-d was purely isolated from the corresponding reaction mixtures by the vacuum distillation method without any ring-closure reaction which might have happened.<sup>4</sup> In contrast, Zhdanov and co-workers<sup>4</sup> reported that the reaction mixture of dimethylmethoxy(chloromethyl)silane with 1a and 1c gave the 2,2-dimethyl-2-silamorpholine derivatives 4 during the vacuum distillation and strongly suggested that 1,6-elimination of trimethylmethoxysilane occurred under this condition as shown in eq 3.



In order to lead 1,5-elimination of trimethylmethoxysilane from the precursors 3a-d, the vacuum sealed tube thermolysis (VSTT) method was adapted. When 3d dissolved in cyclohexane was subjected to VSTT at 300 °C for 3 h, 3b was completely consumed with the formation

(8) Compound 3d: bp 79-80 °C (4 torr); <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 0.08 (s, 9 H), 0.15 (s, 15 H), 2.93 (m, 2 H), 3.35 (m, 2 H), 3.37 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -1.02, 0.00, 1.24, 45.88, 50.00, 65.51. Anal. Calcd for C<sub>11</sub>H<sub>31</sub>O<sub>2</sub>NSi<sub>3</sub>: C, 44.99; H, 10.64; N, 4.77. Found: C, 44.60; H, 10.99; N, 4.79.

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(2) Klebe, J. F.; Finkbeiner, F. J. *J. Am. Chem. Soc.* 1966, 88, 4740-4741. Klebe, J. F.; Finkbeiner, F. J. *J. Am. Chem. Soc.* 1968, 90, 7255-7261.

(3) Wieber, M.; Schmidt, M. Z. *Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* 1963, 18B, 849. Kozyukov, V. P.; Mironov, V. F. *Zh. Obsch. Khim.* 1974, 44, 553-561.

(4) Zhdanov, A. A.; Pakhomov, V. I.; Arkhipov, I. A. *Muanyu Gumi* 1966, 19-20. Zhdanov, A. A.; Pakhomov, V. I.; Arkhipov, I. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1967, 1768-1774. Zhdanov, A. A.; Pakhomov, V. I.; Arkhipov, I. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1970, 392-396.

(5) Compound 3a: bp 71-72 °C (7 torr); <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 0.01 (s, 6 H), 0.02 (s, 9 H), 1.2 (s, 1 H), 2.83 (d of t, <sup>3</sup>J<sub>HH</sub> = 5.5 Hz, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, 2 H), 3.39 (s, 3 H), 3.51 (t, <sup>3</sup>J<sub>HH</sub> = 5.5 Hz, 2 H).

(6) Compound 3b: bp 80-81 °C (10 torr); <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 0.05 (s, 6 H), 0.08 (s, 9 H), 2.52 (s, 3 H), 2.85 (t, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 2 H), 3.33 (s, 3 H), 3.52 (t, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -2.94, 0.00, 35.08, 50.08, 53.01, 61.49. Anal. Calcd for C<sub>9</sub>H<sub>25</sub>O<sub>2</sub>NSi<sub>2</sub>: C, 45.90; H, 10.70; N, 5.95. Found: C, 45.74; H, 10.50; N, 5.93.

(7) Compound 3c: bp 117-118 °C (4 torr); <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 0.03 (s, 9 H), 0.19 (s, 6 H), 3.43 (s, 3 H), 3.49 (s, 4 H), 7.08 (m, 5 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -1.42, 0.05, 49.88, 50.38, 61.70, 121.26, 121.74, 129.51, 148.70. Anal. Calcd for C<sub>11</sub>H<sub>27</sub>O<sub>2</sub>NSi<sub>2</sub>: C, 56.51; H, 9.15; N, 4.71. Found: C, 56.45; H, 9.08; N, 4.74.