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 $\mathrm{Zr\overline{OC(H)}\text{-}}\overline{\mathrm{=C(H)OZr}}$. 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-H} = 2.56 Hz), 5.28 (distal CH, t, J_{H-H} = 2.56 Hz), 5.20 (C_5H_5, s), 0.09 ($SiCH_3$, s); gated nondecoupled ^{13}C NMR (mult, $^1J_{C-H}$ 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 $^1J_{C-C}$ = 82.3 Hz. The corresponding proton coupling constants are $^1J_{C-H}$ = 178 Hz and $^2J_{C-H}$ = 20.4 Hz for carbon A, $^1J_{C-H}$ = 185 Hz and $^2J_{C-H}$ = 25.0 Hz for carbon B, and $^3J_{H-H}$ = 1.3 Hz.

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

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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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Table II. Comparison of the Rates of Hydrosilylation of Acrylonitrile with the Blustein Catalyst

catalyst	silane	conditns[a]	product	yield, %
Bluestein[7]	$HSiCl_3$	40 h, reflux	$Cl_3SiCH_2CH_2CN$	68
present work	$HSiCl_3$	1.5 h, reflux	$Cl_3SiCH_2CH_2CN$	90-95

[a] Both reactions were run by using a 7.5:1:1.2 mol ratio of acrylonitrile/copper catalyst/amine.

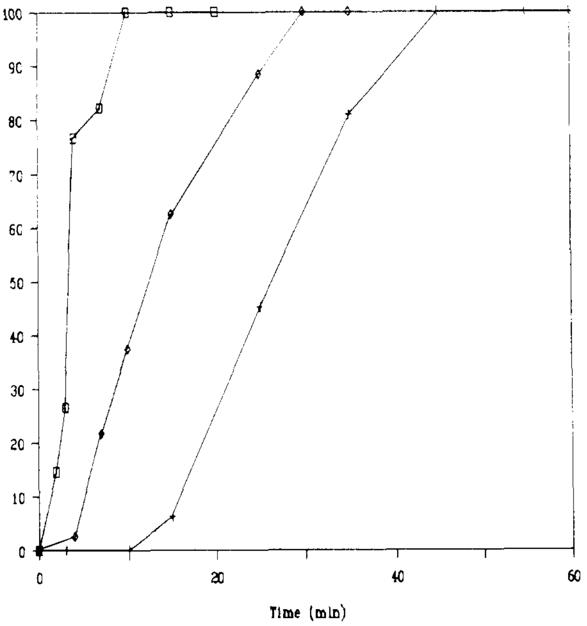

Figure 1. Hydrosilylation of acrylonitrile with $HSiCl_3$ (□), $HSiMeCl_2$ (+), and $HSiPhCl_2$ (◇) under refluxing conditions.

In a typical experiment, 1 g (0.0069 mol) of Cu_2O and 3 mL (0.019 mol) of TMEDA were placed in a 50-mL three-necked round-bottomed flask fitted with a dry ice condenser and a nitrogen inlet. The flask was cooled at 0 °C, and a mixture of 2.3 mL (0.04 mol) of acrylonitrile and 5.05 mL (0.05 mol) of trichlorosilane was added dropwise to the mixture. After the addition was complete, the reaction mixture was heated at reflux for 10 min. (β-Cyanoethyl)trichlorosilane was isolated by distillation (7.4 g, 98%; 60 °C (2 Torr)). The above reaction also was performed in a common ultrasonic laboratory cleaner (Bransonic Model 220), where the flask was positioned at a point that caused the most agitation in the flask. After 2 h of sonication, (β-cyanoethyl)trichlorosilane was collected by distillation (6.03 g, 80%; 60 °C (2 Torr)). Stirring at room temperature gave a 30% yield of (β-cyanoethyl)trichlorosilane (Table I).

To compare our catalyst more directly with the Bluestein catalyst system,[7] we used identical mole ratios of acrylonitrile, copper catalyst, and amine and found a >25-fold rate enhancement (Table II). The results summarized in Table II demonstrate that the functionalized silanes can add to acrylonitrile in good yield and the reactivity of silanes is in the order of $HSiCl_3 > HSiCl_2Ph$, $HSiCl_2Me \gg HSiClPh_2$. No product was observed when $HSiClMe_2$ was used as the silylating agent. Quantitative comparison is made in Figure 1 which shows that $HSiCl_3$ is 3 times more reactive than $HSiPhCl_2$ and 4 times as reactive as $HSiMeCl_2$ based on times required for completion of reaction. The effects of stirring at room temperature, refluxing at 70 °C, and ultrasonic irradiation at room temperature are compared in Figure 2 which shows that refluxing produces the fastest rates and that sonication is significantly faster than room-temperature stirring. Ultrasonic acceleration of reactions involving non-metals, while not as common as those examples in which metals are used, has been reported by several groups.[10] Increased reaction rates are attributed to increased surface area of the solid reagent from cavitation-induced particle size reduction and improved mass transport of liquid reagent to the solid surface via acoustic streaming. Reduction in catalyst affects the rate but not the yield. For example, when the Cu_2O/ TMEDA load is reduced to 10% of our normal runs, 4 h of refluxing are required to reach a 100% product yield.

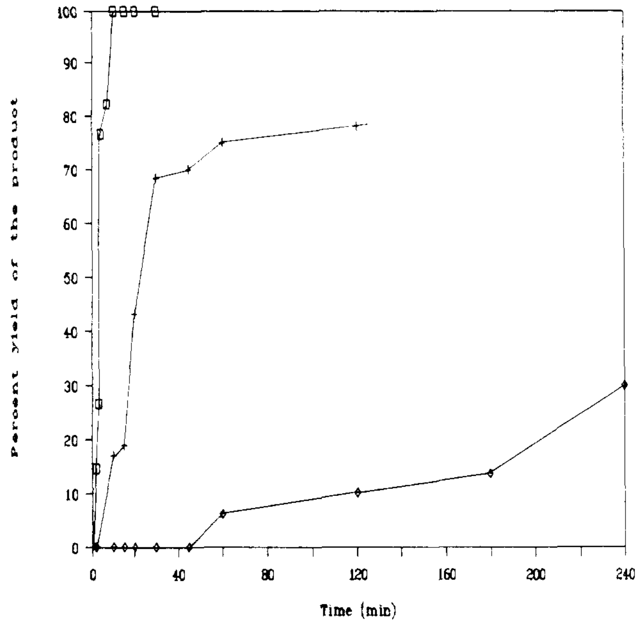

Figure 2. Hydrosilylation of acrylonitrile with $HSiCl_3$, Refluxing (□), ultrasound (+), and stirring (◇).

Cu_2O is recyclable. We found no decrease in the reactivity when product and TMEDA were removed from the flask by distillation, leaving Cu_2O, followed by recharging the vessel with TMEDA, silane, and acrylonitrile. The scope of this catalyst system can be extended to the hydrosilylation of acrylates.[11] We are pursuing that line of investigation and will report our progress in due course.

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Photochemical Skeletal Redistributions of Permethylated Linear and Cyclic Oligosilyl Groups in (η^5-C_5H_5)Fe(CO)$_2$-Substituted Oligosilanes

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Summary: Photochemical treatment of oligosilyl complexes (η^5-C_5H_5)Fe(CO)$_2$–oligosilyl which contain at least four silicon atoms results in very high-yield formation of

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