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Permalink

<https://escholarship.org/uc/item/7vv122hq>

Journal

Chemical communications (Cambridge, England), 53(87)

ISSN

1359-7345

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Publication Date

2017-10-01

DOI

10.1039/c7cc06417a

Peer reviewed

Cite this: *Chem. Commun.*, 2017, 53, 11881Received 16th August 2017,
Accepted 11th October 2017

DOI: 10.1039/c7cc06417a

rsc.li/chemcomm

Efficient and selective catalysis for hydrogenation and hydrosilation of alkenes and alkynes with PNP complexes of scandium and yttrium†‡

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Scandium and yttrium congeneric complexes, supported by a mono-anionic PNP ligand, were studied as catalysts for alkene hydrogenation and hydrosilation and alkyne semihydrogenation and semihydrosilation. The yttrium congener was found to be much more active in all cases, but this greater activity is accompanied by more rapid catalyst decomposition and therefore higher total yields for some of the reactions with the scandium catalyst. Calculations indicate that the reactions may proceed via σ -bond metathesis of the alkyl complexes to form metal hydride intermediates into which alkenes/alkynes insert.

Organometallic complexes of early transition metals in a d^0 electronic configuration are associated with two major types of reactions toward organic substrates, σ -bond metathesis and the insertion of multiple (e.g., C=C) bonds.¹ However, these two reaction steps are rarely combined to form a catalytic cycle.^{1b,2} There have been several advances in recent years employing this approach for hydroamination,^{2d} chain transfer,^{2e} hydroarylation,^{2f} and hydroalkylation^{1b,2g} of olefins. Further advances require greater knowledge of the fundamental reaction steps. Early investigation into the less well-studied of these modes, σ -bond metathesis, revealed that there can be significant differences in rates between scandium and yttrium that span two orders of magnitude (Fig. 1).^{3a} However, beyond these seminal reports, there have been relatively few studies that compare first and second row group 3 metal complexes with the same ligand set, and the role of the metal center has not been extensively explored.³

Recently, a series of PNP-supported scandium alkyl complexes, such as (PNP-Cy)Sc(CH₂SiMe₃)₂ (**1-Sc**) (Fig. 2), were found to react rapidly with hydrogen to form reactive hydride complexes that were trapped by insertion of olefins into the Sc–H bond.⁴ To gain more

Fig. 1 The σ -bond metathesis reaction, comparing the rates of Sc, Y, and Lu congeners in the methane activation reaction.

insight into potential differences between these Sc and Y complexes as catalysts, the congeneric yttrium bis(alkyl) complex **1-Y** was prepared, and its reactions with hydrogen and hydrosilanes were examined. Complexes **1-Sc** and **1-Y** are active catalysts for additions of H₂ and Si–H bonds to olefins, in reactivity that features both σ -bond metathesis and insertion events. Comparisons of these complexes may provide useful underpinnings for catalyst design, and for understanding steric and electronic factors that influence catalytic processes involving four-center transition states.⁵

Complex **1-Y**, (PNP-Cy)Y(CH₂SiMe₃)₂, was prepared by addition of (PNP-Cy)H to a pentane solution of Y(CH₂SiMe₃)₃(THF)₂.⁶ This complex displays a ¹H NMR spectrum that is similar to that of the scandium analogue. It crystallizes as a dimer in the solid state, as determined by X-ray crystallography (see ESI†); however, the room-temperature ¹H NMR spectrum of this complex in benzene-*d*₆ is consistent with a monomer, or with a rapid monomer–dimer equilibrium.

Initial experiments were designed to allow comparison of **1-Sc** and **1-Y** in catalytic alkene hydrogenation reactions. These experiments involved addition of 4 atm of hydrogen to a sample of **1-Sc** or **1-Y** (0.01 mmol) and an olefin (0.2 mmol) in benzene-*d*₆ (1 mL) in an NMR tube. Generation of the active catalyst is presumed to occur by reaction of hydrogen with the bis(alkyl) complexes to release tetramethylsilane and generate the dihydride complex. The catalyst precursor **1-Y** initiates much faster (< 10 min vs. 2 h for **1-Sc** to reach > 99% yield of tetramethylsilane, as monitored by ¹H NMR spectroscopy at 22 °C). Thus, as expected,^{3a} the Y–C bonds are much more reactive than analogous Sc–C bonds toward hydrogenolysis. The much slower reaction of **1-Sc** appears also to be affected by the α -silicon effect, which renders silylated alkyl groups less reactive than

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† Dedicated to Phil Power on the occasion of his 65th birthday.

‡ Electronic supplementary information (ESI) available. CCDC 1569211. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7cc06417a

Fig. 2 Previously reported PNP-supported scandium complexes.

all-carbon groups,⁷ since the bis(neopentyl) analogue of **1-Sc** initiates in < 10 min.

Primary olefins (e.g., 1-octene) were quantitatively hydrogenated to the corresponding alkane over the course of 7 h by 5 mol% **1-Sc** at 22 °C (Table 1, entry 1). The yttrium analogue **1-Y** requires 48 h to reach 90% yield of alkane (Table 1, entry 4). The disubstituted olefin cyclohexene was also hydrogenated under these conditions, although the rates are somewhat slower (62% yield in 7 h for Sc; 10% yield in 48 h for Y, Table 1, entries 2 and 5). The lower rates and yields for cyclohexene are consistent with less efficient hydride trapping by the more hindered, secondary olefins. Since stoichiometric reactions indicated that the metal hydride complexes formed are unstable to decomposition,^{4a} this slower trapping rate is believed to lead to more decomposition and less catalysis.

Owing to the fact that **1-Sc** and **1-Y** catalyze the hydrogenation of primary olefins more rapidly than secondary olefins (Table 1), investigation to determine if these complexes would be competent semihydrogenation catalysts was pursued. The selective semihydrogenation of alkynes to alkenes remains a significant synthetic challenge.^{8,9} Both catalysts proved to be selective for the semihydrogenation of 3-hexyne to *cis*-3-hexene (> 98% for Y, Table 1, entry 6, and 82% for Sc, Table 1, entry 3). In this case as well, the yttrium catalyst suffered from rapid decomposition (observed as loss of ¹H NMR resonances for the catalyst resting state (PNP-Cy)Y(CH=CHC₄H₉)₂), yielding only 22% *cis*-3-hexene; **1-Sc** attained > 98% conversion before significant catalyst decomposition was observed (80% of the Sc catalyst remained as (PNP-Cy)Sc(CH=CHC₄H₉)₂ after consumption of substrates, see ESI†). These data suggest that the yttrium hydride complexes that are formed in this reaction are less stable to decomposition than scandium analogues, leading to lower overall yield due to catalyst decomposition.

Hydrosilylation, a related hydrofunctionalization reaction, introduces the possibility of regiochemical and stereochemical control. Selective semihydrosilylation catalysts are rare,¹⁰ although the vinyl silane products are valuable materials in industry and in organic synthesis as masked ketone functionalities and as

Table 1 Catalytic hydrogenation with **1-Sc** and **1-Y**

Entry	M	Substrate	Time (h)	Select. ^a (%)	Yield ^a (%)
1	Sc	1-Octene	7	> 98	> 98
2	Sc	Cyclohexene	7	> 98	62
3	Sc	3-Hexyne	48	82	82
4	Y	1-Octene	48	> 98	90
5	Y	Cyclohexene	48	> 98	10
6	Y	3-Hexyne	5	> 98	22

Reaction conditions: 1 equiv. substrate, 4 atm H₂, 5 mol% catalyst, 23 °C, benzene-*d*₆, internal std: hexamethylbenzene. ^a Determined by ¹H NMR spectroscopy. Yield: mol pdct/mol starting material, selectivity: mol pdct/mol starting material consumed.

Table 2 Catalytic hydrosilylation with **1-Sc** and **1-Y**

Entry	M	Silane	Alkene	Time (h)	Select. ^a (%)	Yield ^a (%)
1	Sc	PhSiH ₃	1-Hexene	2	> 98	> 98
2 ^b	Sc	PhSiH ₃	Cyclohexene	16	> 98	59
3 ^b	Sc	PhSiH ₃	Cyclohexene	68	> 98	74
4 ^c	Sc	PhMeSiH ₂	1-Hexene	130	> 98	> 98
5 ^c	Sc	PhMeSiH ₂	Cyclohexene	84	N/A	0
6 ^e	Y	PhSiH ₃	1-Hexene	5 min	> 98	> 98
7	Y	PhSiH ₃	Cyclohexene	16	> 98	16
8 ^d	Y	PhMeSiH ₂	1-Hexene	20	> 98	68
9 ^d	Y	PhMeSiH ₂	Cyclohexene	24	N/A	0

Reaction conditions: 1 : 1 alkene : silane, 5 mol% catalyst, 23 °C, benzene-*d*₆.

^a Determined by ¹H NMR spectroscopy. ^b Reaction carried out at 50 °C.

^c Reaction carried out at 80 °C. ^d Reaction carried out at 40 °C. ^e 2 mol% **1-Y**.

coupling partners in cross-coupling reactions.¹¹ While there are some examples of hydrosilylations of alkenes and alkynes with yttrium,^{2c,3b,12} lanthanum,^{12d} and thorium,¹³ there are no examples of semihydrosilylation with scandium and, as such, no corresponding comparison of first- and second-row congeners (Sc and Y) possessing the same ligand set.

The results from alkene hydrosilylation reactions are summarized in Table 2. These catalysts were found to be remarkably selective for a single hydrosilylation product and in some cases they are extremely active, with **1-Y** again initiating faster than **1-Sc** (as monitored by formation of (CH₃)₃SiCH₂SiH₂Ph by ¹H NMR spectroscopy; 1 h for **1-Sc** vs. < 5 min for **1-Y** for > 99% yield of (CH₃)₃SiCH₂SiH₂Ph). For substrates that could produce multiple regioisomers of hydrosilylation products (1-hexene), the less hindered (that is, anti-Markovnikov) addition product was exclusively formed. Regioselectivities of > 98% were obtained in all cases (Table 2, entries 1 and 6). This selectivity may be attributed to steric bulk near the metal center, which favors 1,2- over 2,1-insertion.¹⁴ The resting state of both catalysts is the dialkyl (di-insertion) complex, as determined by NMR spectroscopy (see ESI†). Complex **1-Y** was found to be an extremely rapid catalyst, providing > 98% yield in the hydrosilylation of 1-hexene in < 5 min at 23 °C with as little as 2 mol% catalyst, indicating a turnover frequency of > 500 h⁻¹ (Table 2, entry 6). For comparison, Cp*₂Ln-R lanthanocene catalysts of marks catalyze this reaction with a turnover frequency of 120 h⁻¹ to give 74% yield and 76% regioselectivity for one product.² Indeed, **1-Y** displays turnover frequencies equal to the highest reported for any rare-earth or early transition metal catalyst for this reaction.^{12c} Secondary silanes require heating for the reaction to proceed at a reasonable rate (Table 2, entries 4 and 8). With secondary silanes, the initiation step (and therefore probably the productive σ-bond metathesis step) is much slower, requiring 2 h for **1-Y** and 60 h for **1-Sc**. In accordance with the hypothesis that insertion to form secondary alkyl substituents is disfavored, cyclohexene also required heating to achieve reasonable turnovers (Table 2, entries 2 and 3). The combination of secondary silane and disubstituted olefin afforded no product with either catalyst (Table 2, entries 5 and 9). With more hindered alkenes, **1-Y** does not afford as much product over time as **1-Sc**, though this catalyst initiates faster and reaches its maximum yield much earlier (Table 2, entries 2, 3 and 7).

The partial hydrosilation of alkynes was also efficiently catalysed by **1-Sc** and **1-Y**. With the symmetric, internal alkyne 3-hexyne, both catalysts afford the (*E*)-vinyl silane product of *syn* addition of the silane in high yield (>98%) and with >98% selectivity (Table 3, entries 1 and 6). The unsymmetric, internal alkyne methylphenylacetylene allows for an interesting probe for regioselectivity, since the product with the silyl group *trans* to the methyl group (**2**) is electronically preferred, while the product with the silyl group *trans* to the phenyl group (**3**) is sterically preferred.¹⁵ Complex **1-Y** affords the electronically-preferred product in about 90% selectivity (Table 3, entries 7 and 8), similar to previously reported catalysts.¹⁵ In contrast, **1-Sc** exhibits the opposite preference, producing the sterically-preferred product with about 66% selectivity (Table 3, entries 2 and 3). This difference may be attributed to the different radii of the metal centers, and a more crowded scandium center that exerts greater steric control.

Complex **1-Sc** also proved to be a very efficient catalyst for the anti-Markovnikov partial hydrosilation of terminal alkynes. This reaction is very challenging because of the highly acidic nature of the alkyne C–H bond. Examples of catalysts for this reaction, based on thorium and uranium, require 24–48 h (sometimes with heating) and have low product selectivities of 33–62%.¹³ In contrast, **1-Sc** achieves quantitative conversion with 95% selectivity in 20 min at 23 °C (Table 3, entry 4); **1-Y** exhibited no catalytic activity under the same conditions (Table 3, entry 9).

The mechanisms of these reactions are difficult to ascertain due to the fact that the proposed hydride intermediate is not observed and can only be inferred indirectly from its reactivity with alkenes and alkynes. All reactions are proposed to proceed

Table 3 Catalytic partial hydrosilation with **1-Sc** and **1-Y**

Entry	M	Alkyne	Time (h)	Select. ^a (%)	Yield ^a (%)
1	Sc	EtCCEt	60	> 98	> 98
2 ^b	Sc	MeCCPh	16	33 : 66 2 : 3	55
3 ^b	Sc	MeCCPh	87	33 : 66 2 : 3	80
4	Sc	HCC ⁱ Pr	0.3	95	> 98
5	Sc	HCC ⁿ Pr	2.5	95	90 (68) ^c
6	Y	EtCCEt	3.5	> 98	> 98
7	Y	MeCCPh	10	90 : 10 2 : 3	80
8	Y	MeCCPh	48	90 : 10 2 : 3	89
9	Y	HCC ⁱ Pr	24	N/A	0

Reaction conditions: 1:1 alkyne:PhSiH₃, 5 mol% catalyst, 23 °C, benzene-*d*₆. ^a Determined by ¹H NMR spectroscopy. ^b Reaction carried out at 40 °C. ^c Preparative scale reaction, isolated (distilled) yield 68%.

Fig. 3 Proposed mechanism for catalytic hydrosilation. Hydrogenation is proposed to operate by an analogous mechanism.

by σ -bond metathesis reactions of **1-Sc** or **1-Y** with silanes (or hydrogen) to afford a reactive hydride species. These hydride complexes are trapped by insertion of (for example) olefins to regenerate alkyl complexes, allowing the catalyst to turn over (Fig. 3).

Further complicating analysis of this reaction is that both dihydride and monohydride (PNP)M(H)(alkyl) complexes (also unobserved) are potential catalysts. Generally speaking, the yttrium complexes appear to react more rapidly with H–H and H–Si bonds, but also to decompose more rapidly than the scandium congeners under catalytic conditions. For the yttrium system, competing decomposition is fastest with the most reactive σ -bond metathesis substrates (H₂, primary silanes), implicating hydrides species in the decomposition process. The greater catalytic performance of the scandium congener would therefore seem to relate to the stability of corresponding hydrides, *e.g.* [(PNP)ScH₂]_x, which are more rapidly trapped by the unsaturated substrate. The decomposition product(s) of **1-M** does not appear to be a well-defined material; though soluble in benzene-*d*₆, NMR spectroscopy indicated a complex mixture. Workup and crystallization proved unsuccessful.

Fig. 4 Calculated free energy reaction pathway for **1-Sc** (black) and **1-Y** (blue). All energies are given in kcal mol^{−1}.

To evaluate the feasibility of the proposed mechanism for hydrosilation, DFT calculations were carried out. To save computational time, some truncations were made to the system (described in the ESI†). These truncations relieve some of the steric demands of the system but previous calculations of σ -bond metathesis reactions with these complexes were insensitive to these changes.^{4b} The calculated catalytic pathway is shown in Fig. 4. As expected, the rate-determining step in catalysis was calculated to be the σ -bond metathesis step, with a barrier of 28.8 kcal mol⁻¹ for Sc and 20.5 kcal mol⁻¹ for Y. A separate calculation of the initiation reaction, in which the exchanging group is -CH₂SiMe₃, (not shown in Fig. 4) indicated a slightly higher barrier (29.9 kcal mol⁻¹ for Sc, 27.7 kcal mol⁻¹ for Y). Calculations indicate that the reaction proceeds predominantly *via* a metal-hydride complex as opposed to a metal-silyl complex, since the barrier to formation of the silyl complex is slightly higher than that of the hydride complex (by 1.1 kcal mol⁻¹ for Sc, 7.3 kcal mol⁻¹ for Y). The insertion of olefin (propylene in the calculation) into the methyl hydride complex was found to have a lower barrier for Sc (13.0 kcal mol⁻¹) than Y (17.5 kcal mol⁻¹). This suggests another possibility for scandium's superior performance relative to yttrium: the insertion reaction that traps the reactive hydride species is faster with scandium (as indicated by the lower barrier), leading to less catalyst decomposition.

In summary, efficient and selective hydrogenation, semi-hydrogenation, hydrosilation, and partial hydrosilation catalysts are based on PNP-supported Sc and Y complexes. The Sc and Y complexes follow trends similar to those observed in stoichiometric methane activations, in which σ -bond metathesis is much more rapid with Y and Sc.^{1e,3a} However, this greater reactivity does not necessarily result in a better catalyst, since, in these cases, catalyst decomposition occurs more rapidly. Calculations indicate that relatively less efficient trapping of the reactive metal hydride complexes may be due to a higher barrier to olefin insertion in the yttrium complex than the scandium congener. Different steric environments for the catalysts, due to the difference in radii, lead to marked differences in regioselectivities for the partial hydrosilation of alkynes. Future work will focus on strategies to stabilize the hydride intermediates in order to prevent catalyst decomposition and afford more active and general catalysts.

This work was primarily funded by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AC02-05CH1123. We acknowledge the National Institutes of Health and National Science Foundation for funding of the UC Berkeley College of Chemistry NMR facility under Grant No. S10 RR 03353-01, SRR023679A, 1S10RR016634-01, CHE-0130862,

CHE-8703048, and HE79-26291-A02. DSL acknowledges support of a NSF GRFP.

Conflicts of interest

There are no conflicts to declare.

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