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Orthometallation of *N*-Substituents at the NHC Ligand of [Rh(Cl)(COD)(NHC)] Complexes: Its Role on the Catalytic Hydrosilylation of Ketones

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The rhodium(I)-NHC (NHC = *N*-heterocyclic carbene) complex [Rh(Cl)(COD)(2-methoxyphenyl-NHC-$(CH_2)_3Si(OiPr)_3$)] (**2a**) catalyzes the solvent-free homogeneous hydrosilylation of acetophenone with $HSiMe(OSiMe_3)_2$. Kinetic studies show that **2a** behaves differently to the related homogeneous catalysts [Rh(Cl)(COD)(R-NHC-$(CH_2)_3Si(OiPr)_3$)] (R = 2,6-diisopropylphenyl, (**2b**); R = 2-methoxyethyl (**2c**)). This behavior could be attributable to the participation of different catalytic active species. Indeed, ^1H NMR studies of the reaction of **2a** with $HSiMe(OSiMe_3)_2$ evidenced the formation of a new hydrido-bridged binuclear complex, namely {[Rh($SiMe(OSiMe_3)_2$)(κ-C,C′-R-NHC-$(CH_2)_3Si(OiPr)_3$)]$_2$(μ-H)$_2$} (R = 2-methoxyphenyl, **3**), featuring orthometallated NHC and terminal silyl ligands, which has been proposed as the resting species in the hydrosilylation of acetophenone with $HSiMe(OSiMe_3)_2$ catalyzed by **2a**. Moreover, the heterogeneous catalyst **2a-MCM-41** evidenced a behavior similar to the homogeneous catalyst **2a** in the solvent-free hydrosilylation of acetophenone with $HSiMe(OSiMe_3)_2$.

Introduction

$Si(OR)_3$-functionalyzed metal-complexes have demonstrated great potential for its immobilization on Si-OH functionalized mineral supports.[1,2,3] In this context, we have recently developed a new family of homogeneous $Si(OiPr)_3$-functionalized Rh-NHC (NHC = *N*-heterocyclic carbene) catalysts which have found application as ketone hydrosilylation[4] and benzyl chloride hydrodechlorination[5] catalysts. In addition, the related heterogeneous catalysts, prepared by reaction of $Si(OiPr)_3$-functionalized Rh-NHC homogeneous catalysts with MCM-41, have shown a behavior similar to the corresponding homogeneous systems.[4,5] Taking into account the difficulties to establish the mechanism in heterogeneously catalyzed processes,[6] it would be of interest the use of these $Si(OiPr)_3$-functionalized NHC complexes as soluble models for the active sites of the corresponding supported catalysts. In this regard, it should be mentioned that it has been found that the *N*-substituent of the NHC ligand plays a role on the catalytic activity of the corresponding homogeneous Rh-NHC catalyst in ketone hydrosilylation processes.[4] Thus, Rh-NHC complexes containing bulky *N*-substituents as for instance 2,6-diisopropylphenyl were found to be more active than the related catalysts with less sterically hindered *N*-substituents.[4b]

Herein, we describe the synthesis and characterization of new Rh-NHC based homogeneous, [Rh(Cl)(COD)(2-methoxyphenyl-NHC-$(CH_2)_3Si(OiPr)_3$)] (**2a**), and heterogeneous, **2a-MCM-41**, catalysts containing a 2-methoxyphenyl *N*-substituent at the NHC ligand and therefore with a potential hemilabile character. In addition, the activity of a series of Rh-NHC based heterogeneous catalysts, containing different *N*-substituents at the NHC ligand, in acetophenone hydrosilylation with $HSiMe(OSiMe_3)_2$ has been investigated. As a result from these catalytic studies it has been found that **2a** and the heterogeneous catalysts **2a-MCM-41** exhibit a very different kinetic profile to that of related $Si(OiPr)_3$-functionalized Rh-NHC catalysts with 2,6-diisopropylphenyl or 2-methoxyethyl *N*-substituents at the NHC ligand. In order to shed light on the reasons that cause this different behavior we decided to deepen the study of the reactivity of **2a** towards hydrosilanes in presence or in absence of ketones.

Experimental

General information. All manipulations were performed with rigorous exclusion of air at an argon/vacuum manifold using

standard Schlenk-tube techniques or in a dry-box (MB-UNILAB). Solvents were dried by the usual procedures and distilled under argon prior to use or taken under argon from a Solvent Purification System (SPS). Acetophenone, $HSiEt_3$ and $HSiMe(OSiMe_3)_2$ were purchased from commercial sources and dried over 4A-molecular sieves. $[Rh(\mu\text{-}Cl)(COD)]_2$,[7] 1-(2-methoxyphenyl)-1H-imidazole,[8] $I(CH_2)_3Si(O\textit{i}Pr)_3$,[9] and the complexes $[Rh(Cl)(COD)(R\text{-}NHC\text{-}(CH_2)_3Si(O\textit{i}Pr)_3)]$ (R = 2,6-diisopropylphenyl (**2b**)[4b] and 2-methoxyethyl (**2c**))[4a] were prepared according to methods reported in the literature. NMR spectra were recorded on a Varian Gemini 2000, a Bruker ARX 300, a Bruker Avance 300 MHz or a Bruker Avance 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$). Coupling constants, *J*, are given in hertz. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. TEM microscopy images were collected with an INCA 200 X-Sight from Oxford Instruments with a resolution in energy between 136 eV and 5.9 KeV. Isotherms were obtained on a Quantachrome AUTOSORB by measuring the volume of N_2 absorbed at relative pressures between 0.05 and 0.99 at 77.3 K after drying the sample at 120 ºC *in vacuo.* Pore volume and pore diameter were calculated using the non-local density functional theory (NLDFT) and surface area was calculated using the Brunauer–Emmett–Teller (BET) model.

Preparation of 1-(3-Propyltriisopropoxysilane)-3-(2-methoxyphenyl)-Imidazolium iodide (1). $I(CH_2)_3Si(O\textit{i}Pr)_3$ (1.10 g, 3.0 mmol) was added to an acetonitrile (30 mL) solution of 1-(2-methoxyphenyl)-1H-imidazole (0.44 g, 2.5 mmol), after that the reaction mixture was stirred at 90ºC for 24h. The solvent was removed in vacuo. The residue thus obtained was successively washed with cold Et_2O (2 x 20 mL) and hexane (2 x 20 mL) to give an off-white solid of **1** (1.10 g, 80 %). ^1H RMN plus COSY ($CDCl_3$, 298K, 300Hz): δ 10.01 (s, 1H, NC*H*$_{imd}$N), 7.66 (m, 1H, C*H*Ar), 7.60 (m, 1H, C*H*$_{imd}$), 7.56 (m, 1H, C*H*$_{imd}$), 7.48 (m, 1H, C*H*Ar), 7.10 (m, 2H, C*H*Ar), 4.61 (t, $J_{H\text{-}H}$ = 7.0, 2H, CH_2N), 4.20 (spt, $J_{H\text{-}H}$ = 6.0 Hz, 3H, C*H*-*i*PrO), 3.90 (s, 3H, OC*H*$_3$), 2.05 (m, 2H, -C*H*$_2$-), 1.16 (d, $J_{H\text{-}H}$ = 6 Hz, 18H, C*H*$_3$-*i*PrO), 0.60 (m, 2H, C*H*$_2$Si). $^{13}C\{^1H\}$ RMN ($CDCl_3$, 298 K, 75.46 Hz): δ 151.7 (C_{ipso}-Ar), 137.8 (NC*H*$_{imd}$N), 132.0 (*C*H-Ar), 129.7 (C_{ipso}-Ar), 125.8 (*C*H-Ar), 123.2 (*C*H$_{imd}$), 122.1 (*C*H$_{imid}$), 121.8 (*C*H-Ar), 112.8 (*C*H-Ar), 65.4 (*C*H-*i*PrO), 56.6 (O*C*H$_3$), 52.1 (*C*H$_2$N), 25.6 (*C*H$_3$-*i*PrO), 24.6 (-*C*H$_2$-), 8.5 (*C*H$_2$Si). Mass Spectrometry (ESI^+): m/z 421.2 (M^+-I).

Preparation of [Rh(Cl)(COD)(2-methoxyphenyl-NHC-(CH$_2$)$_3$Si(O*i*Pr)$_3$)] (2a). CH_2Cl_2 (15 mL) was added to a mixture of the imidazolium salt **1** (655 mg, 1.00 mmol) and Ag_2O (232 mg, 1.00 mmol). The reaction mixture was stirred in absence of light at room temperature for 4 h. The resulting mixture was filtered and the solvent was removed in vacuo to yield the silver carbene as an off-white residue. A THF (15 mL) solution of $[Rh(\mu\text{-}Cl)(COD)]_2$ (247 mg, 0.500 mmol) was added to the residue and the mixture was stirred at room temperature for 16 h. The solvent was removed in vacuo and the residue thus obtained was extracted with Et_2O (3 x 20 mL). The Et_2O solution was removed in vacuo and washed with cold hexane (8 mL) to afford a yellow solid of **2a**. Yield 507 mg (76%). Anal. Calcd for $C_{30}H_{48}ClN_2O_4RhSi$: C, 54.01, H, 7.25, N, 4.20. Found: C, 53.99, H, 7.55, N, 4.42. ^1H NMR (C_6D_6, 298 K, 300 MHz): δ 9.13 (m, 1H, C*H*-Ar), 7.08 (m, 1H, C*H*-Ar), 6.98 (m, 1H, C*H*-Ar), 6.69 (d, 1H, $J_{H\text{-}H}$ = 1.5 Hz, C*H*$_{imd}$), 6.48 (m, 1H, C*H*-Ar), 6.41 (d, 1H, $J_{H\text{-}H}$ = 1.5 Hz, C*H*$_{imd}$), 5.50 (m, 1H, C*H*$_{COD}$), 5.39 (m, 1H, C*H*$_{COD}$), 4.59 (m, 2H, C*H*$_2$N), 4.27 (spt, 3H, $J_{H\text{-}H}$ = 6 Hz, C*H*-*i*PrO), 3.38 (m, 1H, C*H*$_{COD}$), 3.11 (s, 3H, C*H*$_3$O), 2.85 (m, 1H, C*H*$_{COD}$), 2.36 (m, 2H, C*H*$_{2COD}$), 2.22 (m, 2H, -C*H*$_2$-), 2.05 (m, 1H, C*H*$_{2COD}$), 1.89-1.39 (m, 5H, C*H*$_{2COD}$), 1.24 (d, 18H, $J_{H\text{-}H}$ = 6 Hz, C*H*$_3$-*i*PrO), 0.81 (m, 2H, C*H*$_2$Si). ^{13}C $\{^1H\}$ NMR (C_6D_6, 298 K, 75 MHz): δ 184.6 (d, $^1J_{Rh\text{-}C}$ = 52 Hz, $RhC_{carbene}$), 153.2 (C_{ipso}), 131.5 (*C*H-Ar), 129.8 (C_{ipso}), 129.4 (*C*H-Ar), 123.4 (*C*H$_{imd}$), 121.1 (*C*H-Ar), 119.8 (*C*H$_{imd}$), 111.1 (*C*H-Ar), 97.7 (d, $^1J_{Rh\text{-}C}$ = 7 Hz, *C*H$_{COD}$), 97.3 (d, $^1J_{Rh\text{-}C}$ = 7 Hz, *C*H$_{COD}$), 67.7 (d, $^1J_{Rh\text{-}C}$ = 14 Hz, *C*H$_{COD}$), 67.3 (d, $^1J_{Rh\text{-}C}$ = 14 Hz, *C*H$_{COD}$), 65.3 (*C*H-*i*PrO), 55.1 (*C*H$_3$O), 53.9 (*C*H$_2$N), 33.9 (*C*H$_{2COD}$), 32.5 (*C*H$_{2COD}$), 29.3 (*C*H$_{2COD}$), 29.1 (*C*H$_{2COD}$), 25.9 (*C*H$_3$-*i*PrO), 25.2 (-*C*H$_2$-), 9.9 (*C*H$_2$Si). Mass Spectrometry ESI^+: m/z 631.1 (M^+-Cl).

Preparation of 2a-MCM-41. A toluene solution (10 mL) of **2a** (100 mg) was added to a suspension of MCM-41 (1.0 g) in 10 mL of wet toluene. The mixture was stirred at room temperature for one hour and after that refluxed for 24 hours. The resulting solid was isolated by centrifugation and washed with toluene (2 x 10 mL), CH_2Cl_2 (2 x 10 mL) and Et_2O (2 x 10 mL) to afford a white solid of **2a-MCM-41** which was dried in vacuo at 60ºC. Yield 0.49 g (90 %). ICP Rh analysis: 6.713 and 9.762 mg/g for batch 1 and 3, respectively. FT-IR: 1627 cm^{-1} (br), ν(C=N) and ν(C=C), 1241 cm^{-1}, 1043 cm^{-1}, 800 cm^{-1} ν(Si-O-Si). ^{13}C-NMR CP-MAS: δ 152.1 (*C*H-Ar), 132.1 (*C*H-Ar), 123.1 (*C*H$_{imd}$), 112.5 (*C*H-Ar), 67.5 (*C*H$_{COD}$), 54.7 (*C*H$_3$O), 52.0 (*C*H$_2$N), 33.0-21.0 (*C*H$_{2COD}$ and -*C*H$_2$-), 9.2 (*C*H$_2$Si).

Homogeneous catalytic hydrosilylation of acetophenone. $HSiMe(OSiMe_3)_2$ (2.0 mL), **2a** (0.02 mmol), acetophenone (2.0 mmol, 0.24 mL) and mesitylene as internal standard (0.24 mL, 2.0 mmol) was stirred at 80ºC. Samples were taken at regular time intervals and studied by gas chromatography (GC).

Heterogeneous catalytic hydrosilylation of acetophenone. $HSiMe(OSiMe_3)_2$ (2.0 mL), **2a-MCM-41** (0.002 mmol of Rh), acetophenone (0.2 mmol, 0.024 mL) and mesitylene as internal standard (0.2 mmol, 0.024 mL) was stirred at 80ºC. Samples were taken at regular time intervals and studied by GC. The catalytic reactions using **2b-MCM-41** (0.002 mmol of Rh) or **2c-MCM-41** (0.002 mmol of Rh) as catalyst precursor were performed using the same procedure above described for **2a-MCM-41**.

Reaction of 2a with excess of $HSiMe(OSiMe_3)_2$ in C_6D_6: formation of {[Rh(SiMe(OSiMe$_3$)$_2$)(*k-C,C*-2-methoxyphenyl-NHC-(CH$_2$)$_3$Si(O*i*Pr)$_3$)]$_2$(μ-H)$_2$} (3). $HSiMe(OSiMe_3)_2$ (0.27 mL, 1.0 mmol), **2a** (33.4 mg, 0.05 mmol) and C_6D_6 (0.5 mL) were placed in a NMR tube. The reaction mixture was heated at 90ºC for 8 hours. Data found for **3**: ^{1}H NMR plus COSY (C_6D_6, 298 K, 300 MHz): δ 8.44 (d, 2H, J_{H-H} = 7.4 Hz, C*H*-Ar), 8.04 (d, 2H, J_{H-H} = 2 Hz, CH_{imd}), 7.11 (t, 2H, J_{H-H} = 7.4 Hz C*H*-Ar), 6.65 (d, 2H, J_{H-H} = 2 Hz, CH_{imd}), 6.49 (m, 2H, J_{H-H} = 7.4 Hz, C*H*-Ar), 5.00 (m, 2H, CH_2N), 4.30 (spt, 6H, J_{H-H} = 6.0 Hz, C*H*-*i*PrO), 4.33 (m, 2H, CH_2N), 3.41 (s, 6H, CH_3O), 2.33-2.18 (m, 4H, -CH_2-), 1.27 (d, 36H, J_{H-H} = 6.0 Hz, CH_3-*i*PrO), 0.88 (s, 4H, CH_2Si), -10.13 (t, J_{Rh-H} = 25.5 Hz, 2H, Rh-*H*-Rh), the resonances due to the protons of the Rh-SiMe(OSiMe$_3$)$_2$ moieties have been assigned according with ^{1}H-^{29}Si{^{1}H} HMBC experiments at 0.51 (s, 6H, Si*Me*(OSiMe$_3$)$_2$) and 0.25 (s, 36 H, SiMe(OSi*Me*$_3$)$_2$). ^{13}C{^{1}H} NMR plus HSQC (C_6D_6, 298 K, 75 MHz): δ 183.0 (d, $^1J_{Rh-C}$ = 47.2 Hz, Rh-$C_{carbene}$), 155.6 (d, $^1J_{Rh-C}$ = 24.5 Hz, Rh-*C*Ar), 146.6 (C_{ipso}), 139.2 (*C*H-Ar), 135.7 (C_{ipso}), 125.1 (*C*H-Ar), 120.2 (*C*H$_{imd}$), 117.9 (*C*H$_{imd}$), 106.9 (*C*H-Ar), 65.3 (*C*H-*i*PrO), 54.9 (*C*H$_3$O), 53.0 (*C*H$_2$N), 26.0 (*C*H$_3$-*i*PrO), 25.2 (CH$_2$*C*H$_2$CH$_2$), 9.44 (*C*H$_2$Si), the resonances due to the carbons of the Rh-SiMe(OSiMe$_3$)$_2$ moieties could not be assigned because of the overlapping with signals of carbons of free silane. ^{29}Si{^{1}H} NMR (C_6D_6, 298 K, 60 MHz) plus ^{1}H-^{29}Si{^{1}H} HMBC: δ -10.5 ppm (d, $^1J_{Rh-Si}$ = 43.5 Hz, Rh-*Si*), -22.19 (s, *Si*(O*i*Pr)$_3$).

Reaction of 2a with excess of $HSiEt_3$ in $(CD_3)_2CO$ at NMR scale. $HSiEt_3$ (0.2 mL), **2a** (33.4 mg, 0.05 mmol) and $(CD_3)_2CO$ (0.3 mL) were placed in a NMR tube. The reaction was monitored by ^{1}H NMR spectroscopy.

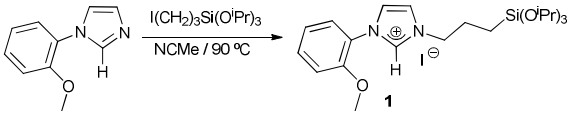
Solvent-free reaction of complex 2a with $HSiEt_3$: formation of {[Rh(SiEt$_3$)(*k-C,C*-2-methoxyphenyl-NHC-(CH$_2$)$_3$Si(O*i*Pr)$_3$)]$_2$(μ-H)$_2$} (4). A mixture of **2a** (100 mg, 0.15 mmol) and $HSiEt_3$ (1.0 mL) was heated at 100ºC during 4 hours. The resulting orange residue was extracted with hexane (10 mL) and the volatiles were removed in high vacuo to yield a yellow oil which has been characterized by NMR as a mixture of **4**, $ClSiEt_3$ and traces of other non-identified rhodium containing species. All attempts of obtain a pure sample of **4** from such mixture have proved fruitless. Data for complex **4**: ^{1}H NMR plus COSY (C_6D_6, 298 K, 300 MHz): δ 8.73 (d, 2H, J_{H-H} = 7.5 Hz, C*H*-Ar), 8.02 (d, 2H, J_{H-H} = 2 Hz, CH_{imd}), 7.06-6.98 (m, 2H, C*H*-Ar), 6.46 (d, 2H, J_{H-H} = 2 Hz, CH_{imd}), 6.43 (m, 2H, C*H*-Ar), 5.28-5.12 (m, 2H, CH_2N), 4.33 (spt, 6H, J_{H-H} = 6 Hz, C*H*-*i*PrO), 4.09-3.92 (m, 2H, CH_2N), 3.31 (s, 6H, CH_3O), 2.25-2.14 (m, 4H, -CH_2-), 1.29 (dvd, 36H, N = 6.5 Hz, CH_3-*i*PrO), 1.04 (t, 18H, J_{H-H} = 8.0 Hz, CH_3-SiEt$_3$), 0.99-0.82 (m, 4H, CH_2Si), 0.57 (q, 12H, J_{H-H} = 8.0 Hz, CH_2-SiEt$_3$), -10.04 (t, J_{Rh-H} = 25.5 Hz, 2H, Rh-*H*-Rh). ^{13}C{^{1}H} NMR plus HSQC (C_6D_6, 298 K, 75 MHz): δ 182.0 (d, $^1J_{Rh-C}$ = 54.4 Hz, Rh-$C_{carbene}$), 154.7 (d, $^1J_{Rh-C}$ = 39.3 Hz, Rh-*C*Ar), 147.2 (C_{ipso}), 139.2 (*C*H-Ar), 136.3 (C_{ipso}), 125.3 (*C*H-Ar), 120.3 (*C*H$_{imd}$), 117.8 (*C*H$_{imd}$), 106.8 (*C*H-Ar), 65.2 (*C*H-*i*PrO), 54.8 (*C*H$_3$O), 53.2 (*C*H$_2$N), 30.0 (CH$_2$CH$_2$CH$_2$), 26.0 (*C*H$_3$-*i*PrO), 11.8 (*C*H$_2$Si), 7.1 (*C*H$_3$-SiEt$_3$), 6.8 (*C*H$_2$-SiEt$_3$). ^{29}Si{^{1}H} NMR (C_6D_6, 298 K 60 MHz): δ 61.0 ppm (d, $^1J_{Rh-Si}$ = 36.0 Hz, Rh-SiEt$_3$), -49.8 (s, *Si*(O*i*Pr)$_3$).

Computational details. Theoretical calculations have been carried out using DFT methods at the B3LYP level[10] using the G09.D01 program package.[11] Full citation is given in supporting information. Dispersion corrections have been added using the D3 scheme proposed by Grimme.[12] The def2-SVP basis set[13] has been selected for all atoms for geometry optimizations and calculation of free energy corrections. The nature of the stationary points has been checked by calculation of vibrational frequencies and intrinsic reactions paths have been traced connecting each transition state with the respective intermediates. All reported energies are Gibbs energies and relative to complex A and isolated molecules.

Results and Discussion

Preparation of the catalyst precursors.

The salt, 1-(3-triisopropoxysilylpropyl)-3-(2-methoxyphenyl)-imidazolium iodide (**1**), used as ligand precursor in this work was prepared in good yield by heating acetonitrile solutions of 1-(2-methoxyphenyl)-1*H*-imidazole and I(CH$_2$)$_3$Si(O*i*Pr)$_3$ at 90 ºC (Scheme 1). Species **1** was isolated as an off-white solid in 80% yield which has been fully characterized by means of ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and mass spectrometry (see experimental section).

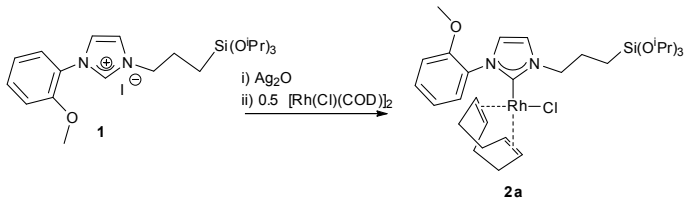


Scheme 1. Preparation of the imidazolium salt **1**.

The reaction of salt **1** with Ag_2O affords solutions containing the corresponding silver-NHC species. Lin´s method of transmetallation[14] of the in situ generated silver-NHC species with [Rh(μ-Cl)(COD)]$_2$ gives the complex [RhCl(COD)(2-methoxyphenyl-NHC-(CH$_2$)$_3$Si(O*i*Pr)$_3$)] (**2a**) (COD = cyclooctadiene) which was isolated as a yellow solid in 76% yield (Scheme 2). Complex **2a** has been fully characterized by elemental analysis, ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and mass spectrometry (ES$^+$).

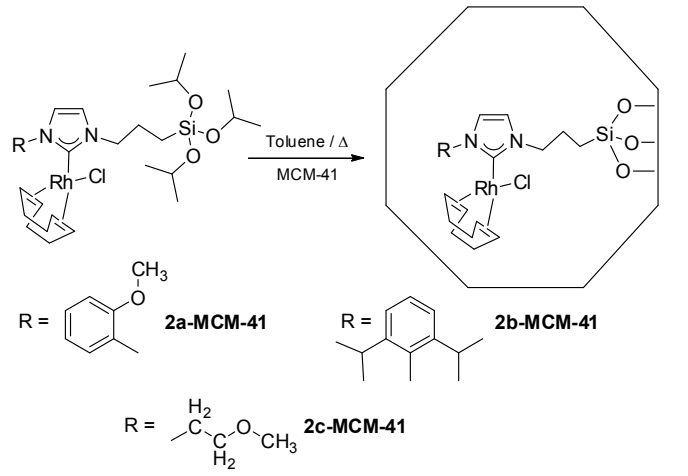
^{1}H NMR spectra of C_6D_6 solutions of **2a** evidenced the presence of the -(CH$_2$)$_3$Si(O*i*Pr)$_3$ moiety. The characteristic resonance due to the CH$_2$Si protons appears as a multiplet at δ 0.81 ppm, low field shifted with respect to that observed for the starting salt **1** which appears as a multiplet at δ 0.60 ppm. The ^{13}C{^{1}H} NMR spectra of **2a** show a doublet resonance at δ 184.6 ppm (J_{Rh-C} = 52 Hz) which confirms the coordination of the NHC ligand to the rhodium atom.[4,5,15] The remaining

resonances of the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2a** are consistent with the structure proposed for such complex in Scheme 2 (see experimental section).



Scheme 2. Preparation of the Rh-NHC complex **2a**.

The preparation of the heterogeneous catalyst **2a-MCM-41** has been carried out following a procedure analogous to that previously reported for the synthesis of **2b-MCM-41** and **2c-MCM-41** (Scheme 3).[4] Thus, the reaction of complex **2a** with MCM-41 (Mobil Composition of Matter Nº 41) in refluxing toluene for 24h afforded, as an off-white solid, the corresponding heterogeneous catalyst which was characterized by ICP analysis, N_2-physisorption/desorption studies and TEM.



Scheme 3. Heterogeneous Rh-NHC-MCM-41 catalysts studied in this work.

ICP analyses of the two different batches of **2a-MCM-41** used in this work show a rhodium loading of 6.713 and 9.762 mg g^{-1} (Table 1). N_2-physisorption/desorption studies showed that the surface area, pore volume and pore diameter of **2a-MCM-41** are lower than the corresponding values obtained for the parent MCM-41, which agree with the covalent immobilization of the species **2a** inside the channels of the mesoporous material (Table 1). The resonances observed in the ^{13}C CP-MAS solid state NMR spectra of **2a-MCM-41** compare well with those observed in the $^{13}C\{^{1}H\}$ NMR spectra of the parent complex **2a**. The most prominent resonances in the ^{13}C CP-MAS solid state NMR spectra are those due to the CH_{imd} (δ 123.1 ppm), CH_2N (δ 52.0 ppm) and CH_2Si (δ 9.2 ppm) carbon atoms.

Table 1. N_2-physisorption/desorption studies and ICP analysis for the support and different preparations of the supported catalyst.

Material	Rh (mg/g)[a]	SA (m^2/g)[b]	PD (Å)[c]	PV (cm^3/g)[d]
MCM-41	-	1070	40.9	1.00
2a-MCM-41[e]	6.713	742	36.2	0.67
2a-MCM-41[f]	9.762	813	30.8	0.62

[a] obtained by ICP analysis. [b] Surface area. [c] Pore diameter. [d] Pore volume. [e] Batch 1. [f] Batch 2.

In addition, transmission electron microscopy (TEM) of **2a-MCM-41** evidenced that the mesoporous structure of the parent material, MCM-41, is maintained throughout the process of immobilization of **2a** (Figure 1).

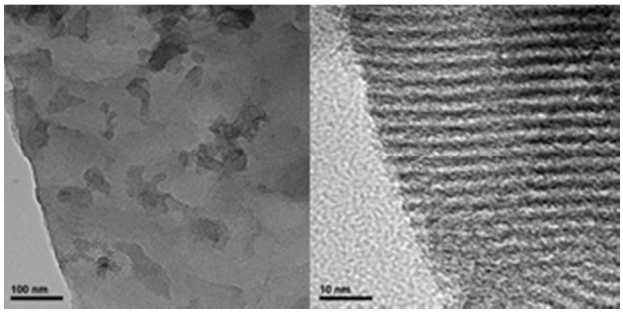


Figure 1. Transmission electron microscopy (TEM) of samples of the heterogeneous catalyst **2a-MCM-41**.

Homogeneously catalyzed hydrosilylation of acetophenone. Rhodium-catalyzed hydrosilylation of ketones is a well-established chemical process.[16] In particular, the catalytic hydrosilylation of acetophenone has proven to be an excellent activity test bench which allows comparison between different [Rh(Cl)(COD)(NHC)] catalysts.[17] In this regard, it should be mentioned that one of our research interest is the study of the potential application of some readily available and environmentally innocuous hydrosilanes, such as $HSiMe(OSiMe_3)_2$, as hydrogen source in catalysis.[4,5,18] Kinetic studies of the solvent-free homogeneous hydrosilylation of acetophenone with $HSiMe(OSiMe_3)_2$ to give the corresponding silylether, namely $PhMeHC\text{-}O\text{-}SiMe(OSiMe_3)_2$, were performed using complex **2a** and the previously reported [Rh(Cl)(COD)(R-NHC-$(CH_2)_3Si(OiPr)_3$)] (R = 2-diisopropylphenyl (**2b**)[4b] or R = 2-methoxyethyl (**2c**)[4a]) complexes as catalyst precursors. A comparison of the results of these studies reveals that the NHC ligand containing a 2,6-diisopropylphenyl *N*-substituent affords the most active catalyitc system (Figure 2). What is surprising, however, is the unusual increase in the activity observed for the homogeneous

catalyst **2a**. Indeed, although **2a** initially is the less active catalyst, an upsurge of the catalytic activity was observed after 50 min that eventually improves the catalytic activity of **2c** (Figure 2). This atypical behaviour evidences a non-innocent role of the 2-methoxyphenyl *N*-substituent of the NHC ligand in this catalytic system.

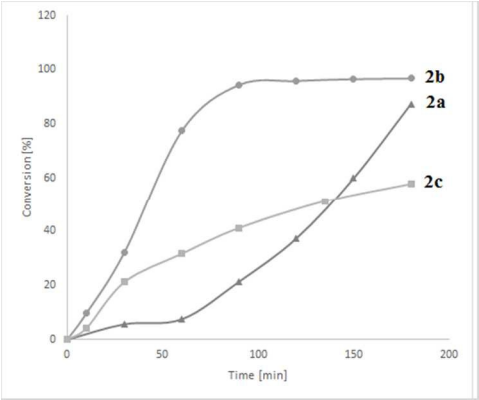


Figure 2. Representation of the conversion of acetophenone (%) versus time (min) for the solvent-free catalytic hydrosilylation of acetophenone with HMTS using the indicated catalytic precursor (1.0 mol%) at 80°C. The lines in Figure 2 represent a continuous path between the experimental data points.

Heterogeneously catalyzed hydrosilylation of acetophenone. Treatment of acetophenone with $HSiMe(OSiMe_3)_2$ at 80ºC for 8h using **2a-MCM-41** (1.0 mol%) as catalyst produces quantitatively the hydrosilylation product, namely PhMeCH-O-$SiMe(OSiMe_3)_2$, which was characterized by comparison of the ^{1}H NMR spectra of the reaction samples with the reported data.[4a] It is worth noting that the heterogeneous catalyst could be recycled and reused for several cycles under the same reaction conditions. Indeed, a decrease on the catalyst performance, from 100% to 90%, was observed only after the fourth cycle. These results compare well with those reported for **2b-MCM-41**[4b] and **2c-MCM-41**.[4a]

The solvent-free catalytic hydrosilylation of acetophenone with $HSiMe(OSiMe_3)_2$ using **2a-MCM-41** as catalyst was monitored by Gas Chromatography (GC). A comparison of the curve obtained for **2a-MCM-41** with the curves obtained using **2b-MCM-41** and **2c-MCM-41** as heterogeneous catalysts[19] evidenced that the *N*-substituent at the NHC ligand plays a relevant role in the activity of these heterogeneous catalytic systems (Figure 3). Indeed, **2a-MCM-41** is initially the less active catalytic system, but after 100 minutes its activity changes, which is evident by the slope change of the curve. Thus, **2a-MCM-41** exhibits better performance than **2c-MCM-41** at long reaction times, which suggests the formation of a different active site. In any case, **2b-MCM-41** was found to be the most active catalyst under these reaction conditions.

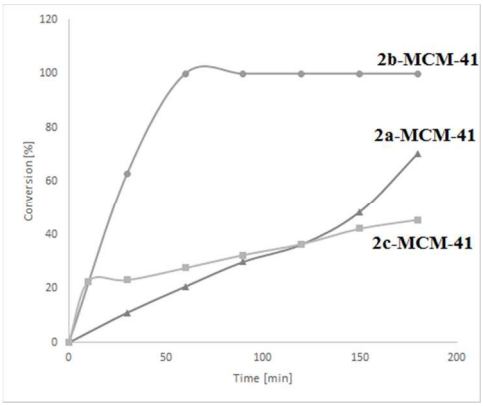


Figure 3. Representation of the conversion of acetophenone (%) versus time (min) for the solvent-free catalytic hydrosilylation of acetophenone with HMTS using the indicated heterogeneous catalysts (1.0 mol%) at 80°C. The lines in Figure 3 represent a continuous path between the experimental data points.

The results showed in Figures 2 and 3 evidenced a certain degree of similarity between the heterogeneous and homogeneous catalytic systems. Indeed, the homogeneous systems have proven to be a model for the qualitative activity of the heterogeneous systems. A quantitative analysis of the results shown in Table 2 revealed that the activity of the heterogeneous catalytic systems follows a similar pattern as that found for the homogeneous catalysts. The 2,6-diisopropylphenyl *N*-substituent exerts a clear positive effect on the catalyst activity of both the homogeneous and heterogeneous catalytic systems (Table 2, entries 2 and 5). In this particular case, the activity of the heterogeneous catalyst has been found to be higher than that of the homogeneous counterpart. The above described kinetic studies show that both the homogeneous, **2a**, and the heterogeneous, **2a-MCM-41**, catalysts follow a similar behaviour. Initially, they exhibit a very low activity but with the course of time an increased catalytic activity was observed for both catalytic systems.

The activities found for species **2** (Table 2) are in the same range of those reported for [Rh(Cl)(COD)(NHC)] catalysts containing peptide-functionalized NHC ligands.[17b-d] In this regard, it is worth noting that the less sterically hindered complex [Rh(Cl)(COD)(1,3-*N*,*N*′-dimethyl-2-ilydene-imidazol)] (1.0 mol %) has been reported as a highly active catalyst precursor for ketones hydrosilylation with H_2SiPh_2 (70 % conversion after 5 min and 90 % conversion after 30 min).[17d]

Table 2. Activity and conversion values obtained for the hydrosilylation of acetophenone with $HSiMe(OSiMe_3)_2$ using $Si(OiPr)_3$-functionalized Rh-NHC complexes or their related supported species (1.0 mol %) as catalysts.

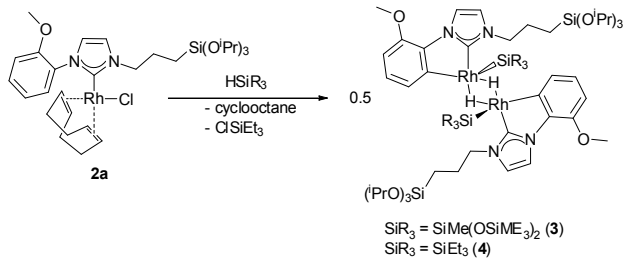
Entry	catalyst	$TOF_{1/2}$ $(h^{-1})^{[a]}$	Conversion (%) 30 min	Conversion (%) 60 min
1	2a	22	6	8
2	2b	74	32	78
3	2c	23	22	36
4	2a-MCM-41	34	11	20
5	2b-MCM-41	139	63	99
6	2c-MCM-41	22	23	28

[a] Turnover frequency number at 50% conversion.

NMR studies of the reaction of 2a with $HSiMe(OSiMe_3)_2$ and $HSiEt_3$. In order to understand the reasons behind the different behavior observed for **2a** compared to **2b** and **2c**, we have monitored the **2a**-catalyzed acetophenone hydrosilylation with $HSiMe(OSiMe_3)_2$ by NMR. Initially, we have studied the reaction of **2a** with $HSiMe(OSiMe_3)_2$. ^1H NMR spectra of the reactions of **2a** with $HSiMe(OSiMe_3)_2$ in C_6D_6 showed no reaction at 25ºC. However, heating at 90ºC the slow disappearance of the resonances corresponding to **2a** and the appearance of the resonances assigned to the new binuclear complex **3** was observed (Scheme 4). After 8 hours complex **3** was the only rhodium containing species observed in solution together with cyclooctane and traces of free cyclooctene (Scheme 4). The NMR data for **3** evidenced a binuclear structure supported by two hydrido-bridged ligands. The most relevant resonance in the ^1H NMR spectra of **3** is a high-field triplet resonance at δ -10.10 ppm ($^1J_{Rh\text{-}H}$ = 25.5 Hz) assigned to the Rh-(μ-H)-Rh moieties. This resonance shows a correlation in the ^1H-$^{29}Si\{^1H\}$ HMBC experiments with a resonance corresponding to the silicon atom bonded to rhodium, Rh-*Si*$Me(OSiMe_3)_2$, which appears as a doublet centred at δ -10.50 ppm ($^1J_{Rh\text{-}Si}$ = 45.7 Hz) in the $^{29}Si\{^1H\}$ NMR spectra of **3** (Figure 4).

The $^{13}C\{^1H\}$ NMR spectra of **3** showed two doublet resonances in the low field region which appeared at δ 183.1 ($^1J_{Rh\text{-}C}$ = 54.0 Hz) and δ 155.8 ppm ($^1J_{Rh\text{-}C}$ = 39.2 Hz). The first one corresponds to the carbene atom of the NHC ligand bonded to rhodium. The latter strongly suggests the orthometallation of the 2-methoxyphenyl *N*-substituent of the NHC ligand to the rhodium atom.[20] This was further confirmed by the remaining resonances which are in agreement with the structure proposed for **3** in Scheme 4 (see experimental section).

The dimeric nature of **3** was corroborated by means of ^1H-DOSY NMR (300 K) spectroscopy of in situ generated C_6D_6 solutions containing complexes of **2a**, **3** and $HSiMe(OSiMe_3)_2$. The resonances of the low field shifted aromatic protons (δ 9.13 ppm; **2a**) and (δ 8.44 ppm; **3**) were used for the determination of the diffusion coefficients (D) of both complexes. The D value obtained for **3**, 4.36 10^{-10} m^2 s^{-1}, is lower than the diffusion coefficient obtained for **2a** (5.88 10^{-10} m^2 s^{-1}). These D values evidenced that in C_6D_6 **3** moves slowly than **2a**. Therefore, this result, based on the known relation between D and molecular size,[21] supports the dimeric structure proposed for **3** in Scheme 4.



Scheme 4. Reaction of complex **2a** with hydrosilanes

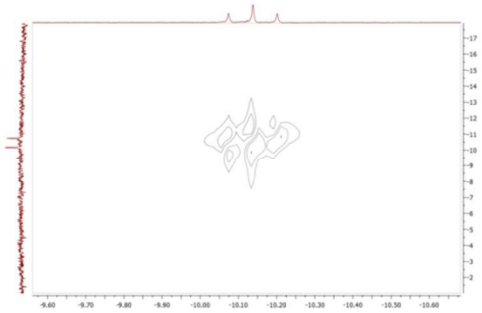


Figure 4. Correlation of the resonance due to the Rh-H-Rh moieties in the ^1H NMR with the $^{29}Si\{^1H\}$ NMR spectrum in the ^1H-$^{29}Si\{^1H\}$ HMQC NMR experiment of the reaction of **2a** with $HSiMe(OSiMe_3)_2$ in C_6D_6 after 24 hours.

The addition of acetophenone to C_6D_6 solutions of $HSiMe(OSiMe_3)_2$ and the in situ prepared species **3** evidenced no reaction at 25ºC. However, when the reaction mixture was warmed to 90ºC the intensity of the resonances assigned to **3** started to decrease and the formation of a mixture of not identifiable rhodium species was observed. Under these reaction conditions the appareance of the resonances corresponding to the acetophenone hydrosilylation product was observed. This fact is in agreement with the in situ formation of an active species energetically less stable than **3** which is supposed to be the responsible for promoting the hydrosilylation process.

With the aim of obtaining more information about the behaviour of **2a** as catalyst precursor in ketone hydrosilylation processes we have explored the reactivity of **2a** with an excess of $HSiEt_3$ using $(CD_3)_2CO$ as reagent and as reaction solvent. ^1H NMR studies of the reaction of hydrosilylation of acetone-d_6 with $HSiEt_3$ in presence of catalytic amounts of **2a** evidenced the slow formation of the hydrosilylation product, namely

$(CD_3)_2CHOSiEt_3$, together with cyclooctane and a new organometallic compound which has been characterized by means of ^1H, $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectroscopy as the binuclear compound **4**, related to **3** (Scheme 4).

^1H NMR spectra of **4** exhibit a characteristic triplet resonance at δ –10.0 ppm ($^1J_{Rh-H}$ = 25.5 Hz) corresponding to the Rh(μ-H)$_2$Rh moiety. This resonance shows a correlation in the ^1H-$^{29}Si\{^1H\}$ HMBC NMR spectra with a resonance corresponding to the Rh-$SiEt_3$ silicon atom which appears as a doublet centred at δ 61.0 ppm ($^1J_{Rh-Si}$ = 36.0 Hz) in the $^{29}Si\{^1H\}$ NMR spectra of **4**. The resonance assigned to the metallated carbon atom of the 2-methoxyphenyl *N*-substituent of the NHC ligand was observed at δ 154.7 ppm ($^1J_{Rh-C}$ = 39.3 Hz) in the $^{13}C\{^1H\}$ NMR spectrum,[20] whereas that of the carbene atom of the NHC ligand appears at δ 182.0 ($^1J_{Rh-C}$ = 54.4 Hz) (see experimental section and supporting information).

All attempts to isolate pure samples of complexes **3** or **4** were fruitless. However, based on the above described NMR experiments it seems reasonable to assume that the binuclear species **3** and **4** are resting states of the corresponding catalytic reactions.

It is worth to mentioning that when analogous reactions were carried out under the same reaction conditions but using the previously reported complex **2b**, instead of **2a**, ^1H NMR spectra evidenced the formation of mixtures of no identified mononuclear Rh-hydride containing species.

Therefore, the role played by the 2-methoxyphenyl *N*-substituent of the NHC ligand is not a consequence of the potential the hemilability of the -OCH_3 moiety at the *N*-substituent of the ligand, but it is supposed to be due to the orthometallation of the aromatic ring which affords a new Rh(III)-NHC active species.

Computational studies on the reaction of 2a with $HSiMe_3$. It has been established that the reaction of [Rh(Cl)(COD)(NHC)] species with hydrosilanes affords the corresponding hydrido complex [Rh(H)(COD)(NHC)] by sigma-bond metathesis.[4,5] Therefore, we assume that the reaction of **2a** with hydrosilanes initially should give the complex [Rh(H)(COD)(2-methoxyphenyl-NHC-$(CH_2)_3Si(OiPr)_3$)] (**5**) which further reacts with the corresponding hydrosilane to afford the binuclear species **3** or **4**. It is reasonable to think that one of the intermediate steps in the process of formation of **3** or **4** from **2a** should entail a classical cyclometallation reaction.[22]

In this regards, it should be mentioned that, in agreement with the above described experimental findings, theoretical calculations at the B3LYP-D3 level on the reaction of [Rh(H)(COD)(2-methoxyphenyl-NHC-Me)] (**A**) (as model of **5**) with $HSiMe_3$ evidenced that the formation of **F** (a model for complexes **3** and **4**) and free cyclooctene (COE) is thermodynamically favoured by 25.2 kcal mol^{-1} (Figure 5) (see supporting information). This reaction could be rationalized as a stepwise process. The initial step corresponds to the oxidative addition of a molecule of silane to the metallic complex **A** across the transition state **TSA-B** showing an energetic barrier of 18.8 kcal mol^{-1} to give the rhodium(III) intermediate **B** which is 9.6 kcal mol^{-1} less stable than **A**. The hydrogenation of one the C=C double bonds of the COD ligand takes place in a two-step manner. Firstly, there is an insertion of the C=C double bond into the metal-hydride via **TSB-C** with a relative energy of 13.7 kcal mol^{-1} to yield intermediate **C**, 2.3 kcal mol^{-1} more stable than the initial system formed by **A** and one molecule of free $HSiMe_3$. The hydrogenation is completed upon reductive elimination to form the C-H bond at the COE ligand and the T-shaped Rh(I) complex **D**. The presence of the 2-methoxyphenyl *N*-substituent at the carbene ligand and the vacancy at the metal, allows the orthometallation of the aromatic ring through **TSD-E** bearing a relative energy of 12.4 kcal mol^{-1} to afford the rhodium(III) intermediate **E**. Finally, the elimination of the COE ligand from **E** and subsequent dimerization of the resulting organometallic fragment forms the binuclear complex **F** (Figures 5 and 6), which is 25.2 kcal mol^{-1} more stable than the initial species. The overall process presents a highest energetic barrier of 18.8 kcal mol^{-1}, corresponding to the oxidative addition of the silane at transition state **TSA-B**.

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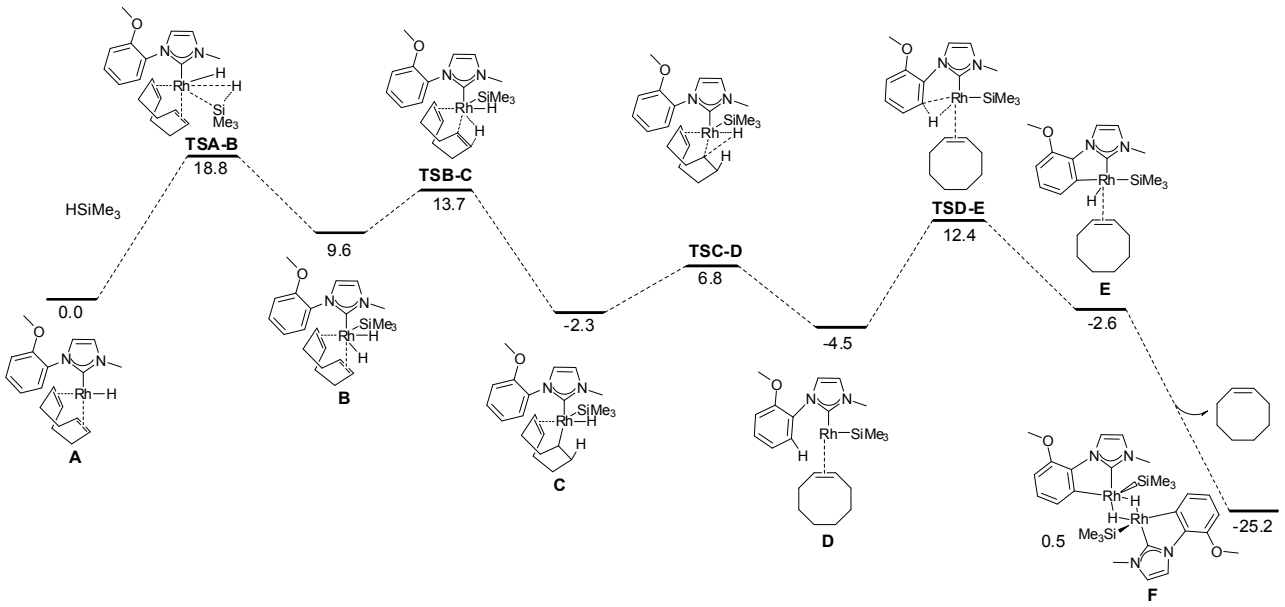

Figure 5. DFT calculated relative Gibbs energy profile (in kcal mol^{-1}) for the reaction of complex **A** with $HSiMe_3$ to yield the binuclear complex **F**.

Taking into account the reactivity of **2a** with hydrosilanes, it is reasonable to suppose that the active site at the heterogeneous catalysts **2a-MCM-41** could behave similarly. However, due to the relatively low rhodium loading observed in **2a-MCM-41** the formation of a binuclear species analogous to species **3** or **4** is less likely. Therefore, the most probable scenario should be the formation of heterogeneous catalysts containing mononuclear rhodium active sites related to the calculated intermediate **E** (Figure 5).

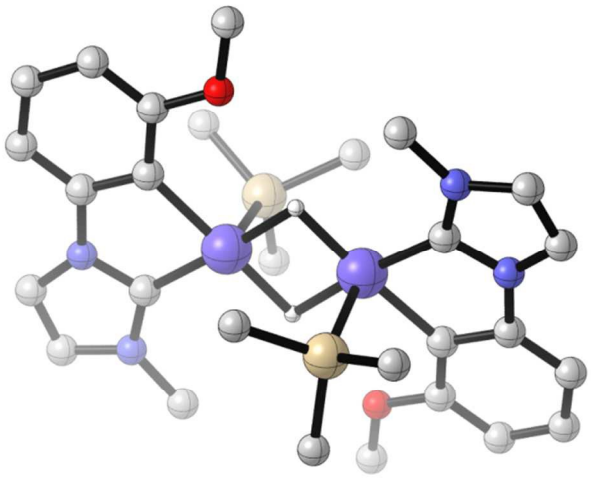

Figure 6. Geometrical representation of the intermediate **F** (as model of **3** and **4**)

The following experimental evidences: i) C_6D_6 solutions of **3** in presence of excess of $HSiMe(OSiMe_3)_2$ remains unchanged after heating at 90ºC, ii) C_6D_6 solutions of acetophenone,

$HSiMe(OSiMe_3)_2$ and the in situ generated species **3** are stable at room temperature but the formation of the corresponding hydrosilylation product was observed after heating at 90ºC, and iii) C_6D_6 solutions of **3** in presence of excess of $HSiMe(OSiMe_3)_2$ react with PCy_3 at 70ºC to afford a mixture of unidentified Rh-H species containing PCy_3 clearly attributed to mononuclear complexes,[23] which support the potential formation of mononuclear active species by thermal activation of the Rh-H-Rh bridges in **3** (see supplementary information).

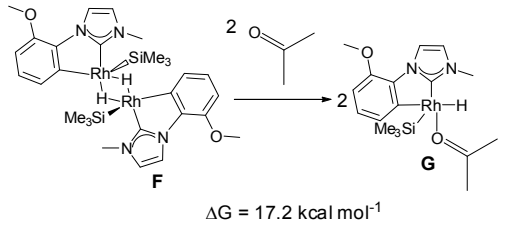

Figure 7. DFT calculated ΔG energy for the reaction of complex **F** with acetone to yield the mononuclear complex **G**.

Indeed, theoretical calculations evidenced that the formation of two equivalents of intermediate **G** starting from the reaction of **F** with two molecules of $(CH_3)_2CO$ requires 17.2 kcal mol^{-1} (Figures 7 and 8), which is agreement with the above mentioned experimental evidences.

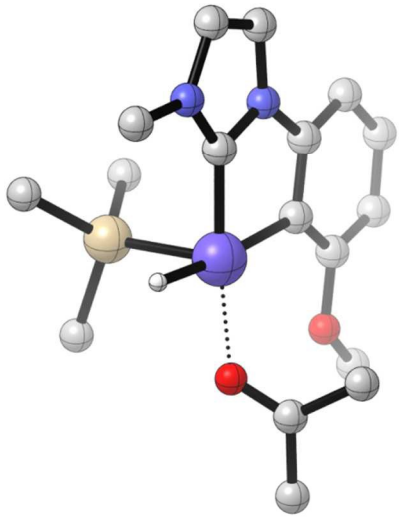

Figure 8. Geometrical representation of the intermediate **G**.

Conclusions

The rhodium(I) complex [Rh(Cl)(COD)(2-methoxyphenyl-NHC-$(CH_2)_3Si(OiPr)_3$)] (**2a**) catalyzes the homogeneous hydrosilylation of acetophenone with $HSiMe(OSiMe_3)_2$. Kinetic studies have shown that **2a** behaves differently to the related homogeneous catalysts [Rh(Cl)(COD)(R-NHC-$(CH_2)_3Si(OiPr)_3$)] (R = 2,6-diisopropylphenyl (**2b**) and 2-methoxyethyl (**2c**)) as a consequence of participation of very different active species. The studies of activity of its heterogeneous counterpart **2a-MCM-41** in acetophenone hydrosilylation also agree with a different active site to those present in **2b-MCM-41** and **2c-MCM-41**.

^1H, $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR studies of the reactivity of **2a** with hydrosilanes together with theoretical calculations evidenced that the orthometallation of the 2-methoxyphenyl *N*-substituent of the NHC ligand affords hydrido-bridged binuclear rhodium(III) complexes featuring terminal silyl ligands. Noteworthy, this species have shown activity in ketone hydrosilylation and thus, they can be considered as precursor for the active mononuclear Rh(III)-H species by bridged-splitting reaction by ketone. This species follow a different reaction mechanism from those Rh-NHC species in which the ortometallacion of the *N*-substituents at the NHC ligand is not possible. Contrary to expectations that orthometallation of the NHC ligand by the metal center is a pathway for catalyst deactivation; we have demonstrated that this process can also lead to active catalytic species.

In addition, it should be noted that in this particular case $Si(OiPr)_3$-functionalized Rh-NHC complexes have proven to be a fairly accurate model of the behavior of their related Rh-NHC heterogeneous catalysts.

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Notes and references

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† Electronic Supplementary Information (ESI) available: details of the computational studies. See DOI: 10.1039/b000000x/

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