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Hydrosilylation of aromatic nitriles promoted by solvated rhodium atom-derived catalysts

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Abstract

Rhodium metal particles, isolated as supported or unsupported powder starting from mesitylene solvated rhodium atoms, catalyse the hydrosilylation of aromatic nitriles to N,N-disilylamines in high conversion at 100°C. Different hydrosilanes ($HSiMe_3$, $HSi(OEt)_3$) can be employed. In the case of cinnamonitrile, the chemoselectivity of the reaction to 2-trimethyl-silyl-3-phenylpropionitrile and (E)- and (Z)-1-di(trimethylsilyl)amino-3-phenyl-1-propene is strongly dependent on the reaction temperature. The commercial rhodium on γ-Al_2O_3 catalyst is considerably less active and selective than the analogous catalyst prepared via Metal Vapour Synthesis (MVS) probably owing to the different dimension and distribution of the metal particles in the two samples as shown by HRTEM analysis. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The hydrosilylation of unsaturated compounds as olefins, acetylenes, imines and oxymes promoted by transition metal catalysts is a widely investigated reaction whether for reduction of unsaturated groups or for introduction of silyls into these ones [1]. However, little is known about the hydrosilylation of C–N triple bonds, being the ciano group considered inert under the usual reaction conditions [2–5]. Only recently, Murai et al. reported a detailed investigation about the hydrosilylation of nitriles catalyzed by $Co_2(CO)_8$ [6,7]. They found that two molecules of trimethylsilane add to the ciano group giving the corresponding N,N-disilylamine in good yield. The authors observed that the reaction proceeds only with trimethylsilane, other silanes ($HSiMe_2Ph$, H_2SiPh_2, $HSi(OEt)_3$, $HSiEt_2Me$ and $HSiEt_3$) being unreactive or giving rise to complex mixtures of products [7].

We recently found that homogeneous and heterogeneous catalysts derived from mesitylene solvated platinum atoms were very reactive

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$$R = H, CH_3, OCH_3, CF_3, COOCH_3$$
$$R' = CH_3, OC_2H_5$$
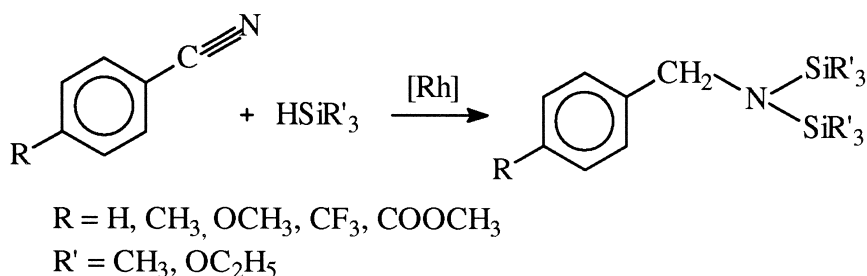
Scheme 1.

in the selective hydrosilylation of dienes and acetylenes [8–10]. We report now that unsupported and supported rhodium metal nanoparticles, similarly prepared from arene solvated rhodium atoms, are excellent precursors for the selective hydrosilylation of aromatic nitriles to the corresponding *N,N*-disilyl derivatives (Scheme 1).

The hydrosilylation of cinnamonitrile has also been investigated and the factors affecting the nitrile vs. carbon–carbon double bond hydrosilylation have also been studied.

2. Experimental

2.1. General

All the operations concerning the Metal Vapour Synthesis (MVS) technique and the catalytic reactions were performed under dry argon atmosphere. Solvents were purified by conventional methods, distilled and stored under argon. The nitriles (benzonitrile, **1**; *p*-methylbenzonitrile, **2**; *p*-methoxybenzonitrile, **3**; *p*-trifluoromethylbenzonitrile, **4**; *p*-carbomethoxybenzonitrile, **5**; *o*-methylbenzonitrile, **6**; cinnamonitrile, *E*-**7**) and the triethoxysilane were commercial products and were degassed and stored under argon before use. Trimethylsilane was prepared according to a literature report [11]. Commercial γ-Al$_2$O$_3$ (AKZO 000-1.5 E product) was dried in oven before the use. Commercial rhodium on γ-Al$_2$O$_3$ (5 wt.% Rh) was an Engelhardt product. The co-condensation of rhodium and mesitylene was carried out in a static reactor previously described [12]. The amount of rhodium present in the MVS solution was determined by X-ray fluorescence analysis [13].

Electron micrographs of the rhodium on γ-Al$_2$O$_3$ catalysts (5 wt.% Rh), prepared by MVS technique and commercially available, were obtained with a Jeol 2000EX microscope equipped with polar piece and top entry stage. Before the introduction in the instrument, the samples, in form of powder, were ultrasonically dispersed in isopropyl alcohol, and a drop of the suspension was deposited on a copper grid covered with a lacey carbon film. Histograms of the metal particle size distribution (MPSD) were obtained by counting onto the micrographs at least 300 particles, and the mean particle diameter (d_m) was calculated by using the formula $d_m = \Sigma d_i n_i / \Sigma n_i$, were n_i was the number of particles of diameter d_i.

The GLC analyses were performed on a Perkin Elmer 8600 gas chromatograph, equipped with a flame ionization detector (FID), using a DB1 column (30 m × 0.53 mm, 5 μm) and helium as carrier gas. The mass spectra were recorded on a Perkin Elmer Q-Mass 910 spectrometer, connected with a Perkin Elmer 8500 gas chromatograph, and on a VG 7070E spectrometer. ^{1}H NMR spectra were recorded on a Varian Gemini 200 instrument at 200 MHz; chloroform-*d* was used as solvent; proton chemical shifts were determined relative to Si(CH$_3$)$_4$ ($\delta = 0$ ppm); coupling constant, *J*, is in hertz. Microanalyses were carried out by the Laboratorio di Microanalisi, Facoltà di Farmacia, Università di Pisa, Italy.

Catalytic runs have been performed in Pirex Carius tubes fitted with Corning Rotaflo Teflon taps.

2.2. Preparation of the rhodium catalysts

2.2.1. Synthesis of the MVS Rh / mesitylene solution

In a typical experiment, rhodium vapour, generated by resistive heating of a tungsten wire surface coated with electrodeposited rhodium (300–400 mg), was co-condensed at liquid nitrogen temperature with mesitylene (40 ml) in the glass reactor chamber of the MVS apparatus in ca. 30 min. The reactor chamber was warmed at the melting point of the solid matrix (ca. -40°C) and the resulting brown solution was siphoned at low temperature in a Schlenk tube. This solution is stable for about a week in a refrigerator at -20°C.

2.2.2. Preparation of rhodium dust, catalyst *B*

The rhodium dust was prepared directly in the Carius tube employed for the catalytic experiment (see below). To 2 ml of the brown Rh/mesitylene solution, containing 6 mg (0.058 mmol) of rhodium/ml, pentane (20 ml) was added and the solution was slowly warmed at room temperature under stirring. After 4 h, the solution becoming colourless, the liquid was removed and the powder obtained was washed with pentane and dried under reduced pressure.

2.2.3. Preparation of metallic rhodium on γ-Al_2O_3, catalyst *C*

The above brown Rh/mesitylene solution (2 ml) was added to a suspension of γ-Al_2O_3 (0.24 g) in toluene (10 ml). The mixture was stirred for 24 h at room temperature. The colourless solution was removed and the light-brown solid was washed with pentane and dried under reduced pressure; Rh/γ-Al_2O_3 catalyst, containing 5 wt.% Rh, was obtained.

The Rh/γ-Al_2O_3 catalyst, containing 1 wt.% Rh, was prepared similarly starting from 2 ml of

the above Rh/mesitylene solution and 1.20 g of Al_2O_3.

2.3. Catalytic hydrosilylation of aromatic nitriles in the presence of rhodium catalysts; general procedure

The nitrile (9.8 mmol) and the hydrosilane (49 mmol) were added to the rhodium catalyst (0.1 mmol) contained in the Carius tube. Using trimethylsilane, the operation was performed at -20°C. The tube was closed and the mixture was stirred at 100°C for 15 h. The liquid was separated by filtration and the excess of hydrosilane was removed in vacuo giving the N,N-disilylamine derivative. Sometimes, a bulb to bulb distillation was performed to get a completely colourless liquid. The yields obtained in the different runs are reported in Tables 1–4. The products have been characterised by elemental analysis, MS spectrometry, ^{1}H NMR spectroscopy and by comparison with literature reports [6,7]; the composition of the reaction mixture obtained in the hydrosilylation of cinnamonitrile was determined by GLC and by ^{1}H NMR analyses.

N,N-Di(trimethylsilyl)benzylamine, **1a**. MS (m/z): 251 (M^+). ^{1}H NMR: δ 0.1 (s, 18H, $-\text{Si}(\text{C}H_3)_3$); 4.13 (s, 2H, $-\text{C}H_2-$); 7.13–7.41 (m, 5H, C_6H_5).

N,N-Di(trimethylsilyl)-p-methylbenzylamine, **2a**. MS (m/z): 265 (M^+). ^{1}H NMR: δ 0.1 (s, 18H, $-\text{Si}(\text{C}H_3)_3$); 2.32 (s, 3H, $-\text{C}_6H_4-\text{C}H_3$); 4.08 (s, 2H, $-\text{C}H_2-$); 7.05–7.18 (m, 4H, $-\text{C}_6H_4-$).

N,N-Di(trimethylsilyl)-p-methoxybenzylamine, **3a**. MS (m/z): 281 (M^+). ^{1}H NMR: δ 0.1 (s, 18H, $-\text{Si}(\text{C}H_3)_3$); 3.86 (s, 3H, $-\text{C}_6H_4-\text{O}\text{C}H_3$); 4.08 (s, 2H, $-\text{C}H_2-$); 6.85 (d, 2H, $-\text{C}_6H_2H_2-$, $J = 8$); 7.25(d, 2H, $-\text{C}_6H_2H_2-$).

N,N-Di(trimethylsilyl)-p-trifluoromethylbenzylamine, **4a**. MS (m/z): 319 (M^+). ^{1}H NMR: δ 0.09(s, 18H, $-\text{Si}(\text{C}H_3)_3$); 4.13 (s, 2H, $-\text{C}H_2-$); 7.35 (d, 2H, $-\text{C}_6H_2H_2-$, $J = 8$); 7.53 (d, 2H, $-\text{C}_6H_2H_2-$). Anal.: Calc. for

Table 1

Catalytic hydrosilylation of aromatic nitriles promoted by rhodium powder (catalyst **B**)[a]

$$\text{ArC}\equiv\text{N} + 2\text{HSiR}_3 \xrightarrow{\text{catalyst } \textbf{B}} \text{ArCH}_2\text{N(SiR}_3)_2 \quad R = Me, OEt$$

Run	Nitrile	Hydrosylane	Conversion %[b]	Product	Yield of product %[c]
1	C_6H_5CN, **1**	$HSiMe_3$	100	$C_6H_5CH_2N(SiMe_3)_2$, **1a**	95(100)
2[d]	C_6H_5CN, **1**	$HSiMe_3$	5	$C_6H_5CH_2N(SiMe_3)_2$, **1a**	(5)
3[e]	C_6H_5CN, **1**	$HSiMe_3$	25	$C_6H_5CH_2N(SiMe_3)_2$, **1a**	(25)
4[f]	C_6H_5CN, **1**	$HSiMe_3$	90	$C_6H_5CH_2N(SiMe_3)_2$, **1a**	(90)
5[g]	C_6H_5CN, **1**	$HSiMe_3$	100	$C_6H_5CH_2N(SiMe_3)_2$, **1a**	(100)
6[h]	C_6H_5CN, **1**	$HSiMe_3$	65	$C_6H_5CH_2N(SiMe_3)_2$, **1a**	(65)
7	$p\text{-MeC}_6H_4CN$, **2**	$HSiMe_3$	100	$p\text{-MeC}_6H_4CH_2N(SiMe_3)_2$, **2a**	95(100)
8	$p\text{-MeOC}_6H_4CN$, **3**	$HSiMe_3$	100	$p\text{-MeOC}_6H_4CH_2N(SiMe_3)_2$, **3a**	95(100)
9[i]	$p\text{-CF}_3C_6H_4CN$, **4**	$HSiMe_3$	100	$p\text{-CF}_3C_6H_4CH_2N(SiMe_3)_2$, **4a**	95(100)
10[l]	$p\text{-MeCO}_2C_6H_4CN$, **5**	$HSiMe_3$	100	$p\text{-MeCO}_2C_6H_4CH_2N(SiMe_3)_2$, **5a**	95(100)
11	$o\text{-MeC}_6H_4CN$, **6**	$HSiMe_3$	< 1	$o\text{-MeC}_6H_4CH_2N(SiMe_3)_2$, **6a**	tr.
12	**1**	$HSi(OEt)_3$	80	$C_6H_5CH_2N[Si(OEt)_3]_2$, **1b**	75(80)
13	**2**	$HSi(OEt)_3$	75	$p\text{-MeC}_6H_4CH_2N[Si(OEt)_3]_2$, **2b**	70(75)
14	**3**	$HSi(OEt)_3$	75	$p\text{-MeOC}_6H_4CH_2N[Si(OEt)_3]_2$, **3b**	70(75)
15	**4**	$HSi(OEt)_3$	75	$p\text{-CF}_3C_6H_4CH_2N[Si(OEt)_3]_2$, **4b**	70(75)
16	**5**	$HSi(OEt)_3$	70	$p\text{-MeCO}_2C_6H_4CH_2N[Si(OEt)_3]_2$, **5b**	65(70)
17	**6**	$HSi(OEt)_3$	< 1	$o\text{-MeC}_6H_4CH_2N[Si(OEt)_3]_2$, **6b**	tr.

[a] Reaction conditions: nitrile (9.8 mmol), hydrosilane (49 mmol), rhodium (0.1 mg atom); $T = 100°C$; time = 15 h.
[b] GLC conversion of the nitrile.
[c] Isolated product yield; GC yield in parenthesis.
[d] Carried out at 25°C.
[e] Carried out at 60°C.
[f] Carried out using trimethylsilane, 29.4 mmol.
[g] Carried out using trimethylsilane, 78.4 mmol.
[h] Carried out for 8 h.
[i] Carried out for 4 h.
[l] Carried out for 7 h.

$C_{14}H_{24}F_3NSi_2$: C, 52.64; H, 7.58; N, 4.39. Found: C, 52.38; H, 7.67; N, 4.41%.

N,N-Di(trimethylsilyl)-*p*-carboimethoxybenzylamine, **5a**. MS (m/z): 309 (M^+). ^{1}H NMR: δ 0.1 (s, 18H, $-Si(CH_3)_3$); 3.85 (s, 3H, $-O-CH_3$), 4.13 (s, 2H, $-CH_2-$); 7.28 (d, 2H, $-C_6H_2H_2-$, $J = 8$); 7.95 (d, 2H, $-C_6H_2H_2-$).

N,N-Di(triethoxysilyl)benzylamine, **1b**. MS (m/z): 431 (M^+). ^{1}H NMR: δ 1.16 (t, 18H, $-CH_2-CH_3$, $J = 7$); 3.75 (q, 12H, $-CH_2-CH_3$); 4.12 (s, 2H, $-CH_2-N$); 7.15–7.50 (m, 5H, $-C_6H_5$). Anal.: Calc. for $C_{19}H_{37}NO_6Si_2$: C, 52.87; H, 8.65; N, 3.25. Found: C, 52.69; H, 8.77; N, 3.36%.

N,N-Di(triethoxysilyl)-*p*-methylbenzylamine, **2b**. MS (m/z): 445 (M^+). ^{1}H NMR: δ 1.16 (t, 18H, $-CH_2-CH_3$, $J = 7$); 2.35 (s, 3H,

$-C_6H_4-CH_3$); 3.75 (q, 12H, $-CH_2-CH_3$); 4.09 (s, 2H, $-CH_2-N$); 7.07–7.45 (m, 5H, $-C_6H_5$). Anal.: Calc. for $C_{20}H_{39}NO_6Si_2$: C, 53.90; H, 8.83; N, 3.15. Found: C, 53.95; H, 8.97; N, 3.12%.

N,N-Di(triethoxysilyl)-*p*-methoxybenzylamine, **3b**. MS (m/z): 461 (M^+). ^{1}H NMR: δ 1.16 (t, 18H, $-CH_2-CH_3$, $J = 7$); 3.75 (q, 12H, $-CH_2-CH_3$); 3.84 (s, 3H, $-C_6H_4-OCH_3$); 4.09 (s, 2H, $-CH_2-N$); 6.89 (d, 2H, $-C_6H_2H_2-$, $J = 8$); 7.27 (d, 2H, $-C_6H_2H_2-$). Anal.: Calc. for $C_{20}H_{39}NO_7Si_2$: C, 52.04; H, 8.52; N, 3.04. Found: C, 51.83; H, 8.65; N, 3.08%.

N,N-Di(triethoxysilyl)-*p*-trifluoromethyl-benzylamine, **4b**. MS (m/z): 499 (M^+). ^{1}H NMR: δ 1.15 (t, 18H, $-CH_2-CH_3$, $J = 7$); 3.73 (q, 12H, $-CH_2-CH_3$); 4.11 (s, 2H,

Table 2

Catalytic hydrosilylation of aromatic nitriles promoted by rhodium on γ-alumina, catalysts $\mathbf{C}$[a]

$$ArC\equiv N + 2HSiR_3 \xrightarrow{\text{catalyst}} ArCH_2N(SiR_3)_2 \quad R = Me, OEt$$
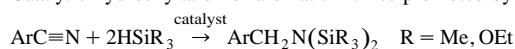
Run	Nitrile	Catalyst	Hydrosilane	Conversion[b]	Product	Yield of product %[c]
18	**1**	Rh/γ-Al$_2$O$_3$ 1%	HSiMe$_3$	80	**1a**	75(80)
19	**2**	Rh/γ-Al$_2$O$_3$ 1%	HSiMe$_3$	75	**2a**	70(75)
20	**3**	Rh/γ-Al$_2$O$_3$ 1%	HSiMe$_3$	75	**3a**	70(75)
21[d]	**4**	Rh/γ-Al$_2$O$_3$ 1%	HSiMe$_3$	50	**4a**	45(50)
22	**1**	Rh/γ-Al$_2$O$_3$ 5%	HSiMe$_3$	80	**1a**	75(80)
23	**2**	Rh/γ-Al$_2$O$_3$ 5%	HSiMe$_3$	75	**2a**	70(75)
24	**3**	Rh/γ-Al$_2$O$_3$ 5%	HSiMe$_3$	75	**3a**	70(75)
25[d]	**4**	Rh/γ-Al$_2$O$_3$ 5%	HSiMe$_3$	45	**4a**	40(45)
26	**1**	Rh/γ-Al$_2$O$_3$ 1%	HSi(OEt)$_3$	65	**1a**	60(65)
27	**1**	Rh/γ-Al$_2$O$_3$ 5%	HSi(OEt)$_3$	65	**1a**	60(65)

[a] Reaction conditions: nitrile (9.8 mmol), HSiR$_3$ (49 mmol), rhodium (0.1 mg atom); $T = 100°C$; time = 15 h.
[b] GLC conversion of the nitrile.
[c] Isolated product yield; GLC yields in parenthesis.
[d] Carried out for 4 h.

$-CH_2-N$); 7.37 (d, 2H, $-C_6H_2H_2-$, $J = 8$); 7.54 (d, 2H, $-C_6H_2H_2-$). Anal.: Calc. for $C_{20}H_{36}F_3NO_6Si_2$: C, 48.08; H, 7.27; N, 2.81. Found: C, 48.10; H, 7.40; N, 3.09%.

N,N-Di(triethoxysilyl)-p-carbomethoxybenzylamine, **5b**. MS (m/z): 489 (M$^+$). ^{1}H NMR: δ 1.16 (t, 18H, $-CH_2-CH_3$, $J = 7$); 3.72 (q, 12H, $-CH_2-CH_3$); 3.86 (s, 3H, $-O-CH_3$); 4.11 (s, 2H, $-CH_2-N$); 7.30 (d, 2H, $-C_6H_2H_2-$, $J = 8$); 7.96 (d, 2H, $-C_6H_2H_2-$). Anal.: Calc. for $C_{15}H_{39}NO_8Si_2$: C, 43.14; H,

9.42; N, 3.36. Found: C, 43.17; H, 9.60; N, 3.43%.

2-Trimethylsilyl-3-phenylpropionitrile, **7a**. GC-MS (m/z): 203 (M$^+$). ^{1}H NMR: δ 0.24 (s, 9H, $-CH_3$); 2.04 (dd, 1H, $CH-CHH-$, $J = 6$ and 9); 2.74–2.84 (m, 2H, C_6H_5-CHH); 7.15–7.40 (m, 5H, C_6H_5). IR (neat): 2221 cm^{-1}.

(Z)-1-Di(trimethylsilyl)amino-3-phenyl-1-propene, **7b**. GC-MS (m/z): 277 (M^+). ^{1}H NMR: δ 0.13 (s, 18H, CH_3); 3.43 (d, 2H, $-CH_2-CH=$, $J = 7$); 5.29 (q, 1H, $-CH_2-$

Table 3

Hydrosilylation of cinnamonitrile, (E)-**7**, with HSiMe$_3$ promoted by heterogeneous rhodium catalysts **B** and **C**[a]
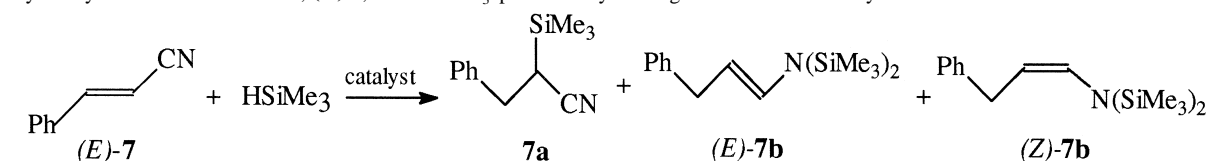
Run	Catalyst	T (°C)	Time (min)	Conversion (%)[b]	Yield of product[c] 7a	(E)-7b	(Z)-7b
28	Rh powder catalyst **B**	100	10	100	82	7	11
29	(Reaction mixture of run 28)	100	240	–	82	7	11
30	Rh powder catalyst **B**	50	360	100	100	–	–
31	Rh powder catalyst **B**	140	5	100	40	26	34
32	Rh/Al$_2$O$_3$ 5% catalyst **C**	100	10	95	84	4	7

[a] Reaction conditions: cinnamonitrile (0.48 ml, 3.9 mmol), HSiMe$_3$ (2.3 ml, 19.5 mmol), rhodium (0.039 mg atom).
[b] GLC conversion of (E)-**7**.
[c] Determined by GLC and ^{1}H NMR.

Table 4
Catalytic hydrosilylation of aromatic nitriles promoted by $HSiMe_3$ with 5 wt.% Rh/γ-Al_2O_3 commercial sample. Comparison with the analogous MVS derived catalyst, $\mathbf{C}$[a]

Run	Nitrile	Catalyst	Conversion (%)[b]	Yield of product (%)[c]
33	**1**	5 wt.% Rh/γ-Al_2O_3 commercial	70	**1a** (28)[d]
34	**2**	5 wt.% Rh/γ-Al_2O_3 commercial	40	**2a** (25)[d]
35[e]	**4**	5 wt.% Rh/γ-Al_2O_3 commercial	35	**4a** (15)[d]
36[f]	(E)-**7**	5 wt.% Rh/γ-Al_2O_3 commercial	5	**7a** (5)
22	**1**	5 wt.% Rh/γ-Al_2O_3 MVS, **C**	80	**1a** (80)
23	**2**	5 wt.% Rh/γ-Al_2O_3 MVS, **C**	75	**2a** (75)
25[e]	**4**	5 wt.% Rh/γ-Al_2O_3 MVS, **C**	45	**4a** (45)
32[f]	(E)-**7**	5 wt.% Rh/γ-Al_2O_3 MVS, **C**	95	**7a** (84); (Z)-**7b** (7); (E)-**7b** (4)

[a] Reaction conditions: nitrile (9.8 mmol); $HSiMe_3$ (49 mmol); rhodium = (0.1 mg atom); $T = 100°C$, time = 15 h.
[b] GLC conversion of the nitrile.
[c] Calculated by GLC.
[d] The other products are high boiling derivatives.
[e] Carried out for 4 h.
[f] Cinnamonitrile = 3.9 mmol; $HSiMe_3$ = 19.5 mmol; rhodium = 0.039 mg atom; time = 10 min.

CH=CH–, $J = 7$); 5.89 (d, 1H, –CH=CH–N, $J = 7$); 7.15–7.40 (m, 5H, –C$_6H_5$).

(E)-1-Di(trimethylsilyl)amino-3-phenyl-1-propene, **7b**. GC-MS (m/z): 277 (M^+). ^{1}H NMR: δ 0.13 (s, 18H, CH_3); 3.28 (d, 2H, –CH_2–CH=, $J = 7$); 5.05 (dt, 1H, –CH$_2$–CH=CH–, $J = 7$ and 13); 5.96 (d, 1H, –CH=CH–N, $J = 13$); 7.15–7.40 (m, 5H, –C$_6H_5$).

3. Results and discussion

3.1. Preparation of the catalytic systems

The catalysts have been obtained according to the well established MVS procedure [12,14]. Rhodium vapour reacts with mesitylene at liquid nitrogen temperature affording a red–brown solid matrix which gives, on melting, solvated rhodium atoms, **A**, soluble and stable at low temperature in the excess of the arene (Scheme 2).

The arene solvated rhodium atoms can be regarded as rhodium-hydrido microclusters [15] and they have been conveniently used as homogeneous catalytic precursors for some interesting reactions such as the selective hydrogenation of olefins and arenes [16] and the selective hydroformylation of conjugated diolefins to unsaturated aldehydes [17].

By further warming at room temperature, the solvated rhodium atoms act as source of rhodium metal particles which can be isolated as unsupported, **B**, and supported, **C**, nanopowders.

The thus prepared rhodium catalysts are active in the hydrosilylation of aromatic nitriles giving selectively N,N-disilylamines (Scheme 1). In particular, the unsupported **B** and supported **C** catalysts show very interesting activity, while the solvated rhodium atoms, **A**, furnish the reaction products in quite low yields.

It is worth noting that the analogously prepared platinum systems, which are very active in the hydrosilylation of olefins and acetylenes, as mentioned above [8–10], are completely ineffective in the title reaction.

3.2. Hydrosilylation of aromatic nitriles with rhodium powder, **B**

The results obtained in the reaction of several aromatic nitriles with $HSiMe_3$ and $HSi(OEt)_3$ using rhodium nanopowder **B** as catalyst are reported in Table 1.

At 100°C benzonitrile, **1**, was completely converted in 15 h to N,N-di(trimethylsilyl)benz-

[A]

Solvated Rh Atoms

pentane
r. t.

γ-Al$_2$O$_3$
r. t.

Rh$_n$
[B]

Rh$_n$/γ-Al$_2$O$_3$
[C]
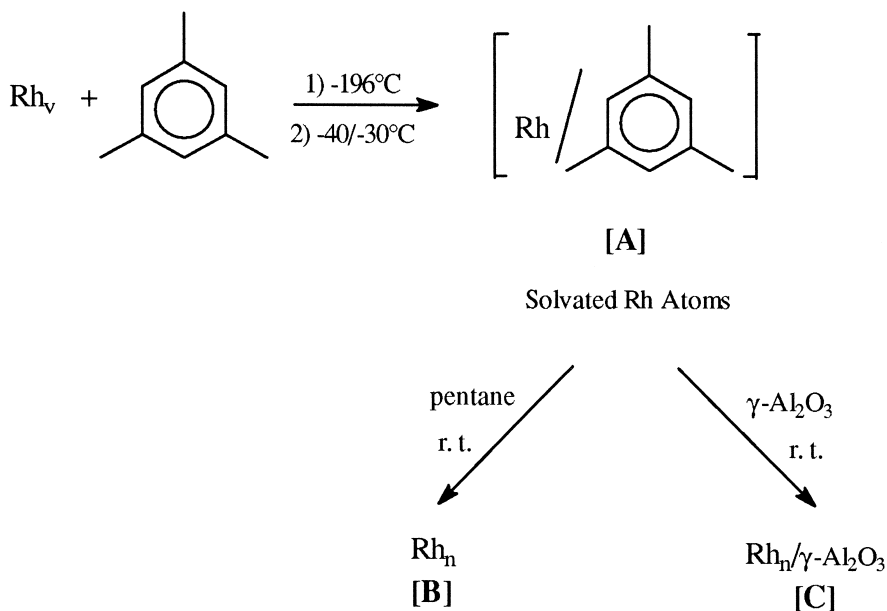
Scheme 2.

ylamine, **1a** (run 1). The reaction proceeds also at 25°C (run 2) and 60°C (run 3) but the conversion in **1a** is significantly lower than at 100°C (5% and 25%, respectively). As far as the influence of the ratio trimethylsilane/benzonitrile, n, in the hydrosilylation rate is concerned, it has been found that $n = 5$ is the minimum ratio that gets the best conversion in the unity of time. For $n = 3$, there is a reduction of the reaction rate (run 4, conv. 90%) and, for $n = 8$, no significant change in the rate is observed (run 5). It is noteworthy that the aldimine C$_6$H$_5$CH=NSiMe$_3$, derived from the reaction of benzonitrile with one molecule of trimethylsilane [2], was never found in the reaction mixture even at partial conversion (run 6).

p-Methylbenzonitrile, **2**, and *p*-methoxybenzonitrile, **3**, containing electron-donating groups, are hydrosilylated to the corresponding bis-*N,N*-disilylamines **2a** and **3a** at the same extent found for benzonitrile (runs 7 and 8). A considerable increase in the reaction rate was observed using *p*-trifluromethylbenzonitrile, **4**, and *p*-carbomethoxybenzonitrile, **5**; the conversion to the corresponding *N,N*-disilylamines **4a**

and **5a** being complete after 4 h and 7 h, respectively (runs 9 and 10). Probably, the CF$_3$ and CO$_2$Me electron-withdrawing groups of **4** and **5** weaken the C–N triple bond facilitating the addition of the hydrosilane. In contrast with the behaviour of the nitriles **1**–**5**, *o*-methylbenzonitrile, **6**, is a very poor reactive in this reaction and the corresponding *N,N*-disilylamine, **6a**, is formed only in traces (run 11), indicating that the activity of the catalyst is affected by the sterical hindrance.

The use of triethoxysilane in the above reactions has also been investigated. This hydrosilane, which is commercially available, was found inactive in the Co$_2$(CO)$_8$-catalyzed hydrosilylation of aromatic nitriles [7]. The results reported in the table indicate that the catalytic hydrosilylation of the nitriles **1**–**5** can be easily performed with rhodium particles **B** giving the corresponding disilylamines **1b**–**5b** in good yields at 100°C after 15 h (runs 12–16). No reaction is observed with the *ortho*-substituted nitrile **6** (run 17). The comparison between runs 1, 7–10, performed with trimethylsilane, and runs 12–16, carried out with triethoxysilane,

indicates that, for the same substrate, the reaction with the first silane is faster than with the last one.

3.3. Hydrosilylation of aromatic nitriles with rhodium on γ-alumina, C

The hydrosilylation of the aromatic nitriles **1**–**4** was performed also in the presence of rhodium supported on γ-alumina, **C**, prepared by deposition, from mesitylene-solvated rhodium solution, of rhodium particles on such support as shown in Scheme 2.

Two samples containing different loadings of metal (1 wt.% Rh and 5 wt.% Rh) were prepared and their catalytic activity was investigated. The results are summarized in Table 2.

The catalyst **C** (1 wt.% Rh) exhibits a good catalytic activity furnishing in the reaction between the nitriles **1**–**4** and trimethylsilane the corresponding N,N-disilylamines derivatives **1a**–**4a** in 50%–80% yields (runs 18–21). Similar results have been obtained using the catalyst **C** with 5 wt.% Rh (runs 22–25). However, the catalysts **C** were less active than catalyst **B**; i.e., with benzonitrile, the yield in **1a** is 80% (run 18 and 22) while it is quantitative with unsupported rhodium dust **B** (run 1) under the same reaction conditions.

Analogous results have been obtained in the hydrosilylation of benzonitrile with triethoxysilane using catalyst **C** (runs 26 and 27).

3.4. Hydrosilylation of cinnamonitrile

The hydrosilylation of cinnamonitrile, (E)-**7**, is of interest because several products can be obtained from this reaction owing to the different reactivity of the double bond and of the ciano group. The reaction has been examined using trimethylsilane in the presence of the previously reported heterogeneous rhodium catalysts and the results are shown in Table 3.

Independently of the nature of the catalyst, the reaction gives a mixture of 2-trimethylsilyl-3-phenylpropionitrile, **7a**, and (E)- and (Z)-1-di(trimethylsilyl)amino-3-phenyl-1-propene, **7b** (Scheme 3), characterised by GC-MS and ^{1}H NMR spectroscopy and by comparison with literature reports [7].

Compound **7a** derives from the hydrosilylation of the C–C double bond while compounds (E)- and (Z)-**7b** are formed by 1,2- and 1,4-addition of two molecules of trimethylsilane to the conjugated system [7].

With rhodium dust (catalyst **B**), the conversion is quantitative in 10 min at 100°C, giving a mixture containing **7a** as main product (82%), and a minor amount of (Z)-**7b** (11%) and (E)-**7b** (7%) (run 28). No change in the composition was observed on the mixture for 4 h at 100°C (run 29) indicating that the formation of the silyl derivatives is irreversible and there is no cis–trans isomerization under these conditions. However, the selectivity is strongly affected by the temperature. In fact, at 50°C, the conversion is quantitative in 6 h with the selective forma-
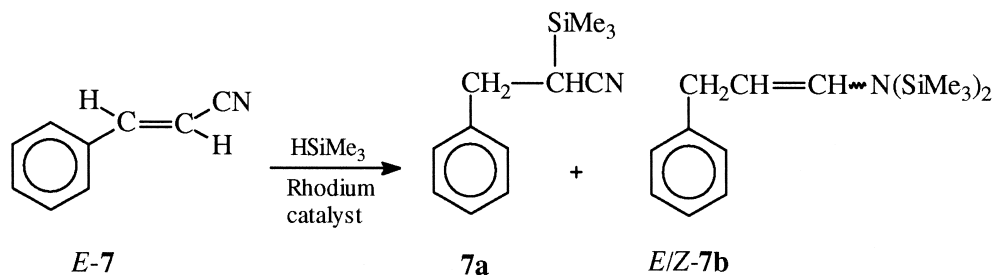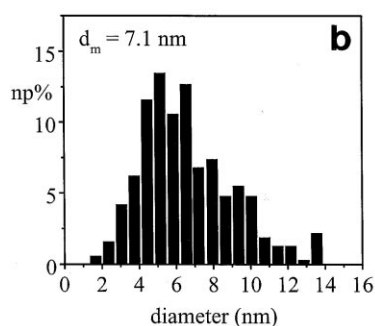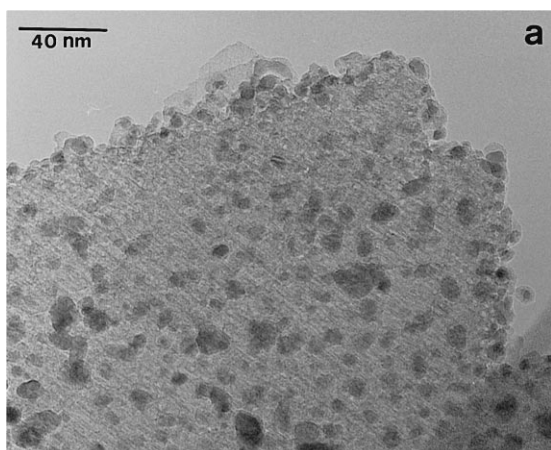

Scheme 3.

Fig. 1. (a) Electron micrograph of the commercial Rh/γ-Al$_2$O$_3$ 5 wt.% Rh catalyst; original magnification ×200,000. (b) Metal particle size distribution.

tion of **7a** (100%, run 30), while at 140°C, cinnamonitrile reacts in 5 min giving (*E*)- and (*Z*)-**7b** in 60% yield (run 31). The supported rhodium catalyst, **C**, behaves very similarly to catalyst **B** (run 32). The results obtained indicate that the C–C double bond reacts more easily than the C–N triple bond.

3.5. Hydrosilylation of aromatic nitriles using a commercial rhodium / γ-alumina catalyst

The hydrosilylation of the aromatic nitriles has also been performed using a 5 wt.% rhodium/γ-alumina catalyst commercially available. The results are reported in Table 4 compared with those obtained with the 5 wt.% rhodium/γ-alumina sample, **C**, derived from mesitylene solvated rhodium atoms.

Under the same experimental conditions, the commercial rhodium sample is considerably less active and selective than the catalyst prepared via MVS. In the hydrosilylation of the nitriles **1**, **2** and **4**, the yield in the corresponding *N*,*N*-disilylamines is very low (runs 33–35), the main products being a complex mixture of high boiling derivatives. In the hydrosilylation of cinnamonitrile, the commercial sample is quite ineffective, giving **7a** in 5% yield only (run 36).

3.6. Characterization of the 5 wt.% rhodium / γ-alumina catalysts

In order to get information on the possible factors responsible for the different catalytic activity shown by the 5 wt.% rhodium/
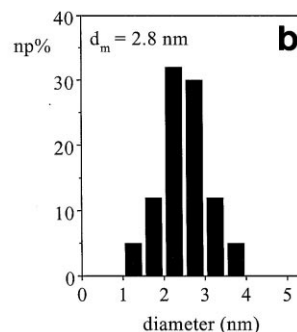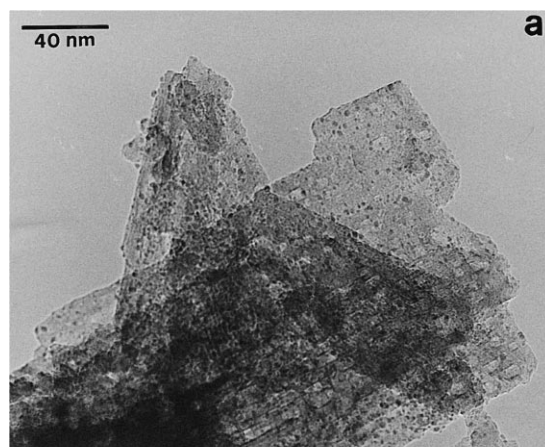

Fig. 2. (a) Electron micrograph of the Rh/γ-Al$_2$O$_3$ 5 wt.% Rh catalyst, **C**, prepared by clustering of solvated metal atoms in the presence of alumina; original magnification ×200,000. (b) Metal particle size distribution.

γ-alumina systems, commercial and MVS derived, their HRTEM analysis has been undertaken and the results are shown in Figs. 1 and 2, respectively.

In the case of the commercial sample (Fig. 1), quite large metal particles are observed, and their size distribution is spread over a broad range between 1.5 nm and 14 nm, with mean diameter $d_m = 7.1$ nm. In the TEM image of the MVS derived catalyst, **C**, (Fig. 2) the metal particles appear homogeneously dispersed onto the support. The statistical analysis of the dimension of these particles resulted in a quite narrow size distribution, lying in the range of 1–4 nm, which means $d_m = 2.8$ nm.

The so large difference in the MPSD of the two samples can reasonably account of their different activity and selectivity [18,19].

4. Conclusions

The results here reported show the first example of rhodium-based systems successfully employed in the heterogeneous catalytic hydrosilylation of aromatic nitriles. Different hydrosilanes can be used and the reaction can be carried out using a wide range of substrates. The hydrosilylation reactions have been performed without a solvent making the collection of the products particularly easy. In this frame it is worth noting that, using toluene or mesitylene as solvents, the yield in N,N-disilylamine derivatives strongly diminishes probably due to a competitive coordination of the aromatic ring to the catalytic centre. This can also account for the quite low catalytic activity of the arene solvated rhodium atoms, **A**, as homogeneous catalytic precursor.

The role of the temperature in affecting the selectivity in the hydrosilylation of cinnamonitrile with MVS-rhodium catalysts, **B** and **C**, is of interest. At low temperature (50°C), only the C–C double bond reacts giving compound **7a**, while at high temperature (140°C), the C–N triple bond becomes more reactive furnishing as

main products (E)- and (Z)-**7b**, deriving from the hydrosilylation at the conjugated system. Interestingly, $Co_2(CO)_8$ exhibits, at low temperature (60°C), a completely different selectivity giving only (E)- and (Z)-**7b**; experimental data at high temperature are not reported [7].

Finally, the comparison of the catalytic activity of the 5 wt.% rhodium/γ-alumina MVS and commercial samples provides an additional indication of the versatility of the metal atom technique in affording interesting new catalytic systems, characterised by very narrow size distributions of unusually active nanostructured metal particles.

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