Manganese Carbonyl Bromide-Catalyzed Alcoholysis of the Monohydrosilane $HSiMe_2Ph$

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Summary: The dimeric manganese carbonyl bromide $[Mn(CO)_4Br]_2$ *is an effective catalyst for the alcoholysis of dimethylphenylsilane in benzene at room temperature. Preparative scale procedures using a 1200:1200:1 mixture of alcohol,* $HSiMe_2Ph$*, and* $[Mn(CO)_4Br]_2$ *(0.084 mol %)* afforded samples of analytically pure alkoxysilanes in good yields. *tert*-Butyl alcohol, for example, gave $(CH_3)_3CO$-$SiMe_2Ph$ in 82% yield after a 35-min reaction time, and allyl and propargyl alcohols quantitatively transformed to their alkoxysilane derivatives, with no evidence of competing hydrosilation of the carbon–carbon multiple bonds. Competitive reactions involving 1:1:1 mixtures of 2-butanol–acetone–$HSiMe_2Ph$ and $[Mn(CO)_4Br]_2$ as catalyst exhibited chemoselective alcoholysis of dimethylphenylsilane. ^1H NMR spectral monitoring of catalyzed reactions between methanol or 2-butanol and $HSiMe_2Ph$ was used in screening other manganese carbonyl complexes as potential $HSiMe_2Ph$ alcoholysis catalysts. Their reaction times varied as follows: $[Mn(CO)_4Br]_2 > Mn(CO)_5Br \gg Mn(CO)_5CH_3 \approx Mn(CO)_5C(O)Ph > Mn(PPh_3)(CO)_4Br > Mn(PPh_3)(CO)_4C(O)CH_3 \gg Mn(CO)_5(SiMe_2Ph) \gg Mn_2(CO)_{10} \approx Rh(PPh_3)_3Cl$ (no reaction). Solvent-dependent turnover frequencies were determined for the $[Mn(CO)_4Br]_2$-catalyzed dehydrocoupling of 2-butanol and $HSiMe_2Ph$ for 0.289 M solutions of 2-butanol and $HSiMe_2Ph$ with 1.4 mol % precatalyst $[Mn(CO)_4Br]_2$: $N_t = 2183$ (THF), 2728 (C_6H_6), and 5457 h^{-1} (CH_2Cl_2). In a second procedure, a preparative-scale reaction in CH_2Cl_2 containing only 0.084 mol % precatalyst but 3.12 M for each reactant afforded a much higher turnover frequency of 11 217 h^{-1}.

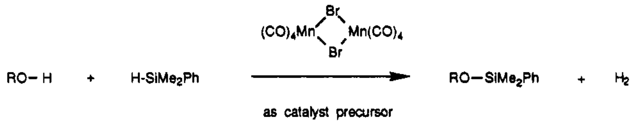
Introduction

A useful organotransition metal catalyst for alcoholysis of hydrosilanes to alkoxysilanes[1] should satisfy several criteria. The catalyst should be sufficiently active to dehydrogenatively couple even tertiary alcohols with the less reactive trialkylsilanes under mild, nonacidic and nonbasic conditions. This catalytic alcohol O-silation activity should be selective in the presence of competing functional groups such as carbon–carbon multiple bonds and carbonyl groups.[2] Further selectivity toward structurally different hydroxylic groups on the same molecule also would be desirable. Finally, a useful hydrosilane alcoholysis catalyst should be easily accessible and moderate in cost.

Of the relatively few transition metal complexes that are established silane alcoholysis catalysts, most are not active with trialkylsilanes.[1] Wilkinson's catalyst, $Rh(PPh_3)_3Cl$, only dehydrocondenses Et_3SiH and alcohols in refluxing benzene,[3,4] and Cp_2TiCl_2/*n*-BuLi[5] only effectively transforms di- and trihydrosilanes to alkoxysilanes. The more reactive catalysts $Co_2(CO)_8$,[6] $[IrCl(C_8H_{14})_2]_2$,[7] *cis*-$PtCl_2(PhCH{=}CH_2)_2$,[8] and $[IrH_2(THF)_2(PPh_3)_3]SbF_6$.[9] all competitively catalyze alkene hydrosilation or hydrogenation (H_2 is a byproduct of alcohol O-silation). Crabtree's catalyst, $[IrH_2(THF)_2(PPH_3)_3]SbF_6$, may be the most reactive, but $Ru(CO)_2(PMe_3)_2Cl_2$[10] and $Rh_2(O_2CC_3F_7)_4$[11] selectively promote silane alcoholysis in the presence of alkene functionalities. We now report that the readily available manganese carbonyl bromides $Mn(CO)_5Br$ and $[Mn(CO)_4Br]_2$[12] are extremely reactive and potentially selective catalysts for alcoholysis of hydrosilanes.

Results and Discussion

The readily available dimeric manganese carbonyl bromide $[Mn(CO)_4Br]_2$[12b] effectively catalyzes the alcoholysis of dimethylphenylsilane in benzene at room temperature. Treatment of the alcohols listed in Table 1 with $HSiMe_2Ph$ and $[Mn(CO)_4Br]_2$ in a 1200:1200:1 ratio afforded their alkoxysilanes in generally high isolated yields. After a 10–20-s induction period, these reactions rapidly evolved gas (presumably H_2) and, in the cases of allylic, propargylic, methyl, and ethyl alcohols, also became noticeably exothermic.



Subsequent studies involving ^1H NMR spectral monitoring of these reactions has established that they were complete when gas evolution ceased.

We used as alternative reaction conditions for 2,2-dimethyl-1,3-propanediol a 2:1 ratio of $HSiMe_2Ph$ to diol in methylene chloride as the solvent (due to solubility

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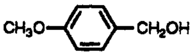
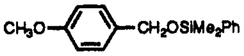
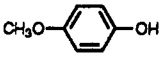
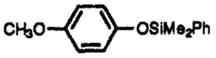
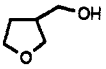
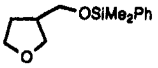
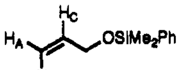
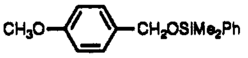
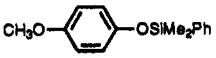
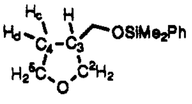
Table 1. Manganese Carbonyl Bromide-Catalyzed Alcoholysis of $HSiMe_2Ph$

starting alcohol	time (min)[a,b]	silyl ether product	NMR yield[c] (%)	isolated yield[a] (%)
CH_3OH	15	CH_3OSiMe_2Ph	95+	93
CH_3CH_2OH[d]	20	$CH_3CH_2OSiMe_2Ph$		92
$CH_3CH_2CH(CH_3)OH$	25	$CH_3CH_2CH(CH_3)OSiMe_2Ph$	95+	82[e]
$(CH_3)_3COH$	35	$(CH_3)_3OSiMe_2Ph$	95+	82[e]
$CH_2{=}CHCH_2OH$	10	$CH_2{=}CHCH_2OSiMe_2Ph$	95+	88
$CH{\equiv}CCH_2OH$	10	$CH{\equiv}CCH_2OSiMe_2Ph$		92
	45		95+	64
	95			36
$BrCH_2CH_2OH$	30	$BrCH_2CH_2OSiMe_2Ph$		88
	25			89
	180[f]		95+	78[e,f]

[a] Preparative scale: alcohol (31.2 mmol), $HSiMe_2Ph$ (4.252 g, 31.2 mmol), and $[Mn(CO)_4Br]_2$ (13 mg, 0.026 mmol, 0.084 mol %) in 10 mL of C_6H_6. Product was isolated by distillation unless otherwise noted. [b] Cessation of gas evolution for preparative-scale reaction. [c] Reaction conditions: alcohol (1.00 mmol), $HSiMe_2Ph$ (136 mg, 1.00 mmol), PhOMe (0.300 mmol, internal standard), and 5 mg (1.0 mol%) of $[Mn(CO)_4Br]_2$ in 600 mg of C_6D_6. Only alkoxysilanes, $ROSiMe_2Ph$, were detected by ^1H and ^{13}C NMR spectroscopy. [d] NMR-scale reaction with $HSiEt_3$ (116 mg, 1.00 mmol) as noted in footnote *a* quantitatively afforded $EtOSiEt_3$, also within 20 min. [e] Product was isolated by column chromatography. [f] Preparative scale: alcohol (15.6 mmol), $HSiMe_2Ph$ (4.252 g, 31.2 mmol), and $[Mn(CO)_4Br]_2$ (13 mg, 0.026 mmol, 0.084 mol %) in 10 mL of CH_2Cl_2.

Table 2. NMR Spectral and Characterization Data for the Alkoxysilanes $RO{-}SiMe_2Ph$

complex	^1H NMR (C_6D_6) (δ)	$^{13}C\{^1H\}$ NMR (C_6D_6) (δ)	bp (°C)	microanal. (%): found (cald) C	microanal. (%): found (cald) H
$HC{\equiv}CCH_2OSiMe_2Ph$	4.06 (d, $J = 2.4$, CH_2), 2.04 (t, $J = 2.4$, CH), 0.32 (s, $SiCH_3$)[a]	137.4 (*ipso*-Ph),[b] 82.4 ($HC{\equiv}C$), 73.5 ($HC{\equiv}C$), 51.3 (CH_2), −1.5 ($SiCH_3$)	180	69.37 (69.42)	7.38 (7.41)
	5.84 (ddt, 1H, H_c), 5.28 (ddt, 1H, $J_{ac} = 17.3$, H_a), 5.00 (ddt, 1H, $J_{bc} = 10.5$, H_b), 4.00 (ddd, 2H, CH_2), 0.31 (s, $SiCH_3$)[a]	138.2 ($CH_2{=}CCH_2$), 137.6 (*ipso*-Ph),[b] 114.0 ($CH_2{=}CCH_2$), 63.9 ($CH_2{=}CCH_2$), −1.6 ($SiCH_3$)	197	68.86 (68.69)	8.50 (8.38)
$EtCH(CH_3)OSiMe_2Ph$	3.63 (qt, 1H, CH), 1.36 (m, 2H, CH_2), 1.03 (d, $J = 6.1$, CH_3CH_2), 0.80 (t, $J = 7.3$, $CHCH_3$), 0.31 (s, $SiCH_3$)[a]	139.0 (*ipso*-Ph),[b] 70.3 (CH), 32.6 (CH_2), 23.4 ($OCHCH_3$), 10.2 (CH_2CH_3), −0.8 ($SiCH_3$)		69.02 (69.17)	9.76 (9.67)
$(CH_3)_3COSiMe_2Ph$	7.64 (m, 2H, Ph), 7.23 (m, 3H, Ph), 1.17 (s, $(CH_3)_3C$), 0.37 (s, $SiCH_3$)	140.7 (*ipso*-Ph),[b] 72.7 ($C(CH_3)_3$), 32.2 ($C(CH_3)_3$), 1.6 ($SiCH_3$)		69.11 (69.17)	9.67 (9.67)
$BrCH_2CH_2OSiMe_2Ph$	3.54 (t, $J = 6.1$, CH_2O), 3.01 (t, $J = 6.4$, CH_2Br), 0.25 (s, $SiCH_3$)[a]	137.6 (*ipso*-Ph),[b] 63.4 (OCH_2), 33.4 (CH_2Br), −1.8 ($SiCH_3$)		46.75 (46.43)	5.83 (5.83)
	7.59 (m, 2H, Ph), 7.22 (m, 5H, Ph + C_6H_4), 6.77 (m, 2H, $CH_3OC_6H_4$), 4.58 (s, CH_2O), 3.29 (s, CH_3O), 0.32 (s, $SiCH_3$)	159.4 (CH_3O–*ipso*-Ph), 149.1 (CH_3O–*p*-C_6H_4), 138.2 (Si–*ipso*-Ph),[b] 133.9 (CH_3O–*o*-C_6H_4), 113.9 (CH_3O–*m*-C_6H_4), 64.9 (CH_2O), 54.7 (CH_3O), −1.5 ($SiCH_3$)	115[c]	70.29 (70.54)	7.36 (7.40)
	7.60 (m, 2H, Ph), 7.21 (m, 3H, Ph), 6.80 (m, 2H, C_6H_4), 6.60 (m, 2H, C_6H_4), 3.27 (s, CH_3O), 0.40 (s, $SiCH_3$)	154.9 (CH_3O–*ipso*-Ph), 149.2 (CH_3O–*p*-C_6H_4), 137.7 (Si–*ipso*-Ph),[b] 133.8 (CH_3O–*o*-C_6H_4), 114.9 (CH_3O–*m*-C_6H_4), 55.0 (CH_3O), −1.6 ($SiCH_3$)	89[c]		
	7.60 (m, 2H, Ph), 7.21 (m, 3H, Ph), 3.61 (m, 4H, OCH_2), 3.34 (d, $J = 7.29$, CH_2), 2.22 (m, 1H, CH), 1.57 (m, 1H, H_c), 1.27 (m, 1H, H_d), 0.28 (s, $SiCH_3$)	137.7 (*ipso*-Ph),[b] 70.6 (C_2), 67.6 (C_5), 64.9 (CH_2), 41.9 (CH), 28.8 (C_4), −1.8 ($SiCH_3$)	135	65.89 (66.05)	8.51 (8.53)
	7.60 (m, 2H, Ph), 7.21 (m, 3H, Ph), 3.44 (s, CH_2), 0.89 (s, CH_3), 0.35 (s, $SiCH_3$)	137.7 (*ipso*-Ph),[b] 68.5 (CH_2O), 38.0 (CMe_2), 21.6 (CH_3), −1.7 ($SiCH_3$)	128[c]		

[a] Phenyl absorptions for $SiMe_2Ph$ at 7.52 (2 H), 7.20 (3 H). [b] Other phenyl ring carbons absorb at 133.5–133.8, 130.0–130.3, and 128.3–128.7. [c] Distilled at 380 mmHg.

reasons for the preparative-scale reactions). Although the initial burst of gas evolution subsided within 25 min, a full 3 h was required before all gas evolution ceased. Under these conditions, the diol transformed to its bis(silyl ether) (Table 1).

Somewhat more of the precatalyst $[Mn(CO)_4Br]_2$, typically 1.0 mol %, was used in C_6D_6 solutions for studies involving ^1H and ^{13}C NMR spectral monitoring of the reactions that are listed in Table 1. All reactions studied quantitatively provided alkoxysilane products, with the presence of diagnostic SiMe NMR absorptions (Table 2) making it particularly straightforward to rule out other products. In particular, we detected no hydrosilation of the carbon–carbon double bond[2] of allyl alcohol even in the presence of 2 equiv of $HSiMe_2Ph$. This result is not surprising in as much as both styrene and cyclopentene remained inert under similar conditions involving $HSiMe_2Ph/[Mn(CO)_4Br]_2$.

A number of other manganese carbonyl complexes were screened as potential $HSiMe_2Ph$ alcoholysis catalysts with methanol (Table 3) and 2-butanol (Table 4). Monomeric $Mn(CO)_5Br$ exhibited diminished activity with respect to $[Mn(CO)_4Br]_2$ (Tables 3 and 4), although it was more reactive than any of the other complexes surveyed. A qualitative ordering of precatalyst activity is as follows:

$$[Mn(CO)_4Br]_2 > Mn(CO)_5Br \gg Mn(CO)_5CH_3 \approx Mn(CO)_5C(O)Ph > Mn(PPh_3)(CO)_4Br > Mn(PPh_3)(CO)_4C(O)CH_3 \gg Mn(CO)_5(SiMe_2Ph) \gg Mn_2(CO)_{10} \approx Rh(PPh_3)_3Cl \text{ (no reaction)}$$

The low to nonreactivity of the manganese silyl and $Mn_2(CO)_{10}$ is consistent with their inability to catalyze either SiH/SiD exchange between $HSiMe_2Et$ and $DSiMe_2Ph$[13] or hydrosilation of aldehydes, ketones, or organometallic acyl complexes.[14] The two manganese bromide and the benzoyl complexes, for example, efficiently catalyze both SiH/SiD exchange and hydrosilation of a carbon–oxygen double bond.

Hilal and co-workers[15] had reported that $Mn_2(CO)_{10}$ (1.25 mol %) slowly catalyzed alcoholysis of $HSi(OEt)_3$ and (in one experimental run) $HSiEt_3$ in toluene at 30 °C. The rates of these reactions decrease in the order *n*-hexane > toluene ≫ tetrahydrofuran (THF). These reactions may be photochemically induced. Barton et al.[16] recently reported that both rhenium and manganese dimers $M_2(CO)_{10}$ require laboratory lighting in order to efficiently catalyze alcoholysis of phenylsilane. Reaction times for the $Re_2(CO)_{10}$-catalyzed hydrosilane alcoholysis decreased in the order *n*-pentane > CH_2Cl_2 > C_6H_6.

An intriguing outcome of screening prospective manganese catalysts was that the acetyl complex $Mn(PPh_3)(CO)_4C(O)CH_3$ only functioned as a very sluggish silane alcoholysis catalyst even with methanol. This acetyl complex, however, is a particularly active hydrosilation catalyst toward aldehydes, ketones, and organometallic acyl complexes.[14] It thus appeared possible that manganese-catalyzed hydrosilane alcoholysis and ketone hydrosilation could occur chemoselectively. We therefore compared $Mn(PPh_3)(CO)_4C(O)CH_3$ and $[Mn(CO)_4Br]_2$ as catalysts for the reactions of $HSiMe_2Ph$ and 1:1 mixtures of acetone and 2-butanol.

In competition reactions, mixtures containing 1.0 mmol of acetone and 2-butanol in 600 mg C_6D_6 were treated with just 1 equiv of $HSiMe_2Ph$ and either $[Mn(CO)_4Br]_2$ or $Mn(PPh_3)(CO)_4C(O)CH_3$ (0.084 mol %) as the catalyst. The manganese bromide catalyst proved to be extremely active; gas evolution ceased within 9 min. Results of subsequent ^1H and ^{13}C NMR spectral monitoring moreover were consistent with chemoselective silane alcoholysis: all of the hydrosilane had converted to the alkoxysilane $CH_3CH(OSiMe_2Ph)CH_2CH_3$, and no acetone hydrosilation was evident. Very few other catalysts that we are aware of chemoselectively dehydrocouple a hydroxyl group and hydrosilane in the presence of a ketone.[9-11]

Interestingly, similar competition reactions but using $Mn(PPh_3)(CO)_4C(O)CH_3$ as the catalyst underwent no transformation over 4 h. The presence of the alcohol inhibited the otherwise facile hydrosilation of acetone.

Turnover frequencies were determined for the $[Mn(CO)_4Br]_2$-catalyzed dehydrocoupling of 2-butanol and $HSiMe_2Ph$ under two sets of conditions. First, initial velocities for the rate of H_2 evolution were measured for 0.289 M solutions of 2-butanol and $HSiMe_2Ph$ with 1.4 mol % precatalyst $[Mn(CO)_4Br]_2$. These initial velocities were converted to turnover numbers that varied with the reaction solvent: $N_t = 2183$ (THF), 2728 (C_6H_6), and 5457 h^{-1} (CH_2Cl_2). In a second procedure, a preparative-scale reaction in CH_2Cl_2 containing only 0.084 mol % precatalyst but 3.12 M for each reactant afforded a much higher turnover frequency of 11 217 h^{-1}.

Values for these turnover frequencies identify a moderately active catalyst system that can be compared with $Ru(CO)_2(PMe_3)_2Cl_2$[10] and $[IrH_2(THF)_2(PPh_3)_3]SbF_6$.[9] The ruthenium complex catalyzes alcoholysis of triethylsilane at 2500 (MeOH) to 70 (*sec*-BuOH) turnovers h^{-1}/mol of catalyst in THF, whereas Crabtree's iridium precatalyst engenders turnover frequencies of 53 000–110 000 h^{-1} (same alcohols and silane in CH_2Cl_2). Recently reported Ni(II) thiosemicarbazone systems slowly catalyze methanolysis of triethylsilane, $N_t \leq 45\ h^{-1}$ (DMSO–C_6H_6).[17]

The O-silation of 2-butanol/$HSiMe_2Ph$ with the manganese bromide precatalysts was investigated in the presence of potential inhibitors. The presence of 1 atm of carbon monoxide during alcohol O-silation, while allowing for the venting of the hydrogen, approximately doubled both the induction and reaction times for the $[Mn(CO)_4Br]_2$ precatalyst. With $Mn(CO)_5Br$ as the catalyst, CO extended both times by a factor of 3 (Table 5). Pyridine (1 and 2 equiv with $[Mn(CO)_4Br]_2$ and $Mn(CO)_5Br$, respectively) immediately terminated catalysis. Less drastic inhibition was achieved by using 2,6-lutidine, which approximately doubled the induction and reaction times.

The manganese carbonyl bromide-catalyzed alcoholysis of $HSiMe_2Ph$ exhibits a reactivity pattern that resembles SiH/SiD exchange between $HSiMe_2Et$ and $DSiMe_2Ph$.[13] These isotope exchange reactions also are catalyzed by $Mn(CO)_5Br$ or $Mn(CO)_5C(O)Ph$ but not by $Mn_2(CO)_{10}$ or $Mn(CO)_5(SiMe_2Ph)$. Modest CO and complete pyridine inhibition also characterize the SiH/SiD exchange. Results of a kinetics study on these reactions (using $Mn(CO)_5C(O)C_6H_4CH_3$ as the precatalyst) were consistent with a pathway that cycles between coordinatively unsaturated $Mn(CO)_4(SiR_3)$ as the active catalysts and the intermediates $Mn(CO)_4H(SiR_3)_2$ (Scheme 1).

A similar pathway could apply to the manganese-catalyzed silane alcoholysis. Bridge cleavage of $[Mn(CO)_4Br]_2$ and CO dissociation from $Mn(CO)_5Br$[18] would afford the same active catalyst $Mn(CO)_4(SiMe_2Ph)$ via the illustrated hydrosilane oxidative addition[19] and HBr reductive elimination sequence.[20] Addition of another 1 equiv of $HSiMe_2Ph$ followed by alcoholysis of a manganese

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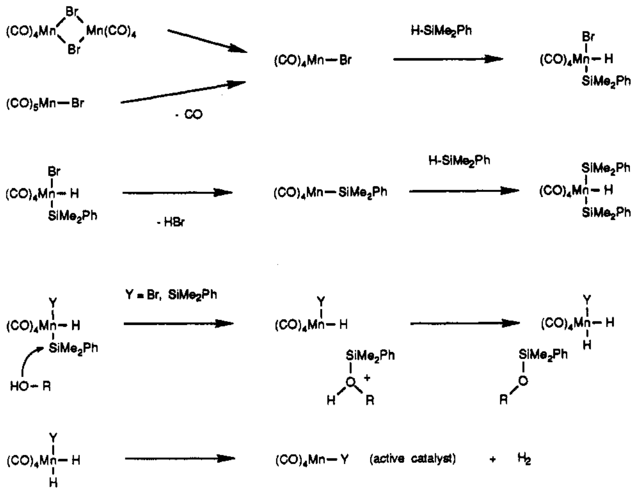
Scheme 1



silyl group on $Mn(CO)_4H(SiMe_2Ph)_2$, as established for stable $Mn(CO)_5(SiR_3)$[22] and $CpMn(CO)_2(\eta^2\text{-H-SiR}_3)$[4d,23] complexes, then provides the alkoxysilane and H_2. Analogous heterolytic cleavage of a metal–silyl bond[19,24] has been proposed previously[1,4a,d,11,15] as the key step in other metal complex-catalyzed silane alcoholysis reactions.

If this working hypothesis for the silane alcoholysis mechanism applies, then the amount of manganese carbonyl bromide precatalyst that converts to active catalyst must be extremely low. IR spectral monitoring of experimental runs containing 2 mol % $[Mn(CO)_4Br]_2$ or $Mn(CO)_5Br$ and 3.33 M in $HSiMe_2Ph$, with or without methanol coreactant present, indicated that the precatalyst was unaltered. With $Mn(CO)_5Br$ catalysis, for example, the absorptivity for the intense ν(CO) at 2049 cm^{-1} did not perceptibly change.

Another plausible pathway, also illustrated above, centers on the unsaturated $Mn(CO)_4Br$ as the active alcohol O-silation catalyst. This $Mn(CO)_4Br$ active catalyst would transform $HSiMe_2Ph$ to its alkoxysilane product through alcoholysis of a subsequent $Mn(CO)_4HBr(SiMe_2Ph)$ intermediate. Alternatively, this intermediate could eliminate $BrSiMe_2Ph$, which would undergo alcoholysis to give the same alkoxysilane product. The released HBr then would add to the manganese center, releasing H_2, to regenerate the active catalyst. Although these latter two pathways account for the manganese carbonyl bromide-catalyzed alcoholysis of $HSiMe_2Ph$, they do not explain the moderate catalytic activity of related manganese carbonyl complexes, viz., $Mn(CO)_5CH_3$ and $Mn(CO)_5C(O)Ph$ (Table 3).

Within the limited set of alcohols considered in this study, the manganese carbonyl bromides $Mn(CO)_5Br$ and $[Mn(CO)_4Br]_2$ are useful catalysts for alcoholysis of hydrosilanes: (1) These catalysts dehydrogenatively couple even tertiary alcohols with the less reactive trialkylsilanes under mild conditions. (2) Catalytic alcohol O-silation evidently occurs in the presence of competing alkene and carbonyl groups. (3) The manganese carbonyl bromide precatalysts certainly are easily accessible and moderate in cost. Our fourth criterion for a useful hydrosilane alcoholysis catalyst, discerning structurally different hydroxylic groups on the same molecule, was not addressed in this study. Future studies will attempt to extend the synthetic scope and selectivity and to probe the mechanistic facets of these manganese carbonyl-catalyzed hydrosilane alcoholysis reactions.

Experimental Section

General Methods. ^1H and ^{13}C NMR spectral data were obtained in C_6D_6 with Varian Unity-500 and Model XL-200 spectrometers; solution infrared spectral data (IR) were acquired on a Perkin-Elmer FT spectrophotometer, Model No. 1600. Silanes, alcohols, $Mn_2(CO)_{10}$, and C_6D_6 were used as received, and benzene was distilled under nitrogen from sodium benzophenone ketyl. The manganese carbonyl precatalysts $Mn(CO)_5Br$,[12a] $[Mn(CO)_4Br]_2$,[12b] $Mn(CO)_5(SiMe_2Ph)$,[14a] $Mn(PPh_3)(CO)_4Br$,[18c,25] $Mn(CO)_5CH_3$,[26] and $Mn(CO)_5C(O)Ph$,[26a,27] $Mn(PPh_3)(CO)_4C(O)CH_3$,[28] and $Rh(PPh_3)_3Cl$[29] were prepared by literature procedures and judged pure by IR and ^1H NMR spectroscopy. $Mn(CO)_5Br$ was sublimed; all organometallic reagents were stored under nitrogen, but catalytic silane alcoholysis reactions were performed without benefit of inert atmosphere. Combustion microanalyses were done by Quantitative Technologies, Bound Brook, NJ.

Catalytic $HSiMe_2Ph$ Alcoholysis. (i) General Preparative-Scale Procedure. The manganese carbonyl bromide $[Mn(CO)_4Br]_2$ (13 mg, 0.0263 mmol) was added to a benzene solution (10 mL) containing the alcohol (31.2 mmol) and $HSiMe_2Ph$ (4.252 g, 31.2 mmol). The 50-mL reaction flask was open to the atmosphere. After a 20–30-s induction period, gas evolution from the pale yellow solutions was pronounced; reactions involving allyl, propargyl, ethyl, and methyl alcohols also were noticeably exothermic. Once the reactions ceased evolving gas, generally within 10–45 min, they were distilled or chromatographed on flash-grade silica gel (fluorescent indicator) with 1:1 methylene chloride–hexane. Isolated alkoxysilanes (Table 1) were spectroscopically (^1H, ^{13}C NMR) and analytically pure (Table 2). NMR spectral data for CH_3OSiMe_2Ph, $CH_3CH_2OSiMe_2Ph$, and $CH_3CH_2OSiEt_3$ agree with that recently reported.[8] No attempt was made to recover or otherwise inactivate the catalyst.

(ii) NMR Spectral Monitoring. C_6D_6 solutions (600 mg) containing the alcohol (1.00 mmol), $HSiMe_2Ph$ (136 mg, 1.00 mmol), C_6H_5OMe as the internal standard (3 mg, 0.03 mmol), and $[Mn(CO)_4Br]_2$ (5 mg, 0.010 mmol) were prepared in a vial and transferred to septum-stoppered NMR tubes. A syringe needle was used between NMR spectral scans to vent the build up of pressure. Cessation of gas evolution closely corresponded to the observed consumption of starting reagents; thus, the same relative ordering of reactivity of alcohols (Table 1) was noted. These reactions were monitored by ^1H NMR spectroscopy using

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(20) Alternatively, manganese η^2-(Si–H) intermediates[19,21] could supplant oxidative addition–reductive elimination sequences[9] in the transforming of $Mn(CO)_4Br$ to $Mn(CO)_4SiMe_2Ph$.

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Table 3. Manganese Carbonyl Catalyst Screening for O-Silation of Methanol with $HSiMe_2Ph$

precatalyst[a]	time (h)	extent of reacn[b] (%)
$Mn(CO)_5CH_3$	0.50	30
$Mn(CO)_5C(O)C_6H_5$	0.50	30
$Mn(PPh_3)(CO)_4C(O)CH_3$	2.5	25
$Mn(CO)_5Br$	0.25	100
$[Mn(CO)_4Br]_2$	0.10	100

[a] Reaction conditions: Mn precatalyst (0.011 mmol, 1.9 mol %), CH_3OH (19 mg, 0.577 mmol), and $HSiMe_2Ph$ (79 mg, 0.577 mmol) in 600 mg of C_6D_6. [b] Reaction was monitored by ^1H NMR spectroscopy; only starting materials and/or CH_3OSiMe_2Ph were detected.

Table 4. Homogeneous Catalyst Screening for O-Silation of 2-Butanol with $HSiMe_2Ph$

precatalyst[a]	time (h)	extent of reacn[b] (%)
$Mn_2(CO)_{10}$	5.0	0
$Mn(PPh_3)(CO)_4Br$	1.5	90^+
$Mn(CO)_5SiMe_2Ph$	7.0	100
$Mn(CO)_5Br$	0.4	100
$[Mn(CO)_4Br]_2$	0.16	100
$Rh(PPh_3)_3Cl$	2.0	0

[a] Reaction conditions: precatalyst (0.011 mmol, 1.9 mol %), $CH_3CH(OH)CH_2CH_3$ (43 mg, 0.577 mmol), and $HSiMe_2Ph$ (79 mg, 0.577 mmol) in 600 mg of C_6D_6. [b] Reaction was monitored by ^1H NMR spectroscopy; only starting materials and/or $CH_3CH(OSiMe_2Ph)CH_2CH_3$ were detected.

delay times and other spectrometer settings that afforded a 5.0% precision for integrations of the SiH and SiMe absorptions (δ 4.58 and 0.32, respectively, for $HSiMe_2Ph$). Between 94 and 99% of the starting hydrosilane was accounted for as alkoxysilane product.

Results also are reported for screening a variety of manganese carbonyl precatalysts (0.011 mmol, 1.9 mol %) for reactions between $HSiMe_2Ph$ and methanol or 2-butanol under conditions that are reported in Tables 3 and 4, respectively.

(iii) CO Inhibition. Four 4-mL vials were charged with benzene solutions (2 mL) containing 2-butanol (43 mg, 0.579 mmol) and $HSiMe_2Ph$ (79 mg, 0.579 mmol). Two of these solutions had been purged with carbon monoxide for 5 min before $Mn(CO)_5Br$ (2 mg, 0.0073 mmol) and $[Mn(CO)_4Br]_2$ (3 mg, 0.0061 mmol) were added, and the vials were capped with serum stoppers. Two syringe needles inserted through the septa maintained a gentle CO flow above the surface of these solutions and retained a net 1 atm with the aid of an oil bubbler. The remaining two vials, open to the air, were treated with the manganese bromide precatalysts. Induction and reaction times (as judged by cessation of gas evolution) are recorded in Table 5.

Table 5. Induction and Reaction Times for Manganese Bromide-Catalyzed O-Silation of 2-Butanol with $HSiMe_2Ph$

	control reacns[b]		1 atm of CO[c]	
catalyst[a]	induction time[d] (s)	completion time[d] (min)	induction time[d] (s)	completion time[d] (min)
$MnBr(CO)_5$	40	25	120	>40
$[Mn(CO)_4Br]_2$	20	<5	35	<10

[a] 1.1 mol % manganese bromide; $CH_3CH(OH)CH_2CH_3$ and $HSiMe_2Ph$, 0.579 mmol in 2 mL of C_6H_6. [b] Set up under open atmosphere. [c] 1 atm of CO maintained; H_2 partial pressure vented. [d] Onset and cessation of gas evolution, respectively.

(iv) Determination of Turnover Numbers. The procedure of Luo and Crabtree[9] was used to measure the H_2 evolution from the catalyzed alcoholysis of $HSiMe_2Ph$ as a function of time and to calculate the initial velocity and turnover number. A benzene solution (2 mL) containing 2-butanol (43 mg, 0.579 mmol) and $HSiMe_2Ph$ (79 mg, 0.579 mmol) was treated with $[Mn(CO)_4Br]_2$ (4 mg, 0.0081 mmol), and the volume of water displaced by the presumed H_2 was monitored. An initial rate of 11.05 M/h was calculated using the equation $v_i = P_{H_2}/[RTV_{soln}][dV_{H_2}/dt]$ and dV_{H_2}/dt = 0.15 mL/s, thus affording a turnover number, $N_t = v_i/[\text{catalyst}]$, of 2728 ± 203 h^{-1} (2σ for three replicate runs). This procedure was repeated using THF and CH_2Cl_2 as solvents: initial velocities of 8.84 and 22.1 M/h, respectively, and N_t values of 2183 and 5457 h^{-1} were obtained. A final preparative-scale reaction (Table 1) was carried out in 10 mL of CH_2Cl_2: initial rate = 29.5 M/h and N_t = 11 217 h^{-1}.

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