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Traceless Chelation-Controlled Rhodium-Catalyzed Intermolecular Alkene and Alkyne Hydroacylation

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Abstract: A new functional-group tolerant, rhodium-catalyzed, sulfide-reduction process is combined with rhodium-catalyzed chelation-controlled hydroacylation reactions to give a traceless hydroacylation protocol. Aryl- and alkenyl aldehydes can be combined with both alkenes, alkynes and allenes to give traceless products in high yields. A preliminary mechanistic proposal is also presented.

Keywords: acylation · rhodium · sulfide reduction · synthetic methods · tandem reactions

Introduction

The use of chelation-control strategies has contributed enormously to the progress of intermolecular alkene and alkyne hydroacylation reactions as synthetically useful transformations.[1] For example, efficient reactions have been developed that rely on C-,[2] N-,[3] O-,[4] S-[5] or P-coordinating substituents,[6] with examples of the coordinating group positioned on either the aldehyde or the alkene/alkyne reaction component.[7] The resultant chelated motif is generally invoked as stabilizing key acyl–metal intermediates (Scheme 1). These reactions now encompass a wide substrate scope and have allowed both enantioselective[7c,8] and regioselective[9] variants to be developed. An inherent feature of chelation-controlled reactions is that the chelating group, which is necessarily present in the starting materials to ensure favourable reactivity, is also present in the product molecules. Derivatization of these controlling groups can provide opportunities for further functionalization of the products,[4d,5a,10] but if an unadorned molecule is required, they represent a limitation of the strategy. Although a number of examples of successful non-chelation-controlled intermolecular hydroacylation reactions is known, they generally require specific substrate combinations or harsh reaction conditions.[11] Herein, we document the development of the first traceless chelation-controlled intermolecular hydroacylation protocol, a process which enjoys the benefits of a chelation-controlled approach – broad substrate scope and mild reaction conditions – but allows the formation of products lacking a superfluous coordinating group.

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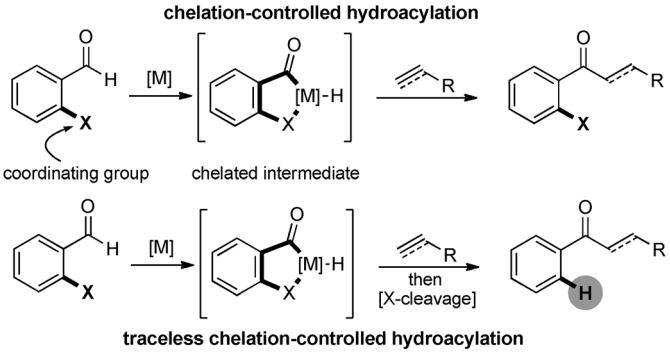
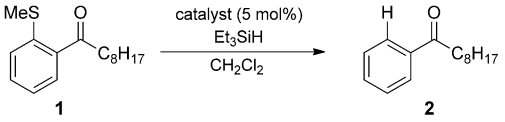


Scheme 1. Chelation-controlled and traceless chelation-controlled alkene/alkyne hydroacylation.

Results and Discussion

The first task in addressing the development of a traceless chelation-controlled hydroacylation protocol was to identify a suitable method of efficiently cleaving the original coordinating group. Based on the advances our laboratory has made in the use of β-S-chelating aldehydes in alkene and alkyne hydroacylation reactions,[5] this chelation motif seemed ideal. However, established methods for the reductive cleavage of simple aryl methyl sulfides to the parent arene are largely limited to those based on Raney nickel or other stoichiometric metal-reducing agents.[12] Given the poor functional group tolerance that such a reductive step would provide, we explored the use of milder reaction conditions by using silane reductants. Silane reductions of aryl methyl sulfides have recently been reported by using nickel and palladium catalysts,[13] although application of both of these methods to our hydroacylation products resulted in the formation of mixtures of ketone hydrosilylation and silyl enol ether products (see the Supporting Information).[14] Based on our recent success in the activation of aryl methyl sulfides with the Rh^{I} catalyst **A** (Table 1) and subsequent application to the development of a new alkyne carbothiola-

Table 1. Catalyst evaluation for sulfide reduction by using ketone **1**.[a]



1 **2**

	Catalyst	T [°C]	Conversion[b]
1	[Rh(DPEphos)(nbd)][BAr^F_4] **A**[d]	80	33 %
2	[Rh(Xantphos)(nbd)][BAr^F_4] **B**[d]	80	15 %
3	[Rh($Cy_2PCH_2PCy_2$)(C_6H_5F)][BAr^F_4] **C**	80	100 % (50 %)[c]
4	[Rh($Cy_2PCH_2PCy_2$)(C_6H_5F)][BAr^F_4] **C**	25	100 % (73 %)[c]
5	[Rh(tBu$_2$PCH$_2$PtBu$_2$)(C_6H_5F)][BAr^F_4] **D**	80	<10 %

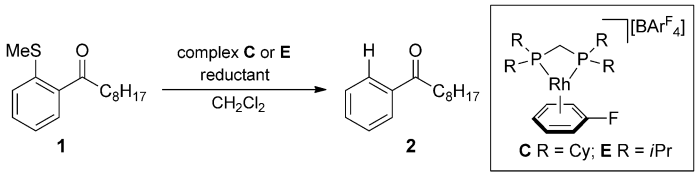
[a] Ar^F = 3,5-$C_6H_3(CF_3)_2$. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Isolated yields in parenthesis. [d] Precatalyst activated with H_2. nbd = norbornadiene.

tion process, we decided to investigate the use of rhodium catalysis for the selective reduction of methyl sulfides.[10] An important goal in exploring this chemistry was to develop a sulfide-reduction process that was tolerant of potentially reactive, synthetically useful, functional groups, such as ketones, esters and halides.

The aryl ketone **1** was selected as a suitable substrate to explore the reduction chemistry, and a number of Rh^I catalysts were evaluated employing Et_3SiH as the reducing agent (Table 1). Although the (2-diphenylphosphinophenyl)-ether (DPEphos) complex **A** provided only moderate conversion to reduced product **2** (Table 1, entry 1), complex **C** was quickly identified,[15] featuring the small-bite-angle ligand bis(dicyclohexylphosphanyl)methane ($Cy_2PCH_2PCy_2$), as an active catalyst for this reaction. Performing this reduction at 80 °C resulted in significant hydrosilylation of the ketone (Table 1, entry 3), although this could be attenuated by reducing the temperature of the reaction (Table 1, entry 4). Under these conditions, complete consumption of the starting material was observed, and the desired product was isolated in 73 % yield.

Next, attention was turned to identifying the optimum reducing agent for this reaction (Table 2). Performing the reaction under an atmosphere of H_2 gas resulted in only partial reduction of the ketone, and no observed SMe cleavage (Table 2, entry 1). The use of phenyl-substituted silanes gave complex mixtures of products, resulting from non-selective reductive cleavage of the SMe group and ketone hydrosilylation (Table 2, entries 2 and 3). We were pleased to see that polymethylhydrosiloxane (PMHS), an inexpensive by-product of the silicone industry,[16] was an effective reducing agent for this reaction (Table 2, entry 4). However, optimal results were obtained when $(EtO)_3SiH$ was employed, resulting in complete conversion in only 15 min when 5 mol % of catalyst **C** was used (Table 2, entry 5). The catalyst loading could be reduced to 1 mol %, which gave complete conversion and a 95 % isolated yield of ketone **2** in one hour (Table 2, entry 6). Complex **E**, containing isopropyl substituents on the phosphorus atoms, displayed even greater reactivity, delivering complete conversion in only 30 min when 1 mol % was used (Table 2, entry 7). Complex **C** was used

Table 2. Optimization of reducing agents for sulfide **1**.[a]



1 **2**

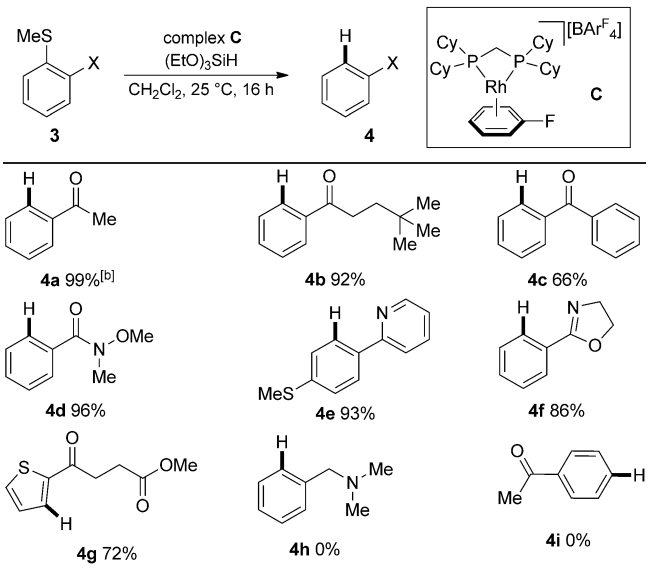
	Catalyst	Reductant	T [°C]	Conversion[b]
1	**C** (5 mol %)	H_2 (1 atm)	80	<10 %
2	**C** (5 mol %)	Ph_2SiH_2	25	complex mix
3	**C** (5 mol %)	$PhSiH_3$	25	complex mix
4	**C** (5 mol %)	PMHS	25	80 %
5[c]	**C** (5 mol %)	$(EtO)_3SiH$	25	100 %
6[d]	**C** (1 mol %)	$(EtO)_3SiH$	25	100 % (95 %)[f]
7[e]	**E** (1 mol %)	$(EtO)_3SiH$	25	100 %

[a] Ar^F = 3,5-$C_6H_3(CF_3)_2$. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Complete in 15 min. [d] Complete in 1 h. [e] Complete in 30 min. [f] Isolated yield in parenthesis.

for further studies; as although both **C** and **E**[17] are bench-stable pre-catalysts, complex **C** can be conveniently prepared from commercially available materials.

Having established mild and efficient conditions for the reductive cleavage of an aryl methyl sulfide in the presence of an *ortho*-ketone group, the role of directing groups in promoting C–S bond cleavage was investigated (Table 3). Substrates with an *ortho*-carbonyl group were well tolerated, with alkyl- and aryl-ketones (**4a–c**), and a Weinreb amide (**4d**) all undergoing selective C–S cleavage. Heterocyclic directing groups could also be employed, with a pyridyl group promoting the chemoselective cleavage of an *ortho*-SMe group in the presence of a *para*-sulfide (**4e**). A substrate containing an *ortho*-oxazoline group was also effective, giving phenyl-oxazoline (**4f**). The thiophene ketone **4g**

Table 3. Directing group effects on aryl sulfide reduction.[a]



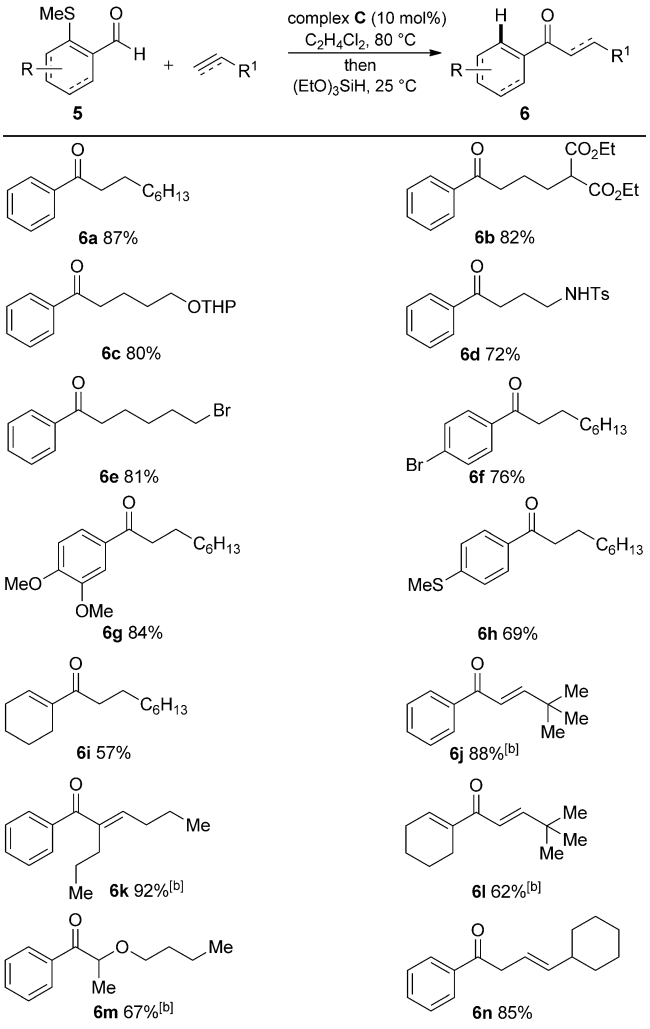
[a] Conditions: **3** (1.0 equiv), catalyst (5 mol %), $(EtO)_3SiH$ (2.0 equiv). Isolated yields. [b] Conversion from ^{1}H NMR spectroscopy.

could also be prepared in good yield, showing the compatibility of this reaction with heterocyclic scaffolds. However, substrate **3h** with a benzylic amine was unreactive. Substrate **3i**, featuring a *para*-disposed acyl group, was also unreactive, thus confirming the requirement for *ortho*-coordination.

We have previously reported that complex **C** is a highly active catalyst for the sulfide-directed hydroacylation of alkenes and alkynes.[15] This raised the exciting possibility of performing hydroacylation reactions, in which the SMe group would act as a directing group for aldehyde C–H activation, followed by reductive cleavage of the C–S bond with the same catalyst. This reaction would give ketone products, in which the thiomethyl group acts as a traceless directing group. Based on the ease with which the thiomethyl substituent can be introduced, by using simple S_NAr chemistry, this combination would provide an attractive route to ketone products. We tested this concept by subjecting the aldehyde **5a** to hydroacylation conditions, employing 10 mol% of catalyst **C** and 1-octene (Table 4). After two hours at 80 °C, the mixture was cooled to room temperature, and $(EtO)_3SiH$ was added. After stirring overnight, we were pleased to find that the ketone **6a** could be isolated in 87% yield. The alkene component of this reaction could be easily varied, and very good functional group tolerance was observed. For example, products featuring ester (**6b**), acetal (**6c**) and sulfonamide (**6d**) groups were all delivered in good yields. This reaction is also highly compatible with both alkyl- (**6e**) and aryl-halides (**6f**), allowing for the possibility of further functionalization of the products. Variation of the aldehyde component of the reaction was also possible. The dimethoxy aldehyde **5g** gave the ketone product in 84% yield, and an aldehyde with both *ortho*- and *para*-SMe groups gave the *ortho*-reduced product in good yield. Pleasingly, the aldehyde scope was not limited to aromatic substrates, as the cycloalkenyl aldehyde **5i** delivered the corresponding α,β-unsaturated ketone. The stability of the enone product **6i** suggested that the products of traceless alkyne hydroacylation could also be accessed. By using the *i*Pr-substituted catalyst **E**, recently reported as a highly active catalyst for alkyne hydroacylation,[17] bulky terminal alkynes, as well as an internal alkyne could be employed, delivering enones **6j** and **6k** in excellent yields. Bis-enones were also accessible (**6l**). Catalyst **E** was also used for the hydroacylation of butyl vinyl ether, which proceeds with high branched selectivity to give the α-substituted ketone **6m**. Finally, the hydroacylation of an allene could be achieved with catalyst **C**, which gave the β,γ-unsaturated ketone **6n** following silane reduction.

The use of catalyst **C** represents a convenient method for tandem hydroacylation/sulfide reduction, because this catalyst is active in both steps, bench stable and easily prepared from commercially available materials. However, the use of the relatively high catalyst loading of 10 mol% for this tandem reaction is not ideal. The amount of catalyst needed can be dramatically reduced if two separate catalysts are employed, each of which have been optimised for the individual steps of the process. We have previously shown that

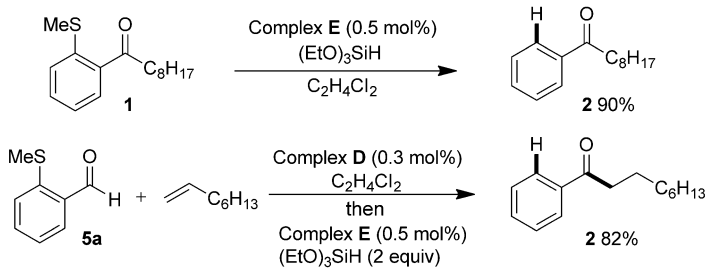
Table 4. Traceless chelation-controlled hydroacylation.[a]



[a] Conditions **5** (1.0 equiv), alkene/alkyne (1.5 equiv), complex **C** (10 mol%), $(EtO)_3SiH$ (2.0 equiv), Isolated yields. [b] Complex **E** was used as catalyst.

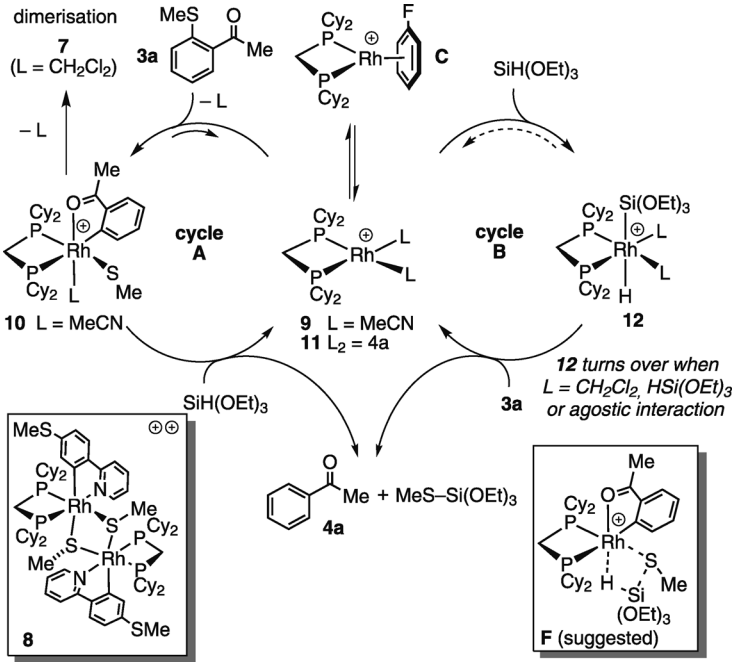
complex **D** (featuring the small bite-angle di(*t*Bu)phosphine) can catalyse the hydroacylation of unactivated alkenes at as low as 0.1% catalyst loading.[15] The most efficient catalyst for the aryl sulfide reduction step is complex **E**,[17] which can efficiently deliver the reduced compound by using only 0.5 mol% loading (Scheme 2). By combining these two catalysts into a one-pot tandem reaction, the traceless hydroacylation product **2** could be isolated in 82% yield, although employing only 0.8 mol% Rh in total (Scheme 2). This represents an efficient method for the synthesis of these valuable ketone products. These two procedures, involving either a single catalyst at higher loading, or two separate catalysts at low loading, are complementary, and allow the choice of either catalyst loading, or the convenience of a simplified reaction procedure, to be the paramount consideration.

We have probed the mechanism of the sulfide reduction process employing precatalyst **C**,[18] with a combination of



Scheme 2. Reduction and traceless HA by using low catalyst loadings.

stoichiometric and catalytic experiments by considering the two likely pathways: C–S bond cleavage followed by addition of silane (cycle A)[13a] or silane addition and then C–S cleavage (cycle B; Scheme 3). Both C–S bond cleavage[10,19]



Scheme 3. Species observed or implicated on the catalytic cycle. In CH_2Cl_2 solvent, L = CH_2Cl_2 or agostic interaction.

and oxidative addition of silanes[20] to Rh centres are established. Addition of **3a** to complex **C** (CH_2Cl_2 solution, 1:1) resulted in the slow consumption of **C** following first-order kinetics ($t_{1/2} = 30 \pm 5$ min) and the formation of a new Rh^{III} species $[Rh(Cy_2PCH_2PCy_2)(\mu\text{-SMe})\{\sigma,\kappa\text{-}C_6H_4(OCMe)\}]_2[BAr^F{}_4]_2$ **7** (see the Supporting Information). NMR data were unable to resolve whether **7** is a monomer or dimer in CH_2Cl_2 solution, but ESI-MS[21] clearly showed a $[M_2]^{2+}$ parent ion ($m/z = 677.27$, calcd 677.26). Complex **7** is formed as an intractable oil on attempted recrystallization, but the closely related complex incorporating pyridyl **3e** (Table 3) did afford crystalline material **8** suitable for X-ray diffraction studies, which showed a dimeric motif with bridging SMe groups, arising from C–S activation and coordination of the 2-pyridyl group (Scheme 3 and the Supporting Information). In compound **7**, coordination of the *ortho*-ketone likely occurs to retain an 18-electron count at each Rh. The NMR data for **7** and **8** are similar, and **8** also showed a $[M_2]^{2+}$ parent ion in the ESI-MS ($m/z = 758.27$, calcd 758.26). Both compounds **7** and **8** are essentially inactive in catalysis, showing that once formed they represent a deactivation pathway for this process in CH_2Cl_2 (or $C_2H_4Cl_2$). An active species is formed upon addition of **3a** to $[Rh(Cy_2PCH_2PCy_2)(MeCN)_2][BAr^F{}_4]$ (**9**)[15] to form $[Rh(Cy_2PCH_2PCy_2)(SMe)\{\sigma,\kappa\text{-}C_6H_4(OCMe)\}(NCMe)][BAr^F{}_4]$ (**10**), rather than the dimer. This reaction is rapid suggesting that dissociation of fluorobenzene is the limiting factor in the reaction of **C** with **3a** in CH_2Cl_2. NMR data suggest that **10** is in rapid equilibrium with **9**/**3a** at room temperature through reversible C–S bond cleavage,[10,19] which can be arrested at −80 °C ($K_{eq} \approx 3$ in favour of **10**). Addition of excess MeCN to this mixture resulted in the near-quantitative conversion to **9**, and ESI-MS of **10** showed it to be monomeric.

Addition of excess final product acetophenone (**4a**) to **C** resulted in the quantitative (as determined by $^{31}P\{^1H\}$ NMR spectroscopy) formation of the η^6-adduct $[Rh(Cy_2PCH_2PCy_2)(\mathbf{4a})][BAr^F{}_4]$ **11**. Compound **11** turns over in catalysis (10 mol%, 25 °C, 100% conversion) at a similar rate to that observed by using **C** (ToF ≈ 60 h^{-1}), consistent with their similar structures and a requirement to dissociate the bound arene prior to catalysis. However, compounds **9** and **10** act considerably faster when used in catalysis (100% conversion, ToF at least 600 h^{-1}), consistent with both the absence of bound arene and their monomeric structures (i.e., **10**). In the absence of MeCN under catalytic conditions (10 mol% **C**), substrate or product (e.g., **3a** or **4a**) presumably coordinate hindering dimerization to **7**, and under these conditions **3e** also turns over. The cycle **A** is completed by addition of $HSi(OEt)_3$ to **10**, which shows the elimination of **4a** (i.e., **11** is formed) and MeS–$Si(OEt)_3$. This process presumably occurs either by sigma-bond metathesis through an η^2-silane,[22] for example, **F**, or oxidative addition to give a Rh^V species.[23] Intermediates, such as **F**, have recently been invoked in reactivity of C–S bonds with silanes.[13a,24] Interestingly, addition of **3a** to pre-catalyst **D** only afforded the Rh^I κ^2-S,O adduct[15] with no C–S activation observed, consistent with the lack of conversion in catalysis (Table 1). Similarly, the lack of reactivity of the DPEphos complex **A** might suggest κ^3-P,O,P coordination[10,25] blocking the vacant site necessary for silane activation (i.e., **F**).

To probe the alternative cycle **B**, addition of excess[26] $HSi(OEt)_3$ to **C** (CH_2Cl_2 solution) resulted in a slow (4 h) reaction to form a Rh^{III} complex tentatively characterised as $[trans\text{-}Rh(Cy_2PCH_2PCy_2)(H)(Si(OEt)_3)(L)_2][BAr^F{}_4]$ (**12**; L = agostic C–H, CH_2Cl_2 or η^2-silane[20,22]). $^1H\{^{31}P\}$ NMR experiments (−80 °C, see the Supporting Information) argue against a dimeric motif with bridging hydride ligands, because a single hydride resonance is observed at δ −7.90 as a doublet [J(RhH) 15 Hz], which resolves into a virtual quar-

tet in the ^{1}H NMR spectrum. Complex **12** is fluxional at room temperature. Addition of **3a**/$HSi(OEt)_3$ to this complex resulted in turnover (10 mol%, ToF $\approx 300\ h^{-1}$) showing that **12** lies on, or is at least connected to, the productive cycle. Addition of one equivalent of **3a** to **12** resulted in rapid formation of **11** and MeS–$Si(OEt)_3$. Interestingly, addition of $HSi(OEt)_3$ to **9** occurred only very slowly, in contrast to the addition of **3a** to **9**. Unfortunately, our data herein do not allow us to discriminate between cycles **A** and **B** in CH_2Cl_2 solvent, and it is possible that both are operating in parallel. However, in the presence of excess MeCN (i.e., **9** as the precatalyst) it is likely that pathway **A** mainly operates, because addition of $HSi(OEt)_3$ to **9** is much slower than catalysis starting from **9**/**3a** and $HSi(OEt)_3$; whereas addition of MeCN to **12** resulted in the formation of the non-fluxional MeCN adduct, that is, L = MeCN (see the Supporting Information), which is inactive in catalysis when using **3a**.

Immediately at the end of catalysis using **C**, unreacted **C** (90%) and **11** (10%) were observed, consistent with the slow (cf turnover) displacement of fluorobenzene by **3a**.[27] The implication of these observations is that the actual active catalyst concentration is much lower than the loadings used. Consistent with this, the MeCN adduct **9** turns over in catalysis much faster than **C**.[15]

Conclusion

A new Rh-catalysed silane-mediated sulfide reduction process, which operates under mild reaction conditions and displays excellent functional group tolerance, was reported. When partnered with an initial Rh-catalysed alkene, alkyne or allene hydroacylation procedure, the overall cascade process gives the products of traceless chelation-controlled hydroacylation. This new process uses the mild reaction conditions and has the substrate scope of chelation-mediated hydroacylation, yet delivers products free of an unwanted coordinating substituent.

Acknowledgements

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