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A New Catalyst for Exclusive β-Hydrosilylation of Acrylonitrile

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Abstract: Acrylonitrile and 2-chloroacrylonitrile react with trichlorosilane in the presence of cobalt chloride and an amine to give the β-adduct in 75-95% yields under mild conditions.

Hydrosilylation of acrylonitrile with halosilanes leads to funtionalized monomers that are easily transformed to alkoxysilanes or organopolysiloxanes of industrial importance.[1] Of the many hydrosilylation catalysts, only a few promote exclusive β-addition of trichlorosilane or methyldichlorosilane to alkenes efficiently. Simple amine and phosphine bases are known to catalyze the β-hydrosilylation of acrylonitrile but require high temperatures and produce modest yields.[2] Typically, α-hydrosilylation of activated terminal olefins (such as acrylonitrile) is the preferred pathway for metal-based catalysts.[3] An important exception is the binary system of copper salts and N,N,N',N' tetramethylethylenediamine (TMEDA) which promotes exclusive β-hydrosilylation of acrylonitriles[4] and acrylates[5] in high yields under mild conditions. However, the methodology does suffer from the generation of solids that inhibit scale-up.

During the course of our effort to develop new catalysts with little or no precipitate, we discovered that $CoCl_2$ and amines will also catalyze exclusive β-hydrosilylation of functionalized olefins. The yields are high (75-95%) and only small quantities of solids are produced.

In a preparative scale experiment, oven dried anhydrous $CoCl_2$ (0.51 g, 4 mmol) and N,N,N'N'-tetramethylethylenediamine (TMEDA) (3 mL, 20 mmol) were dissolved in CH_3CN (5 mL) in a Schlenk tube. This mixture was cooled to –10°C, followed by the simultaneous addition of acrylonitrile (5.2 mL, 80 mmol) and trichlorosilane (12.1 mL, 120 mmol). The resulting mixture was refluxed at 70°C. The reaction was monitored by ^{29}Si and ^{1}H NMR. After 14h, the consumption of acrylonitrile was complete and a small amount of solid was observed. (β-cyanoethyl)trichlorosilane (13.6 g, 90%) was isolated by distillation (60°C, 2 torr) (eq). The results are summarized in the Table.

$$CH_2{=}CXCN \; + \; HSiCl_3 \; + \; CoCl_2\,/\,\text{TMEDA or DMF} \longrightarrow Cl_3SiCH_2CXHCN$$
$$X = H,\ Cl$$

The combination of cobalt chloride and amine is generally effective. The choice of amine is not restricted to TMEDA. Good yields can be obtained with tetraethylethylenediamine (TEEDA) or N,N-dimethylformamide (DMF). On the other hand 1,3-dimethyl-2-imidazolidinone (DMI) was ineffective under the same reaction conditions. Yields appear relatively independent of solvent concentration. Reduction in catalyst load slows the rate

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only slightly and does not diminish yield (entries 2,3). The small amount of solid left after distillation of the β-adduct from the reaction mixture is recyclable but the reaction rate was much slower (only 30% conversion of alkene occurred in 40h). As reported for the hydrosilylation of acrylonitriles in the presence of Cu_2O/TMEDA[4], after recharging the vessel with TMEDA, we found 10 fold increase in the catalytic activity of the solid. This experiment indicated that the metal residues could be recycled as catalyst and accentuates an added advantage of the $CoCl_2$ catalysis.

It is noteworthy that 2-chloroacrylonitrile shows increased reactivity towards trichlorosilane, forming β-adduct in 95% yield at room temperature in 24 h, whereas, methacrylonitrile is completely unreactive even after refluxing 20h at 70°C (entries 6,7).

Table : $CoCl_2$catalyzed hydrosilylation of acrylonitrile

Entry	Alkenes[a]	$CoCl_2$[b] (mmol)	Amine(mmol)	Conditions[c]	Product	Yield %[d]
1	CH_2=CHCN	1.4	TMEDA(4.0)	CD_3CN(0.5mL), 8h	$Cl_3SiCH_2CH_2CN$	92
2	CH_2=CHCN	0.4	TMEDA(2.0)	CH_3CN(15mL), 14h	$Cl_3SiCH_2CH_2CN$	90(85)
3	CH_2=CHCN	0.4	TEEDA(2.0)	CD_3CN(0.5mL), 10h	$Cl_3SiCH_2CH_2CN$	88
4	CH_2=CHCN	0.4	0	DMF(0.9mL),CD_3CN (2mL), 10h	$Cl_3SiCH_2CH_2CN$	75
5	CH_2=CHCN	0.4	0	DMI(0.5mL),CD_3CN (0.5mL),15h	No reaction	_
6	CH_2=CClCN	0.4	TMEDA(1.0)	CD_3CN(0.5mL), 24h	$Cl_3SiCH_2CHClCN$	95(75)
7	CH_2=C(Me)CN	0.4	TMEDA(4.0)	CD_3CN(0.5mL), 20h	No reaction	_

[a]In all cases the alkene / $HSiCl_3$ ratio was 8 mmol : 12 mmol. [b] Oven Dried (~120 °C). [c] Reactions were run at 70°C except for entry 6 which was run at 22°C. [d] Yields were determined by NMR spectroscopy. Yields in parenthesis are isolated yields.

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