Table I. Asymmetric Synthesis of 2-Alkanols through Catalytic Asymmetric Hydrosilylation of 1-Alkenes^{a}

entry	ligand (X in **1**)	1-alkene (**2**)	reactn conditns: temp, °C; time, h	yield^{b} of **3**, %	ratio^{c} of **3**/**3′**	yield^{d} of **5**, %	% ee^{e} (confign)	$[\alpha]_D$, deg (solvent)^{f}
1	**1a** (OMe)	n-$C_4H_9CH{=}CH_2$ (**2a**)	40; 24	91	89/11	70	94 (*R*)	−12.3 (*c* 5.06, EtOH)^{g}
2	**1a** (OMe)	n-$C_6H_{13}CH{=}CH_2$ (**2b**)	40; 24	83	93/7	71	95 (*R*)	
3^{h}	**1a** (OMe)	n-$C_6H_{13}CH{=}CH_2$ (**2b**)	40; 72	97	87/13	70	94 (*R*)	−10.3 (*c* 5.59, EtOH)^{g}
4^{i}	**1a** (OMe)	n-$C_6H_{13}CH{=}CH_2$ (**2b**)	40; 24	97	88/12		91 (*R*)	
5	**1a** (OMe)	n-$C_6H_{13}CH{=}CH_2$ (**2b**)	60; 16	93	89/11		86 (*R*)	
6	**1b** (OPr-*i*)	n-$C_6H_{13}CH{=}CH_2$ (**2b**)	40; 24	88	90/10		91 (*R*)	
7	**1c** (OCH_2Ph)	n-$C_6H_{13}CH{=}CH_2$ (**2b**)	40; 24	85	80/20		95 (*R*)	
8	**1d** (Et)	n-$C_6H_{13}CH{=}CH_2$ (**2b**)	40; 24	80	90/10		93 (*R*)	
9	**1a** (OMe)	n-$C_{10}H_{21}CH{=}CH_2$ (**2c**)	40; 72	90	94/6	75	95 (*R*)	−8.0 (*c* 8.10, EtOH)^{g}
10	**1a** (OMe)	$PhCH_2CH_2CH{=}CH_2$ (**2d**)	40; 24	90	81/19	68	97 (*S*)	+16.7 (*c* 2.40, $CHCl_3$)^{g}
11	**1a** (OMe)	c-$C_6H_{11}CH{=}CH_2$ (**2e**)	40; 24	100	66/34	45^{j}	96 (*R*)	−7.79 (*c* 3.10, Et_2O)^{j,k}

^{a} All reactions were run without solvent in the presence of palladium catalyst prepared in situ by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ and ligand (*S*)-MOP (**1**). The ratio of **2**/$HSiCl_3$/Pd/**1** is 1.0/1.2/0.001/0.002 unless otherwise noted. ^{b} Isolated yield of a mixture of **3** and **3′** by distillation. ^{c} Determined by GLC or ^1H NMR analysis of **3** (and **3′**) or **4** (and **4′**). ^{d} Isolated yield (overall from **2**) of regioisomerically pure alcohol **5**. ^{e} Determined by HPLC analysis of (3,5-dinitrophenyl)carbamate with a chiral column (see text). ^{f} Literature rotations for optically pure (*S*)-**5a**, (*S*)-**5b**, (*S*)-**5c**, (*S*)-**5d**, and (*S*)-**5e** are $[\alpha]_D$ +12.70° (EtOH) (ref 21), $[\alpha]_D$ +9.79° (EtOH) (ref 21), $[\alpha]_D$ +7.94° (EtOH) (ref 21), $[\alpha]_D$ +17.2° (chloroform) (Pikard, R. H.; Kenyon, J. *J. Chem. Soc.* **1914**, *105*, 1115), and $[\alpha]_D$ +8.43° (Et_2O) (Levene, P. A.; Mikeska, L. A. *J. Biol. Chem.* **1927**, *75*, 587), respectively. ^{g} Rotation at 25 °C. ^{h} Reaction with 0.01 mol % of the catalyst. ^{i} Ratio of P/Pd is 1/1. ^{j} Contaminated with 5% of 2-cyclohexylethanol. ^{k} Rotation at 20 °C.

phosphinylbinaphthyl **6**[16] by a sequence of reactions shown in Scheme II.[13,17]

The results obtained for the asymmetric synthesis of 2-alkanols **5** through the hydrosilylation of 1-alkenes **2** are summarized in Table I. All the olefins **2a–e** were transformed efficiently into the corresponding optically active alcohols **5** with enantioselectivity ranging between 94% and 97% ee (entries 1, 2, and 9–11) by the catalytic hydrosilylation–oxidation procedure, the selectivity being highest for the enantioface selection of simple terminal olefins.[1] The regioselectivity forming 2-(silyl)alkanes is surprisingly high[18,19] for the terminal olefins **5a–d** substituted with a primary alkyl group. Lower regioselectivity was observed with vinylcyclohexane (**2e**), which is substituted with a sterically bulky group on the double bond (entry 11). Ligands **1b–d** gave almost the same results as **1a**, indicating that the substituents at the 2′-position on ligand **1** did not have significant effects on the catalytic activity or the selectivity (entries 6–8). It should be noted that the palladium–MOP complex is highly catalytically active, the hydrosilylation taking place with 0.01 mol % of the catalyst (entry 3).

A practical procedure is given for the reaction of 1-octene (**2b**) (entry 3). A mixture of **2b** (2.81 g, 25 mmol), trichlorosilane (4.06 g, 30 mmol), $[PdCl(\pi\text{-}C_3H_5)]_2$ (0.46 mg, 0.0013 mmol, 0.01 mol % Pd), and (*S*)-(−)-MOP-OMe (**1a**, 2.34 mg, 0.005 mmol, 0.02 mol %) was kept stirred at 40 °C for 72 h. The reaction mixture was distilled (bulb-to-bulb) under reduced pressure to give 6.20 g (97% yield) of (trichlorosilyl)octane consisting of 2-silyl and 1-silyl isomers (**3b** and **3′b**, respectively) in a ratio of 87/13, which was converted quantitatively into (triethoxysilyl)octane **4b** (contaminated with regioisomer **4′b**) by treatment with ethanol (5 mL) and triethylamine (10 mL) in ether (600 mL). Oxidation of the triethoxysilane (H_2O_2/KF/$KHCO_3$/MeOH/THF) according to the procedure reported by Tamao[4] followed by removal of a small amount of 1-octanol resulting from **3′b** by the preferential complexation with calcium chloride[20] gave 2.28 g (70% from **2b**) of isomerically pure (*R*)-2-octanol (**5b**)[21] ($[\alpha]^{25}_D$ −10.3° (*c* 5.59, ethanol)). HPLC analysis of the (3,5-dinitrophenyl)carbamate of **5b** (ArNCO/pyridine/toluene) using a chiral stationary phase column (Sumichiral OA-1100, hexane/dichloroethane/ethanol = 100/20/1) demonstrated the enantiomeric purity to be 94%.

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Supplementary Material Available: Experimental details for the preparation of MOPs **1** and their analytical and spectroscopic data (3 pages). Ordering information is given on any current masthead page.

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(17) (*S*)-**1a**: $[\alpha]^{20}_D$ −94.5° (*c* 0.27, chloroform), $[\alpha]^{16}_D$ −59.7° (*c* 1.40, benzene) (ref 13: $[\alpha]^{16}_D$ −59.3° (*c* 1.0, benzene)). (*S*)-**1b**: $[\alpha]^{20}_D$ −90.0° (*c* 0.13, chloroform). (*S*)-**1c**: $[\alpha]^{20}_D$ −96.1° (*c* 0.12, chloroform). (*S*)-**1d**: $[\alpha]^{20}_D$ −85.1° (*c* 0.20, chloroform). Satisfactory spectral and elemental (±0.3% C, H) or MS analytical data were obtained for all compounds listed in Scheme II.

(18) The predominant formation of 2-alkylsilanes from aliphatic 1-olefins has never been observed with any transition-metal catalysts (ref 5).

(19) 3-Alkylsilanes, which would be produced by the hydrosilylation of internal olefins formed by isomerization, were not detected.

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A Highly Stereoselective Olefination of Aldehydes Using New Zinc and Zirconium 1,1-Bimetallic Reagents

Charles E. Tucker and Paul Knochel*

The Willard H. Dow Laboratories
Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48109

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The olefination of carbonyl derivatives by transition metal alkylidene complexes has been one of the most important applications of transition metal chemistry oriented toward organic synthesis.[1] One of the major drawbacks of this methodology has been the extension of the useful reactivity of the methylene transfer reagent $Cl(Cp)_2TiCH_2AlMe_2$[1a-i] to more substituted heterobimetallics. We wish to report a general solution to this problem using new *substituted and highly functionalized* zinc and zirco-

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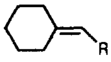
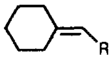
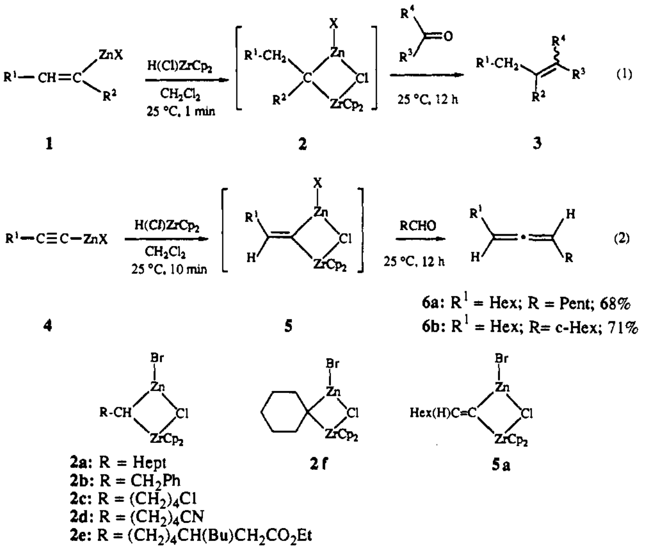
Table I. Preparation of (*Z*)-Polyfunctional Olefins **3** by the Reaction of Aldehydes with the 1,1-Bimetallic Reagents of Zinc and Zirconium **2a–f**

1,1-bimetallic reagent **2**	aldehyde	product of type **3**	*E*:*Z* ratio	yield, %
2a	c-Hex-CHO	c-Hex-CH=CH-Hept (**3a**)	100:0	83
2a	Pent-CHO	Pent-CH=CH-Hept (**3b**)	100:0	73
2a	$MeO_2C(CH_2)_4CHO$	$MeO_2C(CH_2)_4$-CH=CH-Hept (**3c**)	100:0	46
2b	Pent-CHO	$Pent-CH=CHCH_2Ph$ (**3d**)	100:0	89
2c	c-Hex-CHO	$c-Hex-CH=CH(CH_2)_4Cl$ (**3e**)	100:0	64
2d	c-Hex-CHO	$c-Hex-CH=CH(CH_2)_4CN$ (**3f**)	94:6	55
2e	c-Hex-CHO	$c-Hex-CH=CH(CH_2)_4CH(Bu)CH_2CO_2Et$ (**3g**)	97:3	58
2f	PhCHO	 ; R = Ph		83
2f	c-Hex-CHO	 ; R = c-Hex		76

Scheme I



6a: R^1 = Hex; R = Pent; 68%
6b: R^1 = Hex; R= c-Hex; 71%

2a: R = Hept
2b: R = CH_2Ph
2c: R = $(CH_2)_4Cl$
2d: R = $(CH_2)_4CN$
2e: R = $(CH_2)_4CH(Bu)CH_2CO_2Et$

nium 1,1-bimetallic reagents. In the course of our continuing studies on the reactivity of 1,1-bimetalloalkanes of zinc and magnesium,[2] we needed a more general preparation of these reagents[3] allowing the access to a variety of carbon skeletons. Our attention was drawn to the pioneering work of J. Schwartz,[1j–l,4] who demonstrated that various alkenyl organometallics can be hydrometallated leading to several new classes of 1,1-bimetallic reagents. Unfortunately, they did not display a high reactivity and showed a low stereoselectivity in olefination reactions. We have now found that the hydrozirconation of alkenylzinc halides **1** by Schwartz's reagent[5] $H(Cl)ZrCp_2$ *proceeds very smoothly in dry dichloromethane* (25 °C, 1 min) affording the zinc and zirconium 1,1-bimetallic reagents tentatively depicted as **2** (eq 1). These reagents are unstable and decompose after 10 min at 25 °C;[6] however, if a carbonyl derivative such as an aldehyde or a ketone is added immediately after the generation of **2**, then a smooth olefination reaction takes place (25 °C, 12 h) affording an olefin of type **3** in good yields. Thus, the addition of (*Z*)-octenylzinc bromide, prepared by the addition of dry zinc bromide to the corresponding alkenylmagnesium bromide, to $H(Cl)ZrCp_2$ in dry dichloromethane affords a yellow solution of the reagent **2a**. Similarly, a variety of alkenylzinc halides[7] were converted to the corresponding 1,1-bimetallic reagents (**2b–e**). The hydrozirconation reaction shows a remarkable chemoselectivity, and functional groups such as a chloride, cyanide, or ester functionality are tolerated allowing a unique preparation of highly functionalized 1,1-bimetallic reagents. The addition of cyclohexanecarboxaldehyde (0.9 equiv) to **2a** leads to the instantaneous disappearance of **2a** and after 12 h at 25 °C to the formation of (*E*)-1-nonenylcyclohexane as the pure *E*-isomer in 83% yield. Hexanal is converted by **2a** to 100% pure (*E*)-6-tetradecene (73% yield),[8] whereas methyl 6-oxohexanoate[9] reacts chemoselectively with **2a** furnishing the (*E*)-unsaturated ester **3c** (100% *E*) in 46% yield (Table I). The reaction of **2b–f** with aldehydes proceeds with similar high (*E*) selectivities and fair to good yields (49–89%). Ketones such as acetophenone, cyclohexanone, cyclohexenone, or 5,5-dimethyl-3-iodo-2-cyclohexane[9] react readily with **2a** providing 2-phenyl-2-decene (70%; *E*/*Z* 86/14), 1-octylidenecyclohexane (85%), 1-octylidene-2-cyclohexene (82%; *E*/*Z* 1/1), and 5,5-dimethyl-3-iodo-1-octylidene-2-cyclohexene (39%; *E*/*Z* 1/2), respectively. A 1,2-ketoester such as menthyl phenylglyoxylate reacts chemoselectively with **2a** giving Hept-(H)C=C(Ph)-CO_2-menthyl in 87% yield (*E*/*Z* 14/86). Alkynylzinc bromides **4** are also cleanly hydrozirconated by $H(Cl)ZrCp_2$ under our reaction conditions (CH_2Cl_2, 25 °C, 10 min) leading to the 1,1-bimetalloalkenes of zinc and zirconium **5** which react smoothly with aldehydes affording allenes **6** (25 °C, 12 h) in satisfactory yields (eq 2).[1o,10] The olefination of esters such as ethyl benzoate with the reagents **2** did not occur even by performing the reaction

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(6) The hydrolysis of **2a** affords *n*-octane as indicated by GLC analysis and by mass spectrometry. After 10 min at 25 °C, ca. 75% of **2a** has decomposed and the GLC analysis shows a mixture of octane and octene in small amounts (ca. 25%).

(7) The polyfunctional zinc halides **1** required for the preparation of **2c–e** were obtained from the corresponding functionalized alkenyl iodides. Thus, 5-chloro-1-iodopentene (1 equiv) in pentane was treated at −95 °C with BuLi (1.1 equiv) followed after 5 min by the addition of a THF solution of ZnI_2 (1.1 equiv) below −90 °C. Remarkably, this simple procedure can be applied to the preparation of alkenylzinc iodides bearing a cyanide group or an ester function such as **1d** and **1e** which were used for the preparation of **2d** and **2e** (Supplementary Material).

(8) Typical procedure—Preparation of (*E*)-6-tetradecene: A three-necked flask equipped with a gas inlet and a thermometer was charged under argon with dry $ZnBr_2$ (1.13 g, 5 mmol) in 5 mL of dry THF. After cooling to −50 °C, (*Z*)-1-octenylmagnesium bromide (5 mmol; 0.63 M THF solution; *E*/*Z* 15:85) was added dropwise. After warming to 25 °C, the THF was removed under vacuum and replaced by 10 mL of dry CH_2Cl_2. After dissolution, $Cp_2Zr(H)Cl$ (1.29 g, 5 mmol) in 8 mL of CH_2Cl_2 was added at once, followed immediately by hexanal (0.45 g, 4.5 mmol) in 3 mL of CH_2Cl_2. The resulting yellow solution was stirred 14 h at 25 °C. After the usual workup and evaporation of the solvents, the resulting residue was purified by flash chromatography (solvent: hexane) yielding 0.64 g (73% yield) of pure (*E*)-6-tetradecene (purity analysis by GLC).

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in the presence of a base (pyridine).[12]

Interestingly, the olefination of alkylidenemalonates[2d] with the 1,1-bimetallics **2** is also possible and the reaction of diethyl benzylidenemalonate (0.9 equiv) with **2a** in the presence of acetic anhydride (5 equiv, 25 °C, 0.5 h) gives cleanly 1-phenyl-1-nonene (78%; *E*/*Z* 65/35).

In summary, we have shown that zinc and zirconium heterobimetallic reagents of type **2** and **5** can be readily prepared by hydrozirconation. The reaction of organometallics **2** with aldehydes produces *with high stereoselectivity* (*E*)-disubstituted olefins whereas ketones give a *E*/*Z* mixture of stereoisomers. These new zinc and zirconium 1,1-bimetallic reagents show a good functional group compatibility and should become useful reagents for organic synthesis. The determination of the structure and the synthetic scope of these reagents is underway in our laboratories.[13]

Acknowledgment. We thank the National Science Foundation (Grant CHE-8818704), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of Michigan (Office of the Vice President for Research) for support of this research.

Supplementary Material Available: Spectra for new compounds (17 pages). Ordering information is given on any current masthead page.

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Electron Transfer vs Polar Mechanisms. Transition-State Structures and Properties for Reactions of a Cation Radical and a Nucleophile

Jeoung Ki Cho and Sason Shaik*

Department of Chemistry, Ben-Gurion University
Beersheva 84105, Israel

Received April 29, 1991

In response to the intense interest in the mechanistic dichotomy of polar vs electron transfer (ET) pathways in organic reactions,[1] and in a followup to our recent analysis of this dichotomy in reactions of radical ions,[2] we present for the first time ab initio computations of *the isomeric polar and ET transition states* for a nucleophile–electrophile pair modeled by H_2S and $C_2H_6^{\bullet+}$, the latter being in its one-electron σ-bond structure,[3] in eqs 1 and 2.[4] The computations show that the ET-TS does not follow the outer-sphere paradigm but is *inner-sphere and stereoselective* much like its isomer TS of the substitution (SUB-TS) pathway!

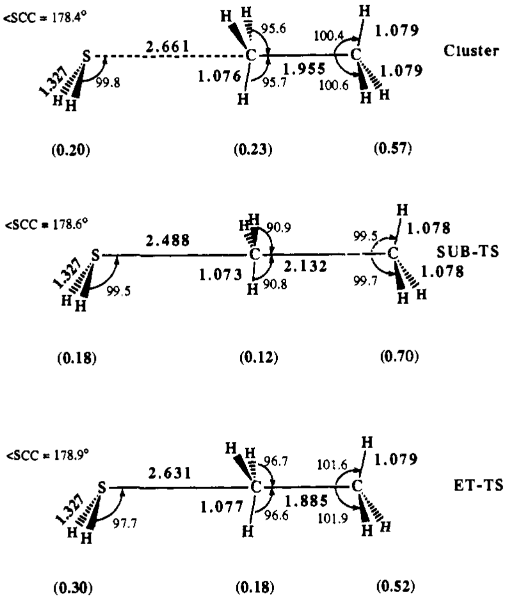
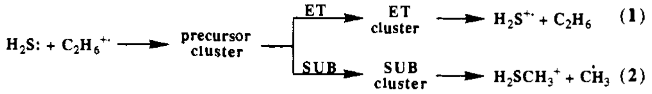


Figure 1. 3-21G*(p) optimized geometries for baskside precursor cluster, substitution TS (SUB-TS), and electron transfer TS (ET-TS). Group spin densities are shown in parentheses below their respective fragments. The $\langle S^2 \rangle$ values are 0.771 (Cluster), 0.775 (SUB-TS), and 0.773 (ET-TS).



The various species in eqs 1 and 2 were computed with the GAUSSIAN 86 and 88 series of programs,[5] using a 3-21G*(p) basis set. The basis set is the standard 3-21G* augmented with first-row polarization functions, taken from the 6-31G* basis set,[6] in order to achieve equivalent cation radical geometries obtained with the latter basis set.[7] Isotope effects were computed with Eyring's equation and analyzed in terms of the contributing components: masses and moments of inertia, excitation, and zero-point energy.[8] All geometries were gradient optimized at the UHF level and characterized by frequency analysis. The interconnection that exists between the critical points in a given pathway were ascertained following ref 9.

The UHF/3-21G*(p) optimized geometries and group spin densities of the lowest energy transition states for the ET and SUB pathways and their *common* ancestor precursor cluster are shown in Figure 1. Table I shows[10] corresponding energetics and

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[1] For a sample of leading references, see: (a) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; *Springer Verlag*: Heidelberg, 1987. (b) Bank, S.; Noyd, D. A. *J. Am. Chem. Soc.* **1973**, *95*, 8303. (c) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212. (d) Kochi, J. K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1227. (e) Chanon, M.; Tobe, M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 1. (f) Chanon, M. *Bull. Chim. Soc. Fr.* **1982**, *209*. (g) Newcomb, M.; Curran, D. P. *Acc. Chem. Res.* **1988**, *21*, 206. (h) Ashby, E. C. *Acc. Chem. Res.* **1988**, *21*, 414. (i) Verhoeven, W. J.; Gersheim, W. V.; Martens, F. M.; van der Kerk, S. M. *Tetrahedron* **1986**, *42*, 975. (j) Lund, T.; Lund, H. *Tetrahedron Lett.* **1986**, *27*, 95. Lund, T.; Lund, H. *Acta Chem. Scand.* **1988**, *B42*, 269.

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