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From Remote Alkenes to Linear Silanes or Allyl Silanes Depending on the Metal Centre

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Abstract: The selective synthesis of linear silanes or allylsilanes from remote alkenes is reported. The cationic and unsaturated, 16 electrons, hydrido-silyl-Rh(III) complex is efficient catalysts for a tandem catalytic alkene isomerization-hydrosilylation reaction at room temperature under solvent-free conditions. The analogue hydrido-silyl-Ir(III) complex is selective for the dehydrogenative silylation, leading to the formation of terminal allylsilanes.

Organosilane compounds are extensively employed in commercial products, such as coatings, paints or sealants.^[1] They also play a significant role in organic synthesis as useful intermediates in various synthetic transformations.^[2] Transition metal-catalyzed hydrosilylation of alkenes is stablished as one of the most common preparation pathways for these compounds.^[3] Platinum catalysts based on Speier's^[4] and Karstedt's^[5] complexes have remained powerful methods in hydrosilylation for years, and first-row transition metals have also been recently studied.^[6] Unsaturated hydrosilylation products are also versatile synthetic intermediates, based on their high stability and non-toxic nature.^[7] They can undergo direct transformations to allyl and vinyl alcohols, or act as nucleophiles in reactions such as Hiyama Sakurai coupling reactions.^[8] Although catalysed or hydrosilylation of alkynes is the general route to these compounds, dehydrogenative silvlation of alkenes has likewise become a useful method of synthesis.^[9] For dehydrogenative silvlation, precious metals like ruthenium or rhodium,^[10] or more recent examples of iron^[11] and cobalt^[12] have proved to be efficient catalysts. Studies of iridium complexes as catalysts in both hydrosilylation and dehydrogenative silylation of alkenes are rare.^[13] One common challenge for the mentioned systems is the formation of terminal silvlated products from internal olefins or olefin mixtures. Internal olefin mixtures being more readily accessible and cheaper than terminal alkenes also add to the interest of this process. Examples of efficient tandem

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isomerization-hydrosilylation of internal alkenes catalysed by iron,^[14] nickel^[15] or cobalt^[6e,16] complexes or nickel nanoparticles^[17] have recently been reported. We have more recently reported on a rhodium silyl complex containing a Si,S-chelating ligand, {Rh(H)[SiMe₂(o-C₆H₄SMe)](PPh₃)₂}[BAr^F₄], as being a very efficient catalyst for this reaction.^[18] These results prompted us to evaluate the viability of related hydrido-silyl rhodium(III) and iridium(III) complexes containing Si,S,S-terdentate ligands as catalysts for the tandem isomerization-hydrosilylation of terminal and internal alkenes.

Here, we report on the catalytic activity of the coordinatively [RhH(SiMe(ounsaturated Rh(III) compound $C_6H_4SMe_{2})(PPh_3)][BAr_{4}]^{[19]}$ (compound 1 in Figure 1) in tandem isomerization-hydrosilylation of internal alkenes to form linear silanes. Moreover, we describe the synthesis and characterization of the coordinatively saturated Ir(III) compounds 1). [IrH(SiMe(o-2-4 Figure (compounds in C6H4SMe)2)(PPh3)(THF)][BArF4] (compound 4 in Figure 1), containing a labile solvent ligand (THF), is selective for the dehydrogenative silylation of internal alkenes, leading to the formation of terminal allyl silanes ..



Figure 1. Compounds used as precatalysts in this work.

The reaction of $[Ir(cod)CI]_2$ with the equimolar amount of the tridentate proligand SiMeH(o-C₆H₄SMe)₂ and PPh₃ afforded the air-stable Ir(III) neutral complex {IrCIH(SiMe(o-C₆H₄SMe)₂)(PPh₃)} (2) (Scheme 1). This compound was characterized in solution by NMR spectroscopy and ESI-MS. Complex 2 is the iridium analogue to the precursor of the rhodium complex 1.





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The ¹H NMR spectrum shows a doublet at -14.13 ppm (J_{P-H} = 17.6 Hz) assigned to the hydrido resulting from the Si–H activation by the metal centre. The signal corresponding to the SiMe unit appears at δ 0.07, and the other two non-equivalent SMe signals are observed at δ 2.65, and 3.41. The ³¹P{¹H} NMR shows a unique signal at 13.3 ppm that indicates a Ir(III) triphenylphosphine complex. An X-ray diffraction study of complex **2** confirms the proposed structure based on NMR spectroscopic data in solution (Figure 2a). The Ir(III) centre is in a pseudo-octahedral geometry. The pincer SiMe(o-C₆H₄SMe)₂ ligand adopts a facial disposition and is coordinated to the metal center by a silyl fragment, and the two thioether moieties. Hydride and triphenylphosphine occupy the two coordination positions *trans* to sulphur atoms, while chloride is located trans to the silyl unit.

Overnight reaction of complex **2** with LiAlH₄ in Et₂O at room temperature allowed the exchange of chloride by hydride to yield complex { $[Ir(H)_2[SiMe(o-C_6H_4SMe)_2](PPh_3)$ } (**3**) (Scheme 2). Otherwise, addition of the NaBAr^F₄ salt to complex **2** in CH₂Cl₂ leads to removal of chloride, and subsequent dissolution in tetrahydrofuran (THF) allows the formation of the cationic compound { $Ir[SiMe(o-C_6H_4SMe)_2](H)(PPh_3)(THF)$ }[BAr^F₄] (**4**) (Scheme 2), where the solvent would then occupy the coordinative vacancy left by the chloride. Attempts to obtain the Ir(III) analogue of **1** proved unsuccessful.



Scheme 2. Synthesis of Complexes 3 and 4.

Experimental ¹H NMR data for 3 shows a single signal for the hydrido at -15.44 ppm (d, J_{P-H} = 14.2 Hz), indicating the equivalence of the two hydride ligands in the molecule. The signals for the SiMe and the equivalent SMe units appear at 1.09 and 2.15 ppm respectively. The ³¹P{¹H} NMR spectrum shows a unique signal at 13.6 ppm corresponding to a Ir(III) triphenylphosphine complex. Isolation of X-ray quality crystals allowed the characterization of compound 3 by single-crystal Xray structural determination (Figure 2b). The coordination geometry for the Ir(III) centre is pseudo octahedral, with the SiMe(o-C₆H₄SMe)₂ spanning one of the octahedron faces. The triphenylphosphine ligand is now located trans to the silyl fragment, while the two hydride ligands are opposite the thioether groups. This disposition could be explained due to the trans influence of the silyl and the hydride groups. In the 1H NMR spectra of complex 4, the signal corresponding to the hydrido is observed at -14.25 ppm (d, JP-H = 14.8 Hz), Other three, integral 3 H methyl signals at 3.30, 2.60, and -0.06 ppm are assigned to the non-equivalent SMe units and the SiMe group in the molecule, respectively. Furthermore, the observation of two signals at 3.57 and 1.70 ppm suggest the presence of coordinated tetrahydrofuran. Formation of 4 is also supported by ESI-MS spectroscopy that shows a molecular ion at m/z = 745.12 (calcd.

745.12), which corresponds to the ion ${Ir[SiMe(o-C_6H_4SMe)_2](H)(PPh_3)}^{\dagger}$ due to loss of THF.

As mentioned previously in the introduction of this paper, we thought useful to extend our studies on the reaction of silanes with internal alkenes using hydrido-silyl-Rh(III) (1) and Ir(III) complexes (2-4) containing terdentate Si,S,S-ligands as precatalysts. Initial hydrosilylation experiments were performed with an equimolar amount of predried trans-2-octene and Et₃SiH using 1 mol% loading of catalyst, without added solvent and under an atmosphere of N₂ (Table 1). The precatalysts used for this initial catalysis experiments were (Figure 1): the unsaturated cationic silyl-hydrido-Rh(III) complex 2, the neutral silyl-dihydrido-Ir(III) complex 3 and the cationic silyl-hydrido-Ir(III) compound 4, which has a labile THF molecule coordinated to the metal centre.



Figure 2 a) Molecular structure of 2. Displacement ellipsoids are drawn at 50% probability level. b) Molecular structure of 3. Displacement ellipsoids are drawn at 50% probability level.^[20]

The rhodium(III) complex 1 was able to catalyse the tandem isomerization-hydrosilylation of trans-2-octene at room temperature with a selectivity of 99% for the linear product triethyloctylsilane 5 (Scheme 3a; Table 1, entry 1). 76% conversion was reached after 12h reaction and further reaction up to 72h allowed 90% conversion. Analogue iridium(III) complex 4 also reached good conversion after 12h, though it require heating up to 50 °C (Table 1, entry 4). However, the observed main silylated compound for this catalyst was the unsaturated allylic triethyl(2-octen-1-yl)silane 6, with a 60% selectivity; this fact indicates that the main catalytic reaction occurring is a tandem isomerization-dehydrogenative silylation (scheme 3b). As expected, ${\bf 6}$ consists of a 3:1 mixture of E/Z isomers. $^{\rm 16c}$ In all cases the silvlation products obtained were selectively anti-Markovnikov. The efficiency of cationic complexes as precatalysts was proved higher as neutral Ir(III) complex 2 was reached only 30% conversion (Table 1, entry 2), with dehydrogenative silylation products being also the main compounds among the final mixture. The difference in the labile nature of the chloride and the tetrahydrofuran can explain the decreased conversion on going from 4 to 2. Complex 3 was inactive for these catalyses (Table 1, entry 3). We propose that the presence of a second hydride instead of chloride or tetrahydrofuran would block the possibility

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of generating a vacant coordination site on the metal centre and thus explain the lack or reactivity of 3.



Scheme 3. a) Tandem isomerization-hydrosilylation of trans-2-octene with Et₃SiH using catalyst 1. b) Tandem isomerization-dehydrogenative silvlation of trans-2-octene with Et_3SiH using catalysts 1 and 4.

Table 1. Hydrosilylation of trans-2-octene with Et₃SiH.^[a]

2

		t ₃ SiH 1 mol% [Rh] or [Ir] Neat 12h	 Silylated products
Entry	Catalyst Terr	iperature (°C)	Conversion (%) ^[b]
1	1	r.t.	76 ^[c]

2 3 3 50 No reaction 73^[d] 4 л 50 [a] Reaction conditions: alkene (0.25 mmol) and Et₃SiH (0.25 mmol) with 1

50

30

mol % of catalyst solvent-free at room temperature, after 12 hours. [b] Conversions determined by $^1{\rm H}$ NMR by silane remaining. [c] >99% selectivity to terminal silane. [d] 60% selectivity to allyl silane.

On view of these results a further study with other internal and terminal alkenes was carried out using cationic 1 and 4 catalysts (Table 2). For catalyst 1, an extraordinary selectivity to linear alkylsilanes was obtained, the minor products being the corresponding unsaturated dehydrogenative silvlation products. Trans-3- and trans-4-octene, which have remote double bonds, also yielded products silvlated in the terminal position selectively, with remarkable conversion of 62% and 60% respectively (Table 2, product 5). Trans-2 and trans-3-hexene yielded the hexylsilane (Table 2, product 7) to reach conversions of 73% and 67% respectively, similar to those observed for trans-2-octene. The highest conversion percentages (90% and 83%) were reached with terminal alkene isomers such as 1-octene and 1-hexene, to yield the corresponding alkylsilane (products 5 and 7). Tertbutylethylene (tbe) and allyltrimethylsilane, both terminal alkenes, led selectively to the formation of 12 and 9, respectively, with almost complete conversion, while 4-bromo-1-butene reached 53% conversion with lower selectivity to 11 after 12 hours. The reaction with styrene afforded 68% conversion under the same reaction conditions, with 82% selectivity to the linear hydrosilylation product 13, whereas styrene derivatives such as α-methylstyrene and 4-chloro-α-methylstyrene gave 29% and 23% conversion to 15 and 16, respectively, with excellent linear selectivity.

Table 2. Hydrosilylation of alkenes with Et_3SiH using complexes 1 and 4. $^{\rm [a,b]}$



[a] Reaction conditions: alkene (0.25 mmol) and Et₃SiH (0.25 mmol) with 1 mol % of complex 1 or 4 solvent-free at room temperature (1) or 50 °C (4) after 12h. [b] Conversions determined by ¹H NMR by silane remaining using 1,2-dichloroethane as internal standard. Selectivity determined by ¹H NMR after work-up of the reaction (value indicated on parenthesis). [c] 43% selectivity to dehydrogenative silylation products. [d] 66% selectivity to dehydrogenative silylation products. [e] 61% selectivity to dehydrogenative silylation products. [f] Experiment carried out at room temperature.

The catalytic activity of complex 4 in dehydrogenative silylation of these alkenes with Et₃SiH was also tested (Table 2). Octene isomers reached similar conversions of 67-73%, the major product being the allylic silvlated compound 6. The presence of

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vinylsilane products in these catalytic reactions was less than 1%. When using hexenes, similar conversions are attained, however the ratio of vinylsilanes increases, to reach 7%, 16% and 14% of the product mixture in the reaction of trans-3-, trans-2- and 1hexene, respectively (See supporting information). Longer chain in octanes might explain the higher allylsilane percentage, as the steric repulsion would lead towards selective β-hydride elimination in the reaction intermediate.^[16c] Higher amounts of dehydrogenative silvlation products were reached, from which 8 was the main species. Allyltrimethylsilane afforded selective 79% conversion to 10, whereas 4-bromo-1-butene underwent very poor reaction. The formation of allylsilane products in the dehydrogenative silylation of styrene, a-methylstyrene, 4-chloro- α -methylstyrene and the is not possible, for they can only yield the vinylsilane species. All of these alkenes exhibit very high selectivity towards the hydrosilylated product except styrene, in which vinylsilane 14 is present in a 68% of the silvlated product. This could once again be explained by steric repulsion caused by methyl groups in α -methylstyrene, 4-chloro- α -methylstyrene, and tbe when the silvlated product is coordinated to Ir that make βhydride elimination unfavourable.^[16c] Hydrosilylation of the successfully yielded linear product 12 to reach 89% of conversion. Notably, the hydrosilylation products of α -methylstyrene and 4chloro- α -methylstyrene with Et₃SiH (15 and 16) were obtained in higher yield (54%) when using the iridium(III) catalyst 4 than when using the rhodium(III) analogue. In alkene dehydrogenative silvlation reactions, the use of a sacrificial hydrogen acceptor (SHA) is usually necessary.^[10-13] The SHA can be the same alkene that reacts with hydrogen to form an alkane. In our case, alkane is not observed upon completion of the reaction. This fact shows that under our conditions, the use of a SHA is no necessary as has been previously reported for other catalytic systems.^{10b} In order to check this, the catalytic dehydrogenative silvlation was carried out adding an extra equivalent of trans-2-octene (SHA). At the end of this reaction the formation of triethyl(2-octenyl)silane was equal and octane was not observed (Figure S.67. Supp. Info.).

In conclusion, an unsaturated silyl-hydrido-Rh(III) complex containing a Si,S,S-terdentate ligand is able to catalyze solvent free tandem isomerization-hydrosilylation of internal alkenes at room temperature to yield linear silanes. The synthesis of an analogue novel iridium(III) complex was also reported. This silyl-hydrido-Ir(III) compound is active in one of the few examples of catalytic tandem isomerization-dehydrogenative silylation of alkenes.

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Keywords: Remote Alkenes • Hydrosilylation • Dehydrogenative Silylation • Rhodium • Iridium

- a) I. Fleming In *Comprehensive Organic Chemistry II*; D. Burton, W. D.
 Ollis, Eds.; Pergamon Press: Oxford, U.K. 1979; p 577. b) D. R. Thomas *Comprehensive Organometallic Chemistry*; W. W. Abel, F. G. A. Stone,
 G. Wilkinson, Eds.; Pergamon Press, Oxford, U.K. 1995; p 114.
- [2] a) J. Michl, Chem. Rev. 1995, 95, 1135. b) S. Bracegirdle, E. A. Anderson, Chem. Soc. Rev. 2010, 39, 4114.
- a) I. Ojima, In *The Chemistry of Organic Silicon Compounds*; S. Patai, Z. Rappoport, Eds.; Wiley-Interscience: New York, 1989; Vol. 2, p 1479. b)
 T. Nakajima, S. Shimada, *RSC Adv.* **2015**, *5*, 20603.
- [4] J. L. Speier, J. A. Webster, G. H. Barnes, J. Am. Chem. Soc. 1957, 79, 974.
- [5] P. B. Hitchcock, F. M. Lappert, N. J. W. Warhurst, Angew. Chem. Int. Ed. 1991, 30, 438; Angew. Chem. 1991, 103, 439.
- [6] a) K. Hirano, H. Yorimitsu, K. Oshima, J. Am. Chem. Soc. 2007, 129, 6094. b) J. C. Mitchener, M. S. Wrighton, J. Am. Chem. Soc. 1981, 103, 975. c) S. C. Bart, E. Lobkovsky, P. J. Chirik, J. Am. Chem. Soc. 2004, 126, 13794. d) Z. Mo, J. Xiao, Y. Gao, L. Deng, J. Am. Chem. Soc. 2014, 136, 17414. e) C. Chen, M. B. Hecht, A. Kavara, W. W. Brennessel, B. Q. Mercado, D. J. Weix, P. L. Holland, J. Am. Chem. Soc. 2015, 137, 13244.
- [7] B. Marciniec, H. Maciejewski, C. Pietraszuk, P. Pawluc, *Hydrosilylation:* A Comprehensive Review on Recent Advances; Springer: London, 2009; p VII-XII.
- [8] a) G. R. Jones, Y. Landais, *Tetrahedron*, **1996**, *52*, 7599. b) Y. Hatanaka
 T. Hiyama, *J. Org. Chem.* **1988**, *53*, 918. c) A. Hosomi, H. Sakurai, *Tetrahedron Lett.* **1976**, 1295.
- [9] a) B. Marciniec, *Coord. Chem. Rev.* 2005, 249, 2374. b) M. Lapointe, F. C. Rix, M. Brookhart, *J. Am. Chem. Soc.* 1997, 119, 906.
- [10] a) Y. Hori, T. Mitsudo, Y. Watanabe, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3011. b)M. P. Doyle, G. A. Devora, A. Nefedov, K. G. High, Organometallics, **1992**, *11*, 549. c) A. Millan, E. Towns, P. M. Maitlis, *J. Chem. Soc., Chem. Commun.* **1981**, 673. d) A. Bokka, J. Jeon, *Org. Lett.* **2016**, *18*, 5324.
- [11] R. N. Naumov, M. Itazaki, M. Kamitani, H Nakazawa, J. Am. Chem. Soc. 2012, 134, 804.
- [12] J. Gu, C. Cai, Chem. Commun. 2016, 52, 10779.
- [13] a)D. C. Apple, K. A. Brady, J. M. Chance, N. E. Heard, T. A. Nile, J. Mol. Catal. 1985, 29, 55. b) M. A. Fernandez, L. A. Oro, J. Mol. Catal. 1986, 37, 151. c) D. Wechsler, A. Myers, R. McDonald, M. J. Ferguson, M. Stradiotto, Inorg. Chem. 2006, 45, 4562. d) E. Calimano, T. D. Tilley, J. Am. Chem. Soc. 2009, 131, 11161. e) C. Cheng, E. M. Simmons, J. F. Hartwig, Angew. Chem. Int. Ed. 2013, 52, 8984; Angew. Chem. 2013, 125, 9154. f) J. A. Muchnij, F. B. Kwaramba, R. J. Rahaim, Org. Lett. 2014, 16, 1330.
- [14] X. Jia, Z. Huang, Nat. Chem. 2016, 8, 157.
- [15] a) I. Buslov, J. Becouse, S. Mazza, M. Montandon-Clerc, X. Hu, Angew. Chem. Int. Ed. 2015, 54, 14523; Angew. Chem. 2015, 127, 14731. b) V.
 Srinivas, Y. Nakajima, W. Ando, K. Sato, S. Shimada, S. Catal. Sci. Tecnol. 2015, 5, 2081.
- [16] a) A. Vasseur, J. Bruffaerts, I. Marek, *Nat. Chem.* 2016, *8*, 209. b) D. Noda, A. Tahara, Y. Sunada, H. Nagashima, *J. Am. Chem. Soc.* 2016, *138*, 2480. c) C. C. H. Atienza, T. Diao, K. J. Weller, S. A. Nye, K. L. Lewis, J. G. P. Delis, J. L. Boyer, A. K. Roy, P. J. Chirik, *J. Am. Chem. Soc.* 2014, *136*, 12108.
- [17] I. Buslov, F. Song, X. Hu, Angew. Chem. Int. Ed. 2016, 55, 12295; Angew. Chem. 2016, 128, 12483.
- [18] S. Azpeitia, M. A. Garralda, M. A. Huertos, *ChemCatChem.* 2017, 9, 1901.
- [19] S. Azpeitia, B. Fernandez, M. A. Garralda, M. A. Huertos, *Eur. J. Inorg. Chem.* 2016, 2891.
- [20] CCDC 1554040 (2), 1554041 (3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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