phosphine (22 μmol) in H_2O (3 mL) in a Schlenk tube was stirred under argon for 1 h. The tube was attached to the vacuum line, and hydrogen was admitted. The tube was then agitated at room temperature under a positive pressure of hydrogen for 2 h. The hydrogen was then removed, the tube sealed under argon, and the ^{31}P NMR spectrum recorded.

Tetrasulfonated BDPP Rhodium(I) Adduct of (*Z*)-α-Acetamidocinnamic Acid, 12. The aqua complex **10** was prepared as above from **4d** (78 mg, 20 μmol) in H_2O (3 mL). This solution was carefully transferred under argon into an NMR tube containing (*Z*)-α-acetamidocinnamic acid (30 mg, 30 μmol) in water (0.5 mL). The tube was sealed under argon and the ^{31}P NMR spectrum recorded.

Hydrogenation. $[Rh(COD)Cl]_2$ and an appropriate amount of the sulfonated phosphine were mixed together in water (5 or 10 mL) for 2 h. This solution was added to the unsaturated substrate dissolved in the organic solvent (ethyl acetate, methylene chloride, or benzene). The two-phase liquid mixtures were transferred to hydrogenation apparatus and shaken until absorption of the theoretical amount of hydrogen when working under atmospheric pressure or for 12 h when working under hydrogen pressure. The organic phase was separated, and in the case of recycling, a solution of the unsaturated substrate was again injected into the apparatus. After reaction, the organic solvent was evaporated, the reaction products were analyzed by ^1H NMR, and the ee was determined by polarimetry using the following rotations for the optically pure compounds: *N*-acetyl-(*S*)-phenylalanine, $[\alpha]^{20}_D = +46.0°$ ($c = 1$, EtOH);[56] *N*-acetyl-(*S*)-phenylalanine methyl ester, $[\alpha]^{20}_D = 101.3°$ ($c = 1$, $CHCl_3$);[57] *N*-benzoyl-(*S*)-phenylalanine, $[\alpha]^{20}_D = -40.3°$ ($c = 1$, MeOH);[53] *N*-acetyl-3-(4-acetoxy-3-methoxyphenyl)-(*S*)-alanine, $[\alpha]^{20}_D = 40.7°$ ($c = 1$, MeOH);[58] (*S*)-methylsuccinic acid dimethyl ester, $[\alpha]^{20}_D = 6.75°$ ($c = 6$, EtOH);[59] *N*-acetyl-(*S*)-phenyl-1-propylamine, $[\alpha]^{20}_D = -137.8°$ ($c = 2.4$, MeOH);[60] (*R*)-1-phenylethyl-*N*-benzylamine, $[\alpha]^{20}_D = +56.2°$ ($c = 1.07$, EtOH);[61] (*S*)-1-phenylethanol, $[\alpha]^{20}_D = -52.5°$ ($c = 2.27$, CH_2Cl_2).[62]

Registry No. **1**, 72689-88-4; **2a**, 117897-88-8; **2b**, 117957-31-0; **2c**, 117957-32-1; **2d**, 102806-81-5; **3**, 77876-39-2; **4a**, 117897-89-9; **4b**, 117897-90-2; **4c**, 117897-91-3; **4d**, 117957-30-9; **5**, 64896-28-2; **6a**, 117897-92-4; **6b**, 117897-93-5; **6c**, 117897-94-6; **6d**, 102806-82-6; **6d**(oxide), 118013-34-6; **7**, 67884-32-6; **8a**, 117897-95-7; **8b**, 117897-96-8; **8c**, 117897-97-9; **8d**, 117897-87-7; **8d**(oxide), 117897-98-0; [**10**(P-P = **2d**)]$^+$, 117939-75-0; [**10**(P-P = **4d**)]$^+$, 117939-79-4; [**11**(P-P = **4d**)]BF_4, 117939-81-8; [**12**(P-P = **4d**)]$^+$, 117939-82-9; **13a**, 55065-02-6; **13b**, 60676-51-9; **13c**, 26348-47-0; **13d**, 55739-56-5; (*R*)-**14a**, 10172-89-1; (*S*)-**14a**, 2018-61-3; (*R*)-**14b**, 21156-62-7; (*S*)-**14b**, 3618-96-0; (*R*)-**14c**, 37002-52-1; (*S*)-**14c**, 2566-22-5; (*R*)-**14d**, 33043-31-1; (*S*)-**14d**, 31269-52-0; **15**, 617-52-7; **16**, 97305-96-9; **17**, 98-86-2; **18**, 14428-98-9; $[Rh(C_2H_4)_2Cl]_2$, 12122-73-5; $[Rh(COD)Cl]_2$, 12092-47-6; $[Rh(COD)_2]PF_6$, 62793-31-1; $[Rh(NBD)_2]BF_4$, 36620-11-8; $[Rh(C_2H_4)_2$(**2d**)$]^+$, 117939-73-8; [Rh(COD)(**2d**)]$^+$, 117939-74-9; [Rh(COD)(**2d**)](PF_6), 118015-57-9; [Rh(COD)(**4d**)]$^+$, 117939-76-1; [Rh(NBD)(**4d**)]BF_4, 117939-78-3; [Rh(COD)(**3d**)]$^+$, 117939-83-0; (*R*)-$CH_3CH(CO_2Me)CH_2CO_2CH_3$, 22644-27-5; (*S*)-$CH_3CH(CO_2Me)CH_2CO_2Me$, 63163-08-6; (*R*)-$PhCH(NHCCO)CH_3)CH_2CH_3$, 57680-92-9; (*S*)-$PhCH(NHCOCH_3)CH_2CH_3$, 20306-86-9; (*S*)-$PhCH(OH)CH_3$, 1445-91-6; (*R*)-$PhCH(CH_3)NHCH_2Ph$, 38235-77-7.

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Communications

Synthesis and Characterization of Binuclear Zirconocenophane Hydrides. The Molecular Structure of $[SiMe_2(C_5H_4)_2][(\eta^5\text{-}C_5H_5)ZrCl(\mu\text{-}H)]_2$

Karuna P. Reddy and Jeffrey L. Petersen*

Department of Chemistry, West Virginia University
Morgantown, West Virginia 26506-6045

Received August 18, 1988

Summary: The reactions of $[SiMe_2(C_5H_4)_2][(C_5H_5)ZrCl_2]_2$ and $[SiMe_2(C_5H_4)_2][(C_5H_5)ZrCl]_2(\mu\text{-}O)$ with stoichiometric amounts of $LiAl(O\text{-}t\text{-}Bu)_3H$ and $LiAlH_4$, respectively, in THF afford convenient routes for the preparation of the corresponding binuclear zirconocenophane hydrides $[SiMe_2(C_5H_4)_2][(C_5H_5)ZrCl(\mu\text{-}H)]_2$ (**1**) and $[SiMe_2(C_5H_4)_2][(C_5H_5)ZrH(\mu\text{-}H)]_2$ (**2**). The molecular structure of **2** has been established by X-ray diffraction. Preliminary results obtained from reactivity studies of **1** with C_2H_4 and ^{13}CO are described.

The bridged bis(cyclopentadienyl) ligand $[X(C_5R_4)_2]^{2-}$ [$X = (CH_2)_n$ (n = 1–3), $SiMe_2$; R = H, Me] has been employed as both a chelating[1] and a bridging[2] ligand in organometallic chemistry. An effort has been undertaken in our laboratories to prepare binuclear zirconocenophane

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hydride complexes in which two electron-deficient d^0 Zr(IV) centers are held in close proximity by a $[X(C_5H_4)_2]^{2-}$ ligand. Wailes, Weigold, and co-workers[3] originally prepared the organozirconium hydride complexes $[(C_5H_5)_2ZrHL]_x$ (L = Cl, H) by the reaction of zirconocene dichloride with $LiAl(O\text{-}t\text{-}Bu)_3H$ and by the treatment of $[(C_5H_5)_2ZrCl]_2O$ with an equimolar amount of $LiAlH_4$, respectively. Although the reactivity displayed by these and related zirconocene hydrides has been examined extensively,[4] the inherent insolubility of $[(C_5H_5)_2ZrHL]_x$ has hindered efforts to determine their molecular structures. Our X-ray diffraction analyses of $[(C_5H_4R)_2ZrH(\mu\text{-}H)]_2$ (R = Me,[5a] CMe$_3$[5b]) have confirmed unequivocally the presence of bridging and terminal hydrides in these related binuclear zirconium complexes. Herein, we present the synthesis and characterization of two new binuclear zirconocenophane hydride complexes, $[SiMe_2(C_5H_4)_2][(C_5H_5)ZrCl(\mu\text{-}H)]_2$ (1) and $[SiMe_2(C_5H_4)_2][(C_5H_5)ZrH(\mu\text{-}H)]_2$ (2). The molecular structure of 1 and preliminary results of its reactivity with C_2H_4 and CO are described.

The addition of two equivalents of $LiAl(O\text{-}t\text{-}Bu)_3H$ to a THF solution of $[SiMe_2(C_5H_4)_2][(C_5H_5)ZrCl_2]_2$[6] affords 1, whereas the reaction of 1 equiv of $LiAlH_4$ with $[SiMe_2(C_5H_4)_2][(C_5H_5)ZrCl]_2(\mu\text{-}O)$[6] provides a convenient route to 2. Both of these zirconocenophane hydride complexes are sparingly soluble in benzene and have been characterized by elemental analysis, hydrolysis, and infrared and ^1H NMR measurements.[8] The Zr–H stretching frequencies of 1390 cm^{-1} for 1 and 1310 and 1535 cm^{-1} for 2 are comparable to those reported for $[(C_5H_5)_2ZrHL]_x$.[3] The hydride resonance in the ^1H NMR spectrum of 1 is a singlet at δ −0.06, whereas the two hydride resonances of 2 appear as two apparent triplets at δ 3.61 and −3.89, consistent with the presence of two bridging and two terminal hydride ligands.[5]

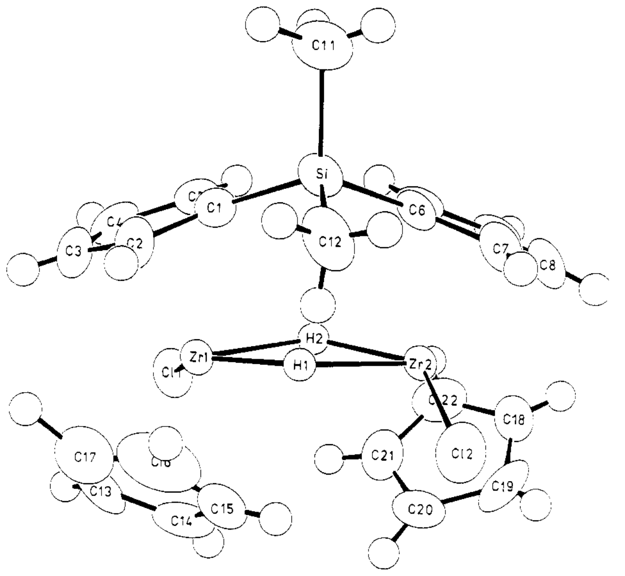

Figure 1. A perspective view of the molecular configuration of $[SiMe_2(C_5H_4)_2][(\eta^5\text{-}C_5H_5)ZrCl(\mu\text{-}H)]_2$ with the atom-labeling scheme for the non-hydrogen atoms. The thermal ellipsoids were scaled to enclose 50% probability. For clarity the radii of the spheres for the hydrogen atoms were reduced arbitrarily. Pertinent interatomic distances (Å) and angles (deg) within the $[ZrCl(\mu\text{-}H)]_2$ core: Zr1–Cl1, 2.526 (1); Zr2–Cl2, 2.521 (1); Zr1–H1, 1.75 (4); Zr1–H2, 2.05 (4); Zr2–H1, 2.08 (4); Zr2–H2, 1.84 (4); Zr1···Zr2, 3.4502 (5); H1–Zr1–H2, 53 (1); H1–Zr1–Cl1, 127 (1); H2–Zr1–Cl1, 77 (1); H1–Zr2–H2, 52 (1); H2–Zr2–Cl2, 128 (1); H1–Zr2–Cl2, 78 (1); Zr1–H1–Zr2; 128 (2); Zr1–H2–Zr2, 125 (2).

Direct structural information about the molecular configuration of 1 has been provided by an X-ray diffraction analysis.[9] The solid-state structure, as shown in Figure 1, illustrates that 1 exists as a discrete binuclear zirconium complex with two hydride ligands bridging the two Zr centers. The Zr···Zr separation of 3.4502 (5) Å is only 0.01 Å shorter than that found in $[(C_5H_4R)_2ZrH(\mu\text{-}H)]_2$.[5] The central $Zr_2Cl_2(\mu\text{-}H)_2$ moiety deviates significantly from planarity with a Cl1–Zr1···Zr2–Cl2 torsional angle of 36.9 (1)°. Presumably, this feature is a consequence of the bridging $[SiMe_2(C_5H_4)_2]^{2-}$ ligand, which prevents a mutually planar alignment of the three frontier orbitals[10] available for each of the two canted "zirconocene-like" centers. The relatively long Zr–Cl bonds of 2.523 Å (av) reflect the reduction of π-donation from the Cl p_π orbitals to the Zr atoms. Although the X-ray determined hydride positions are inherently inaccurate, they offer qualitative insight into the nature of the zirconium–hydride interactions. The Zr–H bonds arising from the interaction of each H 1s orbital with an *inner* Zr hybrid orbital are significantly longer than the Zr–H bonds which utilize one of the remaining *outer* Zr hybrid orbitals. The nonplanarity of the $Zr_2Cl_2(\mu\text{-}H)_2$ core leads to a less favorable orbital overlap for the internal Zr–H bonds, thereby producing asymmetric three-center, two-electron Zr–H–Zr bonding interactions in 1.

Reactivity studies of 1 have led to several interesting preliminary observations. The reaction of 1 equiv of ethylene with 1, for example, proceeds slowly at 85 °C with

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(8) (a) $[SiMe_2(C_5H_4)_2][(C_5H_5)ZrCl(\mu\text{-}H)]_2$: ^1H NMR (C_6H_6-d_6) δ 6.49, 6.09, 5.61, 5.26 (C_5H_4, m), 5.92 (C_5H_5, s), 0.37 ($SiCH_3$, s), −0.06 (Zr-H-Zr, s); IR (KBr disk) ν_{Zr-H} 1390 cm^{-1}; hydrolysis, hydride/Zr ratio = 0.95:1. Anal. Calcd for $Zr_2Cl_2SiC_{22}H_{26}$: C, 46.20; H, 4.58. Found: C, 46.01; H, 4.92. (b) $[SiMe_2(C_5H_4)_2][(C_5H_5)ZrH(\mu\text{-}H)]_2$: ^1H NMR (C_6H_6-d_6) δ 6.72, 5.90, 5.40, 4.88 (C_5H_4, m), 5.59 (C_5H_5, s), 3.61 (Zr–H, t, J_{H-H} = 7.5 Hz), 0.47 ($SiCH_3$, s), −3.89 (Zr-H-Zr, t, J_{H-H} = 7.5 Hz); IR (KBr disk) ν_{Zr-H} 1310, 1535 cm^{-1}; hydrolysis, hydride/Zr ratio = 1.94:1. Anal. Calcd for $Zr_2SiC_{22}H_{28}$: C, 52.53; H, 5.61. Found: C, 51.31; H, 6.04.

(9) Crystal data for $[SiMe_2(C_5H_4)_2][(C_5H_5)ZrCl(\mu\text{-}H)]_2$: space group $P2_1/c$, a = 13.282 (4) Å, b = 9.642 (2) Å, c = 17.896 (5) Å, β = 100.21 (2)°, V = 2256 (1) Å^3, Z = 4, d_{calcd} = 1.684 g/cm^3. All 2968 unique reflections ($\pm h,k,l$), which were collected on a Picker goniostat controlled by a Krisel Control automation system within a detector range of $5° < 2\theta < 45°$ with Zr-filtered Mo K_α radiation, were used in the structure determination. Data collection, reduction, and refinement procedures have been described previously.[5a] Full-matrix least-squares refinement (based on F_o^2) with anisotropic temperature factors for the 27 nonhydrogen atoms and isotropic temperature factors for the 26 hydrogen atoms converged with final discrepancy indices of $R(F_o)$ = 0.035, $R(F_o^2)$ = 0.043, and $R_w(F_o^2)$ = 0.069 with σ_1 = 1.62 for the 2668 data with $F_o^2 > \sigma(F_o^2)$.

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the evolution of ethane[11] and the formation of $[SiMe_2(C_5H_4)_2][(C_5H_5)Zr(\mu\text{-}Cl)]_2$ (**3**).[12] Alternatively, thermolysis of **1** in toluene at 130 °C quantitatively eliminates 1 equiv of H_2 within 12 h, producing only this diamagnetic binuclear Zr(III) species **3**.[13] The reaction of **1** with ^{13}CO at 85 °C proceeds with the reductive coupling of two molecules of ^{13}CO resulting in the formation of a cis enediolate bridge.[15] The 16-line ABXY splitting pattern[16] observed for this C_2 fragment in the gated-nondecoupled ^{13}C NMR spectrum, however, indicates an unsymmetrical mode of coordination which might correspond to one of the oxygen atoms being bound to both Zr atoms, such as ZrOC(H)=C(H)OZr. Current efforts are aimed at further evaluating the use of mechanically linked, binuclear zirconocene hydride complexes for the sequential hydrogenation or reductive coupling of these and related substrates.

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Supplementary Material Available: Summary of crystal data and data collection parameters and tables of positional and thermal parameters, interatomic distances and bond angles for hydrogen atoms, and least-squares planes of $[SiMe_2(C_5H_4)_2][(C_5H_5)ZrCl(\mu\text{-}H)]_2$ (10 pages); a listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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(11) Ethane was identified by GC/MS measurements (*m/e* 30) and by its characteristic proton resonance at δ 0.79 in $C_6H_6\text{-}d_6$.

(12) $[SiMe_2(C_5H_4)_2][(C_5H_5)Zr(\mu\text{-}Cl)]_2$: ^1H NMR ($C_6H_6\text{-}d_6$) δ 5.43 (proximal CH, t, $J_{H\text{-}H}$ = 2.56 Hz), 5.28 (distal CH, t, $J_{H\text{-}H}$ = 2.56 Hz), 5.20 (C_5H_5, s), 0.09 ($SiCH_3$, s); gated nondecoupled ^{13}C NMR (mult, $^1J_{C\text{-}H}$ in Hz) δ 114.2 (bridgehead C, s), 112.4 (proximal CH, dq, 164.8), 104.2 (distal CH, dq, 169.7), 103.3 (C_5H_5, d qt, 172.1), −0.66 ($SiCH_3$, q, 119.7); UV λ_{max} 474 nm. Anal. Calcd for $Zr_2Cl_2SiC_{22}H_{24}$: C, 46.36; H, 4.25. Found: C, 47.00; H, 4.51.

(13) A structurally similar binuclear fulvalene Zr(III) species, $(\eta^5{:}\eta^5\text{-}C_{10}H_8)[(C_5H_5)Zr(\mu\text{-}Cl)]_2$, has been prepared by the comproportionation of $(C_5H_5)_2ZrCl_2$ and $(C_5H_5)_2Zr(PMe_3)_2$.[14]

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(16) The two ^{13}C resonances appear at δ_A 136.9 and δ_B 130.8 with $^1J_{C\text{-}C}$ = 82.3 Hz. The corresponding proton coupling constants are $^1J_{C\text{-}H}$ = 178 Hz and $^2J_{C\text{-}H}$ = 20.4 Hz for carbon A, $^1J_{C\text{-}H}$ = 185 Hz and $^2J_{C\text{-}H}$ = 25.0 Hz for carbon B, and $^3J_{H\text{-}H}$ = 1.3 Hz.

A New Catalyst for the Efficient and Selective β-Hydrosilylation of Acrylonitrile. Effect of Ultrasound

Amirthini B. Rajkumar and Philip Boudjouk*

Department of Chemistry, North Dakota State University
Fargo, North Dakota 58105

Received September 20, 1988

Summary: The hydrosilylation of acrylonitrile to give exclusively the β-adduct was effected in yields of 70–100% under mild conditions using a new two-component catalyst system consisting of tetramethylethylenediamine and cuprous oxide. Ultrasonic waves significantly increase the rate of hydrosilylation over room-temperature stirring.

Table I. Hydrosilylation of Acrylonitrile Catalyzed by Cu_2O and Tetramethylethylenediamine

expt	silane	conditns[a]	product	yield,[b] %
1	$HSiCl_3$	10 min, reflux	$Cl_3SiCH_2CH_2CN$	95–100
2	$HSiCl_3$	2 h,)))	$Cl_3SiCH_2CH_2CN$	80
3	$HSiCl_3$	4 h, stir	$Cl_3SiCH_2CH_2CN$	30
4	$HSiMeCl_2$	45 min, reflux	$MeCl_2SiCH_2CH_2CN$	98–100
5	$HSiMeCl_2$	6 h,)))	$MeCl_2SiCH_2CH_2CN$	60
6	$HSiMeCl_2$	18 h, stir	$MeCl_2SiCH_2CH_2CN$	11
7	$HSiMe_2Cl$	24 h, reflux	no reaction	
8	$HSiMe_2Cl$	10 h,)))	no reaction	
9	$HSiMe_2Cl$	10 h, stir	no reaction	
10	$HSiPhCl_2$	30 min, reflux	$PhCl_2SiCH_2CH_2CN$	98–100
11	$HSiPhCl_2$	4 h,)))	$PhCl_2SiCH_2CH_2CN$	70–75
12	$HSiPhCl_2$	21 h, stir	$PhCl_2SiCH_2CH_2CN$	32
13	$HSiPh_2Cl$	24 h, reflux	$Ph_2ClSiCH_2CH_2CN$	5–10
14	$HSiPh_2Cl$	12 h, 12 h	no reaction	
15	$HSiPh_2Cl$	18 h, stir	no reaction	

[a] All reactions, except runs 1, 4, 7, 10, 13, and were run at 30 °C by using a 0.04:0.06:0.0069:0.019 mol ratio of acrylonitrile/silane/Cu_2O/TMEDA, while reactions 1, 4, 7, 10, and 13 were run with 0.04:0.05:0.0069:0.019 mol ratios. All reactions were run in the absence of solvent. [b] Yields are based on product isolated by distillation.

While there is an abundance of catalysts that are useful in promoting the addition of the Si–H bond across alkenes and alkynes,[1] relatively few agents efficiently catalyze the hydrosilylation of acrylonitrile. In particular, catalysts that lead to exclusively β-addition to the double bond in acrylonitrile are rare and generally give low yields. These include tertiary amines,[2] platinum on carbon,[3] Raney nickel,[4] amides,[5] and phosphines.[6]

The two most effective catalysts are a three-component system (CuCl/*n*-Bu_3N/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA)) developed by Bluestein which requires temperatures of 50–126 °C for 40 h to give 75% yields of β-adduct[7] (7.5:1:1.2 mol ratio of reactants/CuCl/amines) and a binary system of a copper compound (Cu_2O, CuCl, or $Cu(acac)_2$) and an isocyanide developed by Svoboda et al.,[8] which requires heating to 120 °C for 2 h to give 70–75% yields of β-adduct (9:0.1:0.3 mol ratio of reactants/Cu catalysts/isocyanide).

In this communication we report a new two-component catalyst consisting of cuprous oxide and TMEDA that promotes exclusively β-hydrosilylation of acrylonitrile in high yields under mild conditions. We also observed that ultrasound, which is often used to promote heterogeneous reactions,[9] is very effective in accelerating this reaction.

$$CH_2{=}CH{-}CN + R_3SiH \xrightarrow[Cu_2O,\ TMEDA]{)))} R_3Si{-}CH_2{-}CH_2CN$$

$$R_3 = Cl_3,\ Cl_2Me,\ Cl_2Ph,\ ClPh_2$$

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