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PtCl₂/XPhos: A highly efficient and readily available catalyst for the hydrosilylation of propargylic alcohols[†]

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A highly regioselective hydrosilylation of propargylic alcohols has been developed using an *in situ* prepared PtCl₂/XPhos catalyst system. The reaction is tolerant of many functional groups and exhibits excellent regio and geometric selectivity.

The hydrosilylation of alkynes is a powerful reaction resulting in a stereodefined alkene with a useful functional handle for further synthetic elaboration. There are many catalysts that promote this reaction and late transition metal catalysts can be especially efficient.^{1,2} In particular, platinum complexes such as Speier's catalyst $[H_2PtCl_6]$ and Karstedt's catalyst $[Pt_2(dvs)_3]^3$ can produce high catalyst turnovers, however the selectivity can be poor.^{4,5}

A solution to this problem was found through the use of bulky trialkylphosphine ligands⁶ and more recently the use of platinum N-heterocyclic carbene complexes.⁷ These sterically encumbered catalysts can impart high levels of selectivity on the reactions. Of note, was the development of the (dvs)Pt–Pt–Bu₃ catalyst which exhibits high activity with a high level of selectivity.^{6a} The drawbacks to these methods are the cost of the Pt(0) precatalysts and the pyrophoric nature of the phosphines required.

Alami reported that a combination of Pt(II) salts and bulky dialkylarylphosphines, such as XPhos, catalysed the hydrosilylation of alkynes.⁸ The reaction proceeded in good yields and excellent selectivities, however a large catalyst loading is required, typically 5 mol% Pt and 10 mol% phosphine.

We required a rapid and reliable method for the synthesis of β -silyl alyllic alcohols **2** that was tolerant of significant steric encumbrance. Panek previously reported the use of the highly reactive (dvs)Pt–Pt–Bu₃ catalyst for the regioselective hydrosilylation of propargylic alcohols,⁹ however no examples of sterically congested propargylic alcohols were reported. We speculated that we could modify the reaction reported by Alami to combine the catalytic activity of the bulky Pt(0) catalyst with the selectivity and operational ease of the air stable Pt(II) system. Herein we report the use of air and moisture stable Pt(II) salts and Buchwald phosphines to yield the requisite vinyl silanes using a wide range of propargyl alcohols exclusively as the β -isomer with the *E*-geometry.

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We began by examining but-3-yn-2-ol 1a (Table 1), the reaction proceeded well with 5 mol% $PtCl_2$ and 10 mol% XPhos, analogous to the conditions reported by Alami,⁸ producing a single regio and geometric isomer in excellent yield. In the absence of XPhos the regioselectivity was diminished with only a 9:1 selectivity being observed. Further optimisation lead to the catalyst loading being reduced with excellent yields still being produced at just 1 mol% catalyst, however below this the reaction becomes sluggish and lower yields are observed. The amount of silane used could also be lowered but again, a pronounced slowing of the reaction is observed.

The substrate scope for secondary propargylic alcohols is examined in Table 2. The reaction is tolerant of alkyl, branched alkyl and aryl groups **2a–h** with typical yields 80–91% using just 1 mol% PtCl₂ and 2 mol% XPhos.

More functionalised substrates could also be incorporated with heteroaromatics and alkenes being well tolerated with good yields and selectivities shown for the alkyne.¹⁰ Propargyl alcohol itself **1b** is a poor substrate for this reaction with low yields being obtained.

The reaction is even more efficient when tertiary propargylic alcohols are used (Table 3). The catalyst loading may be reduced further to just 0.5 mol% and excellent yields of the corresponding vinyl silanes produced. Dialkyl **4a–c** and diaryl groups **4d** are tolerated well as are a combination of the two **4e**. Cyclic propargylic alcohols **4f–h** are also excellent substrates and even those bearing basic heteroatoms **4g–h** are well tolerated.

We also examined the use of different silanes in the reaction, as phenyldimethylsilane was used throughout (Table 4). Other

Table 1 Optimisation Studies

OH Me 1a		PtCl ₂ , XPhos PhMe ₂ SiH, THF 50 °C, 12h		OH Me SiMe ₂ Ph 2a	
Entry	mol% PtC	l ₂ /Xphos	Eq. R ₃ SiH	$β: \alpha \text{ Ratio}^a$	Yield $(\%)^b$
1	5/10		1.6	> 99 : 1	93
2	5/0		1.6	> 91 : 9	72
3	2/4		1.5	> 99 : 1	93
4	1/2		1.5	>99:1	91
5	0.5/1		1.5	> 99 : 1	74
6	1/2		1.1	>99:1	83
^a Deter	mined by ¹ H	I NMR. ^b	Isolated vield	l of pure B-iso	mer.

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 Table 3
 Tertiary Propargylic Alcohol Scope



trialkyl silanes were attempted and triethylsilane was a very efficient coupling partner. Triiso-propylsilane was presumably too hindered as no reaction was observed and starting material was recovered. Triethoxysilane coupled efficiently providing access to vinyl trialcoxysilanes **8c** which can be used in Hiyama cross-coupling chemistry.¹¹ Aryl silanes undergo the reaction to form triaryl vinyl silanes. Interestingly silanes containing multiple hydrides can undergo multiple couplings. Diphenyl-silane can couple with two equivalents of alkyne to afford divinyl silanes **8e** and phenylsilane can couple with three equivalents to provides trivinyl silanes **8f**.¹²

We also examined whether we could perform a one-pot hydrosilylation/Hiyama-Denmark cross-coupling reaction.¹³ Table 4Alternative Silane Scope



The hydrosilylation of **3a** with 1,1,3,3-tetramethylsiloxane proceeded smoothly to form the intermediate bis-hydrosilylated product,¹⁴ which was treated with TBAF and iodobenzene in the presence of Pd_2dba_3 as a catalyst to afford the cross-coupled product **6** in 71% yield (eqn (1)).



Aside from hydrosilylation, other hydrometallations can be efficiently catalyzed by this system. Pinacol borane can perform a hydroboronation on TMS protected propargylic alcohol in good yields (eqn (2)).¹⁵ Although the reaction to form **8** does proceeds uncatalysed, much higher yields are obtained, with faster reaction times than previously reported using less pinacol borane.¹⁶



We also examined internal alkynes to investigate whether the Lewis basic oxygen atom was co-ordinating to the metal and directing the addition¹⁷ or whether the regioselectivity was based purely on steric factors.¹⁸ The first substrate attempted was but-2-yn-1-ol **9**, which gave a 1 : 1 mixture of regioisomers. This clearly disproves that the oxygen is directing the addition and that pure sterics govern the regioselectivity. When a cyclohexyl group is introduced at the propargylic position **11** an increase in β -selectivity with a 3.2 : 1 ratio of **12**a : **12b** being observed (eqn (4)), which is in line with what one would expect based on the steric environment of the alkyne.

When the terminal alkyne position of propargyl alcohol was substituted with a phenyl group 13, modest selectivity was



observed with the β -isomer **14a** prevailing in a 4.1:1 ratio (eqn (5)). This is contrary to the steric environment around the alkyne and is clearly showing preference for hydride attack at the more electrophilic terminus of the alkyne.¹⁹ Indeed, Alami observed this effect when applied to the palladium catalyzed hydrostannylation of 13, with 4:1 regioselectivity for β-substitution being observed.²⁰ They also showed that the regioselectivity in these systems directly correlated to the Hammett σ -value for substituted benzene rings with the β -isomer favoured in all cases. If the steric environment at the β-position is increased greatly by installing a *tert*-butyl group 15. the regioselectivity of the reaction can be switched to give solely the α -isomer. No traces of the β -isomer 16a was observed with only the α -isomer **16b** being formed in good yield. A single regioisomer could again be obtained when the propargylic position is was highly substituted compared to the β -position 17. In this instance only the β -isomer 18a was observed again in good yield (eqn (7)). The results in eqn (6)and (7) demonstrate that the steric environment around the alkyne plays a pivotal role in determining the selectivity of the products. However, when the alkyne is polarised an electronic bias is present, such as eqn (5), the regiochemistry will be dictated by the attack of the hydridic hydrogen at the more electron deficient terminus.

In conclusion we have demonstrated the power of the PtCl₂/ XPhos catalyst system to perform hydrometallations across alkynes. The reaction works particularly well for sterically encumbed tertiary propargylic alcohol and a single regioisomer is always obtained. The regioselectivity of internal alkynes was also probed and we discovered that a combination of steric and electronic factors governed the regioselectivity.

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