Supporting Information

A Family of Rhodium(I) NHC Chelates Featuring O-containing Tethers for Catalytic Tandem Alkene Isomerization-Hydrosilylation

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Figure S1. ¹H NMR spectrum (296 K, 500 MHz, CDCl₃) of complex **2**.



Figure S2. ${}^{13}C$ { ${}^{1}H$ } NMR spectrum (296 K, 125 MHz, CDCl₃) of complex 2.



Figure S3. Comparison of the ¹H NMR spectra (THF- d_8) of the crude reaction mixtures obtained from the KHMDS deprotonation of the cationic rhodium NHC complex **3** (top) and the neutral rhodium-NHC complex **1** (bottom). The ¹H NMR study confirms that both synthetic routes lead to same compound: complex **2**.



Figure S4.¹H NMR spectrum (296 K, 300 MHz, CDCl₃) of complex 3.



Figure S5. ^{13}C {¹H} NMR spectrum (296 K, 101 MHz, CDCl₃) of complex 3.



Figure S6. ¹⁹F NMR spectrum (296 K, 376 MHz, CDCl₃) of complex **3**.



Figure S7. ¹¹B NMR spectrum (296 K, 96 MHz, CDCl₃) of complex 3.



Figure S8. ¹H NMR spectrum (296 K, 300 MHz, THF-d₈) of complex 4.



Figure S9. ¹³C {¹H} NMR spectrum (296 K, 125 MHz, THF-*d*₈) of complex **4**.



Figure S10. ¹⁹F NMR spectrum (296 K, 282 MHz, THF-*d*₈) of complex **4**.



1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0 -0.2 -0.4 -0.6 -0.8 -1.0 -1.2 -1.4 -1.6 -1.8 -2.0 -2.2 -2.4 -2.6 -2.8 -3.0 -3.2 -3.4 -3.6 -3.8 -4.0 -4.2 -4.4 fl (ppm)

Figure S11. ¹¹B NMR spectrum (296 K, 96 MHz, THF- d_8) of complex **4**.



Figure S12. Comparison of the ¹H NMR spectra (296 K, 300 MHz, THF-d₈) of complex **4** obtained from **3** + Ta(CH^{*t*}Bu)(CH₂^{*t*}Bu)₃ (bottom) *vs* the crude reaction mixture of complex **2** treated with BF₃·THF (top) leading to same compound **4**.



Figure S13. ¹⁹F NMR spectrum (296 K, 282 MHz, THF-d₈) of the supernatant from the crude reaction from $\mathbf{3} + \text{Ta}(\text{CH}^{t}\text{Bu})(\text{CH}_{2}^{t}\text{Bu})_{3}$, establishing the existence of a Ta-F moiety.



Figure S14. DRIFT (296 K, in KBr under argon) spectrum for 2.



Figure S15. DRIFT (296 K, in KBr under argon) spectrum for 3.



Figure S16. DRIFT (296 K, in KBr under argon) spectrum for 4.



Figure S17. Kinetic profile of the reaction using 0.1 (pale red) and 0.01 (dark red) mol% catalytic loading of complex **2** for the hydrosilylation of 3,3-dimethylbut-1-ene with MD^HM at room temperature. The reaction is monitored by ¹H NMR. The %conversion corresponds to the conversion of TBE; mass balance analysis shows that 100% selectivity towards the corresponding hydrosilylation product is obtained.



Figure S18. ¹H NMR spectrum (296 K, 300 MHz, THF-d₈) of the reaction between complex **2** and two equivalents of MD^HM, carried out in THF-d₈ (*) at 0°C and quiclky transferred into the NMR spectrometer at r.t. for analysis. The ¹H NMR reaction monitoring shows the quick formation of a rhodium hydride intermediate with a characteristic resonance at δ = -13.04 ppm (¹J_{Rh-H} = 23.8 Hz) which is unstable and degrades into a complex mixture of unidentified species at r.t.

Characterization of the silylated products:

Most hydrosilylation products were previously reported in literature.[1]

1,1,1,3,5,5,5-heptamethyl-3-(4-phenylbutyl)trisiloxane



¹H NMR (300 MHz, CDCl₃): δ 7.25-7.18 (m, 2H, *H9*), 7.15-7.08 (m, 3H, *H8*+*H10*), 2.56 (dd, J 78, 7.6 Hz, 2H, *H6*), 1.65-1.54 (m, 2H, *H5*), 1.38-1.27 (m. 2H, *H4*), 0.49-0.42 (nfom, 2H, *H3*), 0.04 9s, 18H, *TMS*), -0.04 (s, 3H, *H3*).

¹³C NMR (75 MHz, CDCl₃): δ 143.0 (*C9*), 128.6 (*C10* or *C11*), 128.4 (*C11* or *C10*), 125.7 (*C12*), 35.9 (*C8* or *C7*), 35.2 (*C7* or *C8*), 23.0 (*C6*), 17.6 (*C5*), 2.0 (*C2*), -0.1 (*C4*).

²⁹Si NMR (60 MHz, CDCl₃): δ 6.7 (*Si1*), -21.3 (*Si3*).

HRMS (ESI+) m/z calculated for $[C_{17}H_{34}Si_3O_2Na]$ + 377.1759, found 377.1759.

The product is a colorless liquid (121 mg) obtained in 76% isolated yield.

1-(bicyclo[2.2.1]heptan-2-yl)-1,1,1-3-5,5,5-heptamethyltrisiloxane (exo isomer)



¹H NMR (300 MHz, CDCl₃): δ 2.24-2.19 (m, 2H), 1.55-1.48 (m, 2H), 1.48-1.42 (m, 1H), 1.36-1.27 (m, 2H), 1.19 (apparent dd, J 6.6, 2.1 Hz, 2H), 1.09 (ddt, J 9.2, 3.5, 1.7 Hz, 1H), 0.46 (ddd, J 9.0, 7.2, 1.3 Hz, 1H, *H5*_{endo}), 0.09 (s, 18H, *H2*), -0.03 (s, 3H, *H4*).

¹³C NMR (75 MHz, CDCl₃): δ 37.8, 37.5, 36.9, 34.0, 31.8, 30.4, 29.2, 2.0 (*C*2), -1.3 (*C*4).

The spectroscopic data correspond to the reported data for the *exo*-isomer in a mixture of exo-endo products.[2] Selective formation of *endo*-isomer has been previously obtained with a Pt-catalyst.[3]

HRMS (ESI+) m/z calculated for $[C_{14}H_{32}Si_3O_2Na]^+$ 339.1602, found 339.1601.

The product is a colorless liquid (126 mg) obtained in 89% isolated yield.

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- [2] D. Noda, A. Tahara, Y. Sunada, H. Nagashima, Non-Precious-Metal Catalytic Systems Involving Iron or Cobalt Carboxylates and Alkyl Isocyanides for Hydrosilylation of Alkenes with Hydrosiloxanes, J. Am. Chem. Soc. 138 (2016) 2480–2483. https://doi.org/10.1021/jacs.5b11311.
- [3] R. Bandari, M.R. Buchmeiser, Polymeric monolith supported Pt-nanoparticles as ligand-free catalysts for olefin hydrosilylation under batch and continuous conditions, Catal. Sci. Technol. 2 (2012) 220–226. https://doi.org/10.1039/C1CY00351H.

NMR data for 1,1,1,3,5,5,5-heptamethyl-3-(4-phenylbutyl)trisiloxane

Figure S19. ¹H NMR (300 MHz, CDCl₃) spectrum:



Figure S20. ¹³C {¹H} NMR (75 MHz, CDCl₃) spectrum:



Figure S21. ²⁹Si {¹H} NMR (60 MHz, CDCl₃) spectrum:



NMR data for 1-(bicyclo[2.2.1]heptan-2-yl)-1,1,1-3-5,5,5-heptamethyltrisiloxane (exo isomer)

Figure S22. ¹H NMR (300 MHz, CDCl₃) spectrum:



Figure S23. ¹³C {¹H} NMR (75 MHz, CDCl₃) spectrum:

