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Communications

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

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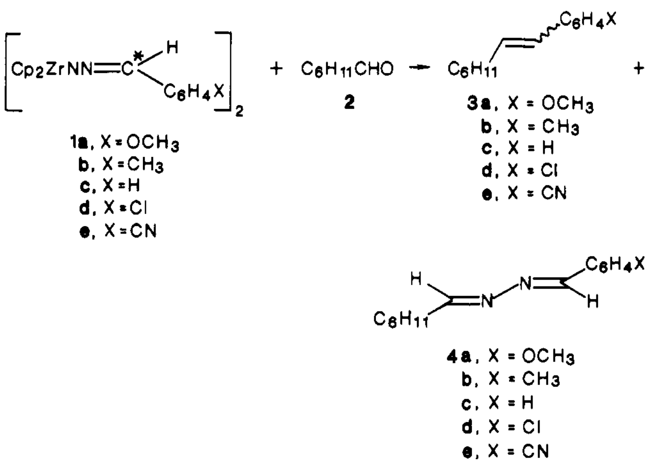
Summary: The reaction between Zr(IV) "metalloazines" and aldehydes affords unsymmetrical olefins and azines. Relative rates for formation of these species (and corresponding yields) were found to depend on the electron-donating ability of the metalloazine and on the electron-accepting ability of the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

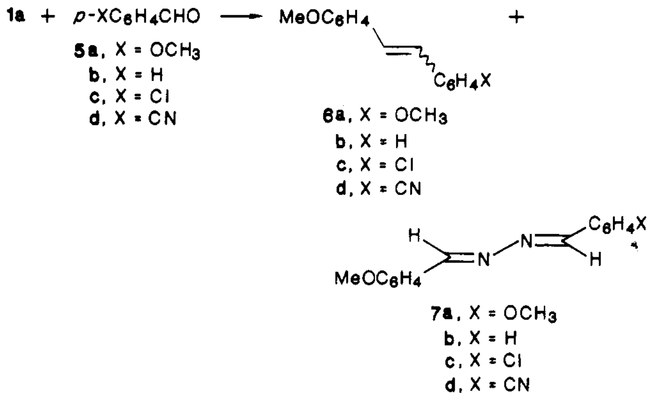
Zr(IV) "metalloazines" prepared[1] from Cp$_2$Zr^{IV}XY and hydrazone derivatives of aldehydes or ketones are susceptible to electrophilic attack at either the hydrazone group carbonyl-derived carbon C* or at Zr-N, as shown by their reaction with organic carbonyl compounds (Schemes I and II). The olefination 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 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 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 μL of benzaldehyde (distilled from 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 C$_6$D$_6$ (with dioxane, 0.006 71 M, added as an internal standard) at 10 °C. The growth of signals at 3.60 (-OCH$_3$, **6b**) and 8.63 ppm (-N=C(H)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 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[2] was obtained for olefination and shows that electron-donating groups enhance the rate for olefin for-

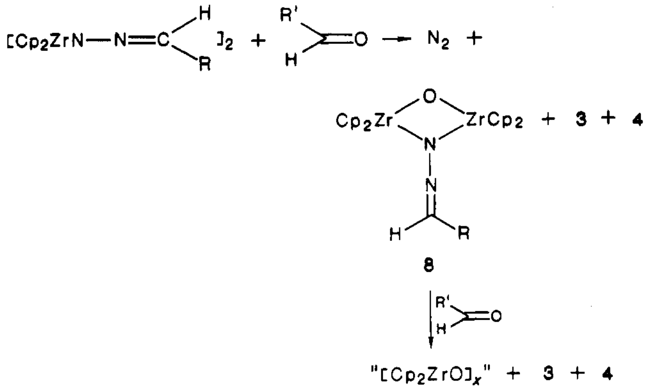
Scheme I



Scheme II



Scheme III



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(1) Arvanitis, G.; Schwartz, J.; Van Engen, D. *Organometallics* **1986**, *5*, 2157.

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

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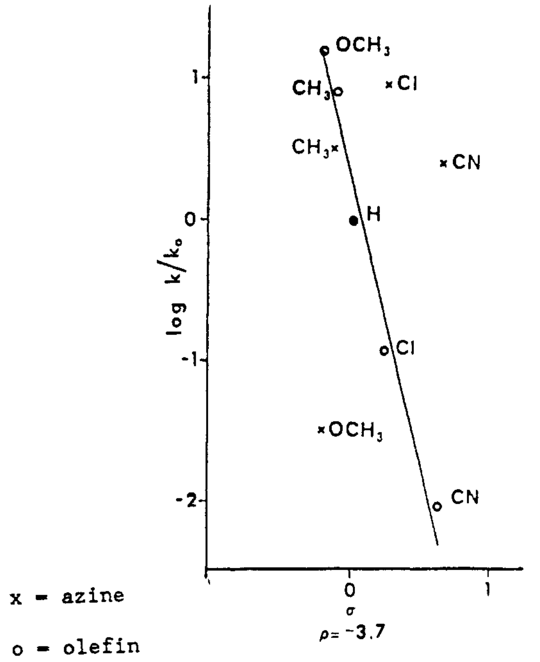


	azine formation		olefin formation		
	k, M min^{-1}	log k/k_0	k, M min^{-1}	log k/k_0	Hammett σ
1a	5.0×10^{-3}	-1.5	9.1×10^{-2}	1.2	-0.27
1b	3.7×10^{-2}	0.51	6.6×10^{-2}	0.89	-0.17
1c	2.2×10^{-2}	0	2.7×10^{-2}	0	0
1d	5.6×10^{-2}	0.92	1.1×10^{-2}	-0.92	0.23
1e	3.3×10^{-2}	0.40	3.5×10^{-3}	-2.0	0.63

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

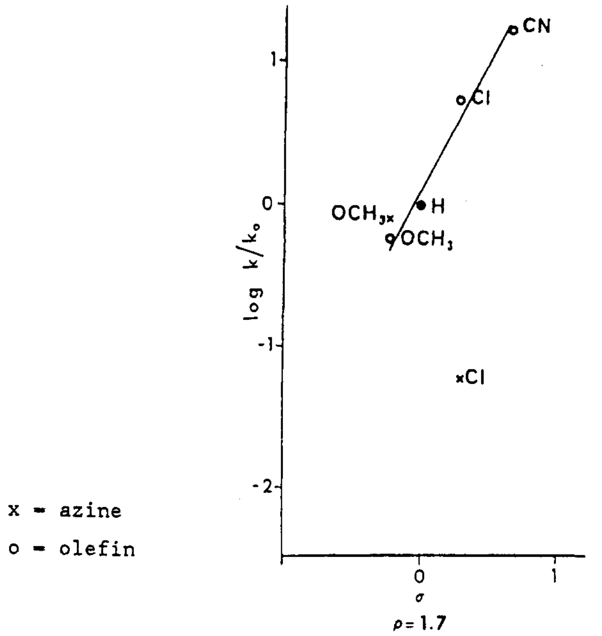
Table I. Final Yields for Reactions of Metalloazines and Aldehydes

	olefin,[a] %	azine,[a] %
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

[a] Determined by GC with internal standard.

mation;[3] no such trend exists for formation of the unsymmetrical azine.[5]

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 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[6] (but not necessarily in the one leading to olefin).



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

[a] Yield azine = 0.

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

Benzaldehyde and less easily reduced cyclohexanecarboxaldehyde ($E_{1/2} = -1.15$ V vs. -1.85 V vs. SCE for the analogue pentanal[7]) react with **1a** at comparable rates ($k_2 = 1.73 \times 10^{-2}$ vs. 4.81×10^{-2} M min^{-1}), 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.[8] Control of product distributions of olefins and azines is now undergoing study in order to make zirconium "metalloazines" useful as reagents for organic synthesis.

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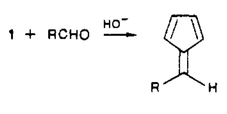
(3) We find that the electronegativity of the metal center also is related to olefin formation. The analogous Ti complex $[CpTi(Cl)\text{-}NNCHPh]_2$[4] prepared from $CpTiCl_3$ and $H_2NNCHPh$ reacts with cyclohexanone to give only the unsymmetrical azine.

(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



(6) (a) We thank a reviewer for bringing this to our attention. (b) Note the correlation with ν_{CO} for the substituted benzaldehydes (0.25 M in CCl_4): **5a**, 1701 cm^{-1}; **5b**, 1708 cm^{-1}; **5c**, 1712 cm^{-1}; **5d**, 1717 cm^{-1}.

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

(8) These trends correspond to a negative ρ value for Scheme I and a positive ρ value for Scheme II, analogous to the reaction[9] of $X\text{-}C_6H_4COCl$ and $X\text{-}C_6H_4NH_2$ 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; $C_6H_{11}CH_3$, 2043-61-0; *P*-$(OCH_3)C_6H_4COH$, 123-11-5; PhCHO, 100-52-7; *p*-ClC_6H_4CHO, 104-88-1; *p*-$(CN)C_6H_4CHO$, 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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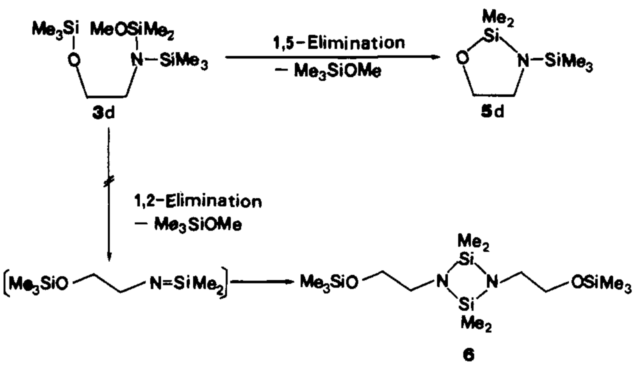
Summary: The vacuum sealed tube thermolyses of $Me_3SiOCH_2CH_2NRSiMe_2(OMe)$ (R = Me, Ph, $SiMe_3$) gave new heterocyclic compounds, 2,2,3-trimethyl-2-siloxazolidine, 2,2-dimethyl-3-phenyl-2-siloxazolidine, and 2,2-dimethyl-3-(trimethylsilyl)-2-siloxazolidine, through the 1,5-elimination of trimethylmethoxysilane, 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,[1] although 2-siloxazolidones[2] and 2,2-dimethyl-3-oxa-2-silaindoline[3] 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 could be formed from a ring-closure reaction through an intramolecular transalkoxylation,[4] 1-(trimethylsiloxy)-2-(*N*-substituted-*N*-(methoxydimethylsilyl)amino)ethanes (**3a–d**) were prepared. The reactions of dimethylmethoxychlorosilane (**2**) with (2-(*N*-substituted amino)ethoxy)trimethylsilanes (**1a** and **1b**) gave compounds **3a**[5] and **3b**[6] in 48 and 49% yields, respectively (eq 1). Compounds **3c**[7] and **3d**[8] 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).

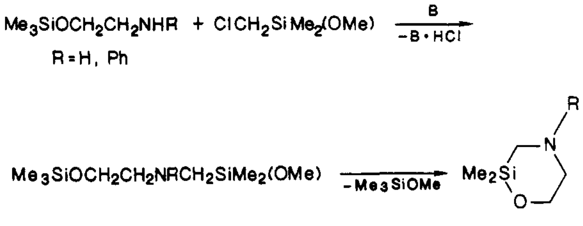
Scheme I



$$\underset{\substack{\mathbf{1a},\ R = H\\ \mathbf{1b},\ R = Me}}{Me_3SiOCH_2CH_2NHR} + \underset{\mathbf{2}}{Me_2Si(OMe)Cl} \xrightarrow[-B\cdot HCl]{B} \underset{\substack{\mathbf{3a},\ R = H\\ \mathbf{3b},\ R = Me}}{Me_3SiOCH_2CH_2NRSiMe_2(OMe)} \quad (1)$$

$$\underset{\substack{\mathbf{1c},\ R = Ph\\ \mathbf{1d},\ R = SiMe_3}}{Me_3SiOCH_2CH_2NHR} \xrightarrow[\text{ii. } Me_2Si(OMe)Cl,\ 0\ °C]{\text{i. } n\text{-BuLi, } -78\ °C} \underset{\substack{\mathbf{3c},\ R = Ph\\ \mathbf{3d},\ R = SiMe_3}}{Me_3SiOCH_2CH_2NRSiMe_2(OMe)} \quad (2)$$

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.[4] In contrast, Zhdanov and co-workers[4] 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.



(3)

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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

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[1] Mehrotra, R. C.; Bajaj, P. *J. Organomet. Chem.* **1970**, *24*, 611–621. Mehrotra, R. C.; Bajaj, P. *J. Organomet. Chem.* **1970**, *25*, 359–365.

[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. *Muánya* 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); ^1H NMR (CCl_4) δ 0.01 (s, 6 H), 0.02 (s, 9 H), 1.2 (s, 1 H), 2.83 (d of t, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 8.2 Hz, 2 H), 3.39 (s, 3 H), 3.51 (t, $^3J_{HH}$ = 5.5 Hz, 2 H).

[6] Compound **3b**: bp 80–81 °C (10 torr); ^1H NMR (CCl_4) δ 0.05 (s, 6 H), 0.08 (s, 9 H), 2.52 (s, 3 H), 2.85 (t, $^3J_{HH}$ = 6.0 Hz, 2 H), 3.33 (s, 3 H), 3.52 (t, $^3J_{HH}$ = 6.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −2.94, 0.00, 35.08, 50.08, 53.01, 61.49. Anal. Calcd for $C_9H_{25}O_2NSi_2$: 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); ^1H NMR (CCl_4) 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); ^{13}C NMR ($CDCl_3$) δ −1.42, 0.05, 49.88, 50.38, 61.70, 121.26, 121.74, 129.51, 148.70. Anal. Calcd for $C_{14}H_{27}O_2NSi_2$: C, 56.51; H, 9.15; N, 4.71. Found: C, 56.45; H, 9.08; N, 4.74.

[8] Compound **3d**: bp 79–80 °C (4 torr); ^1H NMR (CCl_4) 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); ^{13}C NMR ($CDCl_3$) δ −1.02, 0.00, 1.24, 45.88, 50.00, 65.51. Anal. Calcd for $C_{11}H_{31}O_2NSi_3$: C, 44.99; H, 10.64; N, 4.77. Found: C, 44.60; H, 10.99; N, 4.79.

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