Synthesis of Monophasic Hybrid Organic−Inorganic Solids Containing [η6-(Organosilyl)arene]chromium Tricarbonyl Moieties

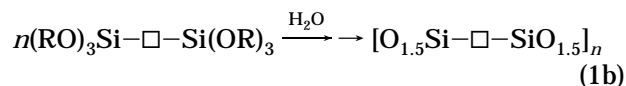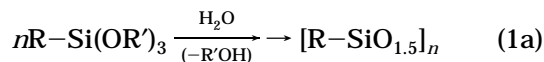Geneviève Cerveau, Robert J. P. Corriu,* and Cédric Lepeytre

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Silica gel containing benzenechromium tricarbonyl units have been obtained from molecular organosilicon precursors. The hydrolytic sol−gel polymerization of $[\eta^6\text{-}C_6H_5\text{Si-}(OMe)_3]Cr(CO)_3$ (**1**), $[\eta^6\text{-}1,4\text{-}C_6H_4RR']Cr(CO)_3$ $[R = R' = Si(OMe)_3$ (**2**), $R = R' = CH_2Si(OMe)_3$ (**3**), $R = R' = CH_2CH_2Si(OMe)_3$ (**4**)], $\{\eta^6\text{-}1,3,5\text{-}C_6H_3[Si(OMe)_3]_3\}Cr(CO)_3$ (**5**), under nucleophilic catalysis by fluoride ion (NH_4F), have led quantitatively to new monophasic hybrid organic−inorganic silica gels. The derived xerogels **X** were characterized by FT IR, ^{13}C and ^{29}Si solid state CP MAS NMR spectroscopies. The silicon−carbon bond and the tricarbonylchromium ligand were retained within the gel. The major environment of the Si atoms corresponded to a T_2:CSi(OR)(OSi)$_2$ substructure for **X2**−**X4**, a T_3:CSi(OSi)$_3$ one for **X1** and a Ts:CSi(OR)$_2$-(OSi) in the case of **X5**. In most cases, these were amorphous materials that exhibited low specific surface areas (~10 m^2 g^{-1}). Upon heating the xerogels **X1**, **X2**, and **X4** at 400 °C under an argon flow, weight losses corresponding to complete carbon monoxide elimination were obtained, leading to chromium in a low oxidation state within the solid.

Introduction

The sol−gel process, offering unique possibilities for the elaboration of inorganic solids,[1] has recently proved to be of great interest for the preparation of hybrid organic−inorganic materials.[2] The monophasic hybrid materials obtained by hydrolysis and polycondensation of substituted alkoxysilanes containing nonhydrolyzable Si−C bonds,[3,4] are opening interesting perspectives and wide possibilities in changing the nature of the organic moiety. In the case of RSi(OR')$_3$, the hydrolysis−polycondensation leads to a solid in which most of the organic groups are located at the surface[5,6] (eq 1a) and the resulting silsesquioxanes have been explored as models for the silica surface,[7] as ceramic precursors,[8−10] or to anchor metal complex moieties to a silica matrix.[11]

$$n\text{R}-\text{Si}(\text{OR}')_3 \xrightarrow[(-\text{R'OH})]{\text{H}_2\text{O}} [\text{R}-\text{SiO}_{1.5}]_n \quad \text{(1a)}$$

$$n(\text{RO})_3\text{Si}-\square-\text{Si}(\text{OR})_3 \xrightarrow{\text{H}_2\text{O}} [\text{O}_{1.5}\text{Si}-\square-\text{SiO}_{1.5}]_n \quad \text{(1b)}$$

In the case of polysilylated molecules,[3,4] solids with the organic unit incorporated into the silica matrix were obtained (eq 1b).

It has been pointed out that the formation of these materials is kinetically controlled,[3c] and relationships have been established between the properties of the solid and the nature of the organic groups, linear rigid rod[12,13] or more flexible structures[14,15] leading to completely different solids. Furthermore, a short-range organization has been evidenced by using chemical reactivity.[16,17]

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1997.

(1) (a) Brinker, C. J.; Scherer, G. W. *Sol-gel Science*; Academic Press: London, 1990, and references therein. (b) Hench, L. L.; West, J. K. *Chem. Rev.* **1990,** *90,* 33.

(2) (a) Schmidt, H. K. *Mater. Res. Soc. Symp. Proc.* **1984,** *32,* 327. (b) Schmidt, H. K. *Inorganic and Organometallic Polymers*; ACS Symp. Ser. No. 360; American Chemical Society: Washington, DC, 1988; p 133. (c) Schmidt, H. K. *Mater. Res. Soc. Symp. Proc.* **1990,** *180,* 961 and references therein. (d) *Hybrid Organic-inorganic Composites*; ACS Symp. Ser. No. 585; American Chemical Society: Washington, DC, 1994. (e) *New J. Chem.* **1994,** *18,* 989. (f) Judenstein, P.; Sanchez, C. *J. Mater. Chem.* **1996,** *6,* 511.

(3) (a) Cerveau, G.; Chorro, C.; Corriu, R. J. P.; Lepeytre, C.; Lère-Porte, J. P.; Moreau, J.; Thépot, P.; Wong Chi Man, M. *Hybrid Organic-Inorganic Silica Materials*; ACS Symp. Ser. No. 585; American Chemical Society: Washington, DC, 1995; p 210 and references therein. (b) Cerveau, G.; Chevalier, P.; Corriu, R. J. P.; Lepeytre, C.; Lère-Porte, J. P.; Moreau, J.; Thépot, P.; Wong Chi Man, M. *Tailor-made Silicon-Oxygen compounds From molecules to materials*; Corriu, R., Jutzi, P., Eds.; Vieweg Publishers: 1996; p 273 and references therein. (c) Corriu, R. J. P.; Leclercq, D. *Angew. Chem., Int. Ed. Engl.* **1996,** *35,* 1420 and references therein.

(4) Loy, D. A.; Shea, K. J. *Chem. Rev.* **1995,** *95,* 1431 and references therein.

(5) Schubert, U.; Hüsing, N.; Lorenz, A. *Chem. Mater.* **1995,** *7,* 2010.

(6) Cerveau, G.; Corriu, R. J. P.; Aubagnac, J. L.; Combarieu, R.; de Puydt, Y., to be published.

(7) Feher, F. J.; Newman, D. A.; Walzer, J. *J. Am. Chem. Soc.* **1989,** *111,* 1741.

(8) Laine, R. M.; Blum, Y.; Hamlin, R. D.; Chow, A. *Ultra Structure Processing of Advanced Ceramics*; MacKenzie, D. J., Ulrich, D. J., Eds.; Wiley-Interscience: New York, 1988; p 761.

(9) Yu, Y. F.; Mah, T. I. *Ultra Structure Processing of Advanced Ceramics*; MacKenzie, D. J., Ulrich, D. J., Eds.; Wiley-Interscience: New York, 1988; p 773.

(10) (a) White, D. A.; Oleff, S. M.; Boyer, R. D.; Budringer, P. A.; Fox, J. R. *Adv. Ceram. Mater.* **1987,** *2,* 45. (b) White, D. A.; Oleff, S. M.; Fox, J. R. *Adv. Ceram. Mater.* **1987,** *2,* 53.

(11) Breitscheidel, B.; Zieder, J.; Schubert, Y. *Chem. Mater.* **1991,** *3,* 559.

(12) (a) Corriu, R. J. P.; Moreau, J. J. E.; Thépot, P.; Wong Chi Man, M. *Chem. Mater.* **1992,** *4,* 1217. (b) Corriu, R. J. P.; Moreau, J. J. E.; Wong Chi Man, M. *J. Sol-Gel Sci. Technol.* **1994,** *2,* 87.

(13) Shea, K. J.; Loy, D. A.; Webster, O. *J. Am. Chem. Soc.* **1992,** *114,* 6700.

(14) (a) Oviatt, H. W., Jr.; Shea, K. J.; Small, J. H. *Chem. Mater.* **1993,** *5,* 943 and references therein. (b) Choi, K. M.; Shea, K. J. *Chem. Mater.* **1993,** *5,* 1067. (c) Choi, K. M.; Shea, K. J. *J. Phys. Chem.* **1994,** *98,* 3207. (d) Choi, K. M.; Shea, K. J. *J. Am. Chem. Soc.* **1994,** *116,* 9052. (e) Loy, D. A.; Jamison, G. M.; Baugher, B. M.; Russick, E. M.; Assink, R. A.; Prabakar, S.; Shea, K. J. *J. Non-Cryst. Solids* **1995,** *186,* 44.

(15) Antony, A.; Corriu, R. J. P.; Moreau, J. J. E.; Wong Chi Man, M. unpublished results.

In this paper, we describe, for the first time, monophasic organic−inorganic hybrid solids elaborated from organometallic molecules. Surprisingly despite the interesting possibilities afforded by this type of spacer, only the hybrid materials obtained from very stable ferrocene precursors have been previously reported.[18] The introduction of metallic centers into solids is of great interest since these centers can induce interesting physical properties, such as redox, paramagnetism, dipole moments, optical properties, etc. Until now, attempts have only been made in the case of biphasic systems in which the "dopant" can be removed by simply washing the solid. The main reason originates certainly in the high reactivity of the metallic centers and their tendency to induce partial or complete decomposition, which induces difficulties for the synthesis of precursors as well as for the elaboration of the solids. We have chosen to consider the case of arenechromium tricarbonyl precursors since we have shown in a previous paper the chemical stability of solids containing some aryl $Cr(CO)_3$ units obtained by direct complexation of xerogels elaborated from aromatic precursors.[19] In this case only some of the aromatic groups were complexed due to the lack of accessibility of aryl groups. We are describing now the preparation and the identification of xerogels obtained from pure arene $Cr(CO)_3$ containing one, two, or three $Si(OMe)_3$ groups.

Results and Discussion

Preparation of the Precursors. Compounds **1−5** (Scheme 1) have been prepared by direct thermal reaction[19,20] of the corresponding organosilyl arenes with the acetonitrile complex $(CH_3CN)_3Cr(CO)_3$ without solvent according to eq 2, illustrated in the case of **2**.
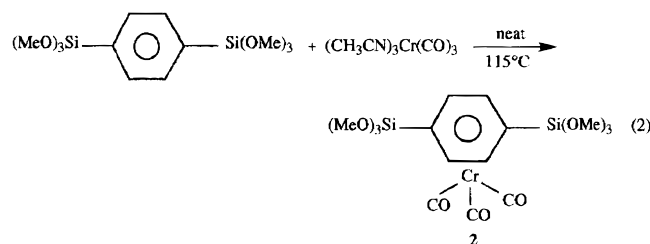
The progress of the reaction was monitored by IR spectroscopy. The heating was stopped when the $\nu(CO)$ bands at 1915, 1841, and 1792 cm^{-1} due to $(CH_3CN)_3Cr(CO)_3$ had disappeared and the new carbonyl stretching vibrations in the 1970−1880 cm^{-1} region stopped increasing. The residue was taken up with hexane, some insoluble decomposition material was eliminated by filtration and the resulting bright yellow solution was

(16) Corriu, R. J. P.; Moreau, J. J. E.; Thépot, P.; Wong Chi Man, M. *Chem. Mater.* **1996**, *8*, 100.

(17) (a) Corriu, R. J. P.; Moreau, J. J. E.; Thépot, P.; Wong Chi Man, M.; Chorro, C.; Lère-Porte, J. P.; Sauvajol, J. L. *Chem. Mater.* **1994**, *6*, 640. (b) Corriu, R. J. P.; Moreau, J. J. E.; Thépot, P.; Wong Chi Man, M.; Chorro, C.; Lère-Porte, J. P.; Sauvajol, J. L. *Synth. Met.* **1994**, *62*, 233.

(18) (a) Cerveau, G.; Corriu, R. J. P.; Costa, N. *J. Non-Cryst. Solids* **1993**, *163*, 226. (b) Audebert, P.; Calas, P.; Cerveau, G.; Corriu, R. J. P.; Costa, N. *J. Electroanal. Chem.* **1994**, *372*, 275. (c) Audebert, P.; Cerveau, G.; Corriu, R. J. P.; Costa, N. *J. Electroanal. Chem.* **1996**, *413*, 89.

(19) Cerveau, G.; Corriu, R. J. P.; Lepeytre, C. *J. Mater. Chem.* **1995**, *5*, 793.
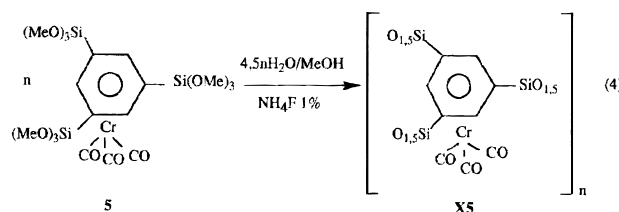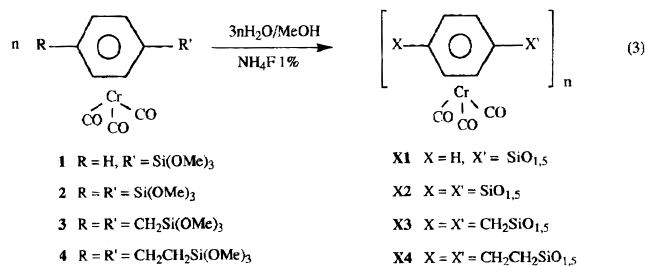
(20) Moran, M.; Cuadrado, I.; Pascual, M. C.; Casado, C. M. *Organometallics* **1992**, *11*, 1210.

Scheme 1. Gel Precursors 1−5
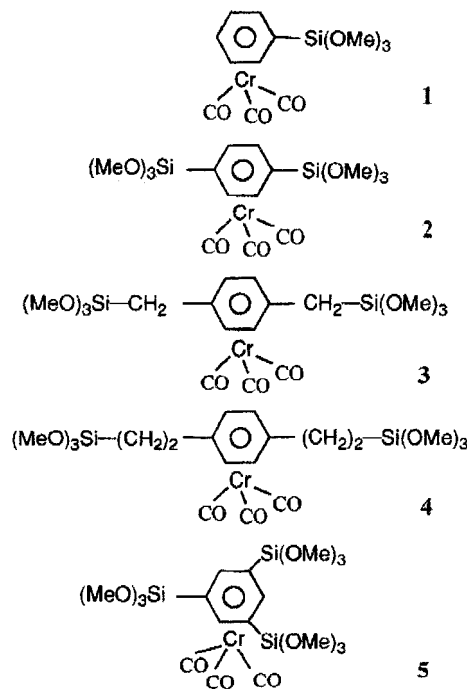
cooled at −25 °C to give air- and light-sensitive yellow solids, isolated in moderate yields (30−40%) as analytically pure yellow crystals (except for **4** which is an oil[20]). The analytical and spectroscopic data for all the new complexes are given in the Experimental Section.

Synthesis and Characterization of Organic−Inorganic Hybrid Gels. The xerogels **X1−X5** were prepared by sol−gel polymerization of **1−5** under nucleophilic catalysis,[21] using NH_4F (1 mol %; eq 3 and 4). Transparent yellow gels generally formed within a

1 R = H, R' = $Si(OMe)_3$
2 R = R' = $Si(OMe)_3$
3 R = R' = $CH_2Si(OMe)_3$
4 R = R' = $CH_2CH_2Si(OMe)_3$

X1 X = H, X' = $SiO_{1.5}$
X2 X = X' = $SiO_{1.5}$
X3 X = X' = $CH_2SiO_{1.5}$
X4 X = X' = $CH_2CH_2SiO_{1.5}$

very short period of time with **X2**, **X3**, **X4** (several seconds to few minutes). **X1** precipitates after 2 min and **X5** gels after 31 days (Table 1). After standing for ca. 7 days, the gels were powdered, washed with acetone and ether, and dried in vacuo. The resulting solids were analyzed and characterized by FTIR and solid-state ^{13}C and ^{29}Si CP MAS NMR spectroscopies.

(21) Corriu, R. J. P.; Leclercq, D.; Vioux, A.; Pauthe, M.; Phalippou, J. *Ultrastructure Processing of Advanced Ceramics*; Mackenzie, J. D., Ulrich, D. R., Eds.; Wiley: New York, 1988; p 113.
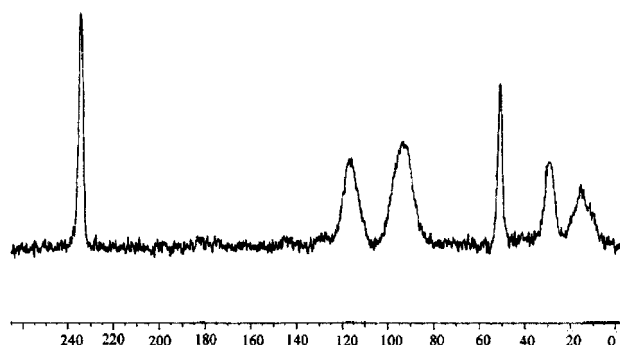
Table 1. Hydrolysis and Polycondensation of Precursors 1–5

xerogel	gel time (min)	surface[a] (m² g⁻¹)	C/Si calcd	C/Si found	Cr/Si calcd	Cr/Si found
X1	2[b]	<10	9	8.72	1	0.95
X2	1	588	4.5	4.6	0.5	0.48
X3	c	18	5.5	6.15	0.5	0.35
X4	5	<10	6.5	6.8	0.5	0.5
X5	4.46×10^4	<10	3	3.78	0.33	0.28

[a] BET Surface from multipoint analysis of N_2 adsorption isotherm. [b] Fast precipitation of solid. [c] Instantaneous gel at ~30 °C.

Table 2. ¹³C CP MAS NMR Chemical Shifts (δ, ppm) of Poly(organosilsesquioxanes) X1–X5

xerogels	CH_2Si	CH_2–Ar	residual CH_3O	complexed aromatic	CO
X1				94	233
X2			51.8	94	231
X3	21		51.4	93; 106	234
X4	15	29	51	93; 115	234
X5			51	88; 103	230

Figure 1. ¹³C CP MAS NMR spectrum of xerogel **X4**.

Table 3. ²⁹Si CP MAS NMR Chemical Shifts (δ, ppm) of Poly(organosilsesquioxanes) X1–X5[a]

	silicate substructure[b]		
	OR RO–Si–O–Si C	OSi RO–Si–O–Si C	OSi Si–O–Si–O–Si C
xerogels	(T1)	(T2)	(T3)
X1			−77; −79
X2		**−70**[c]	
X3	−56	**−63**	−71
X4	−50	**−58**	−67
X5[d]	**−63**	−70	

[a] Major resonances are in bold characters. [b] R = H, Me. [c] Broad signal (−55 < δ < −85) centered at −70 ppm. [d] Assignments have been made by comparison with the corresponding noncomplexed gels.[12a]

Figure 2. ²⁹Si CP MAS NMR spectra of xerogels (a) **X4** and (b) **X5**.
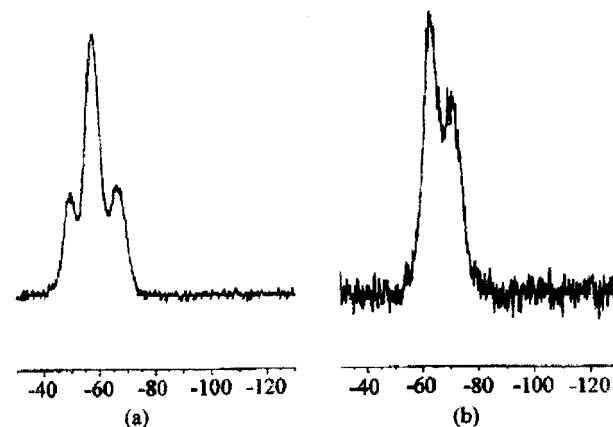
The obtained materials in all cases deviated from the ideal stoichiometry and contained numerous un-cross-linked units with residual hydroxy and methoxy groups. The carbon-to-silicon and chromium-to-silicon ratios calculated from elemental analysis measurements are reported in Table 1 and confirm the presence of these residual groups and the conservation of the $Cr(CO)_3$ ligand in the solids. FT IR spectra of dried gels showed bands at 3415 and 2845 cm⁻¹ attributable to the presence of Si–OH and Si–OMe groups, respectively. The most interesting features arose from the examination of the ν(CO) region where strong bands at ~1900 and 1970 cm⁻¹ confirmed the presence of $Cr(CO)_3$ units. The conservation of the molecular structure of the precursor in the gel and the absence of cleavage of the Si–C bond during the gelation process was established by NMR spectroscopy. ¹³C solid-state MAS NMR clearly revealed the expected aromatic resonances at δ = 94 ppm for **X1** and **X2** and δ ~ 90 and 110 ppm in the case of **X3**–**X5** corresponding to aromatic $Cr(CO)_3$ complexed carbons. A signal at δ ~ 233 ppm indicated the presence of CO ligands. Signals corresponding to CH_2 groups in the gels **X3** and **X4** appeared respectively at δ = 21 ppm for **X3** and δ = 15 and 29 ppm for **X4**. A minor resonance at δ = 51 ppm arises from residual methoxy carbons.

These characteristics are reported in Table 2, and Figure 1 shows ¹³C NMR spectrum of **X4** as an example. The absence of any ²⁹Si resonances attributable to SiO_4 units[22] (in the range −100, −110 ppm) confirms that no cleavage of the SiC bond is occurring. ²⁹Si NMR,

which is sensitive to the second neighbor,[23] also provides structural information about the silicate framework within the gel. The gels showed resonances corresponding to branched silicates with a degree of polycondensation around the central silicon atom corresponding to T_1, T_2, and T_3 units.[23] Chemical shifts and assignments of signals are reported in Table 3. Some representative spectra of the gels are presented in Figure 2. A high degree of condensation has been obtained with precursor **1**, an enhanced intensity of the ²⁹Si NMR signal corresponding to the fully condensed T_3 substructure being observed. Xerogels **X2**–**X4** showed the central peak corresponding to the substructure T_2:$CSi(OR)(OSi)_2$ as major resonance (Figure 2a).

Thus the bulky $Cr(CO)_3$ complexed precursors are leading to similar degrees of condensation than the corresponding noncomplexed precursors.[12a] The precursor **5** with nine possible condensation directions, leads to a poorly cross-linked oxide polymer where the major environment around the silicon atom is T_1:$CSi(OR)_2$-(OSi) (Figure 2b) instead of a major environment T_2 around the silicon atom observed with the corresponding 1,3,5-tris(trimethoxysilyl)benzene.[12a] Thus the presence of the $Cr(CO)_3$ moiety seems to hinder the polycondensation reaction.

The solid-state properties of the gels have been partially investigated. The X-ray powder diffraction

(22) Mägi, M.; Lippmaa, E.; Samoson, A.; Engelhardt, G.; Grimmer, A. R. *J. Phys. Chem.* **1984**, *88*, 1518.
(23) Williams, E. A. *NMR Spectroscopy of Organosilicon Compounds* in the Chemistry of Organic Silicon Compounds; Pataï, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 511.
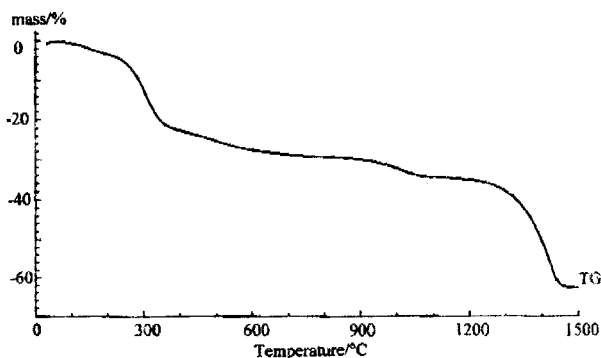
Figure 3. TGA curve of **X3**.

Table 4. Weight Losses Deduced from TGA of Gels X1−X5

	weight losses $\Delta m/m$(%)				
	250−350 °C			400−1050 °C	1200−1500 °C
xerogel	calcd[a]	found[b]	found[c]	found	found
X1	31.6	28	32.5	15	20
X2	26.5	20	24.7	10	24
X3	24	20		12	30
X4	22.5	20	23.2	14	26
X5	23	22[d]		4	28

[a] Weight loss of carbon monoxide based on the ideal stoichiometry. [b] From TG analyses. [c] From pyrolysis at 400 °C. [d] Weight loss from 250 to 400 °C.
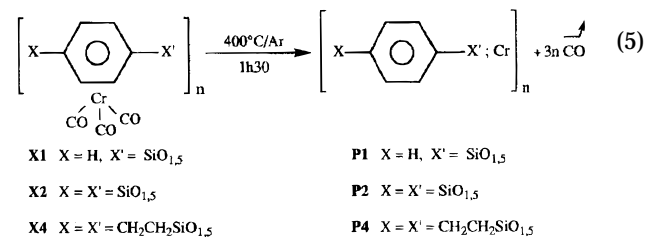
pattern showed no crystallinity in all cases. The materials are amorphous and no long-range order was detected. N_2 BET measurements gave the specific surface areas reported in Table 1. It is interesting to note that these specific surface areas are in the same range as those obtained for the corresponding noncomplexed solids prepared in the same experimental conditions[24] with the exception of **X5** which exhibits a surface area less than 10 m² g⁻¹ as compared to the surface area of 1004 m² g⁻¹ observed with the corresponding noncomplexed xerogel.

Thermogravimetric analyses (TGA) under argon were performed from room temperature to 1500 °C. In the case of **X1**−**X4**, the pyrolysis takes place in three steps. The TGA curve of **X3** is presented in Figure 3 as an example. For **X5** only two steps are observed. During the first step, between 250 and 350 °C, the weight losses correspond to the escape of carbon monoxide. Experiments performed by using TG/MS detected CO (m/z 12, 16, 28) almost exclusively. Some methanol evolution observed at the beginning of the treatment between 20 and 100 °C corresponded to residual polycondensation reactions. This is confirmed by the comparison of the calculated weight losses (deduced from the ideal stoichiometry) and the experimental ones (deduced from TG analyses; Table 4). In the second step, between 400 and 1050−1200 °C, only low weight losses between 10 and 15% are observed. In the third step, between 1200 and 1450 °C a large escape of carbon monoxide is detected, indicating that carbothermal reduction takes place. It is interesting to note that this carboreduction occurs at a lower temperature than in the case of phenylsilsesquioxane or other organosilsesquioxanes.[25] For **X5**, the

first step, between 250 and 400 °C corresponds to the escape of carbon monoxide and the second one between 1150 and 1450 °C is indicative of the carbothermal reduction.

X-ray analysis of the ceramics obtained after the carbothermal reduction revealed the presence of mainly SiC and Cr_3C_2 in the case of **X1**, **X3**, and **X4**, mainly formation of SiC and $Cr_{5-x}Si_{3-z}C_{x+z}$ in the case of **X2**, SiC, $Cr_{5-x}Si_{3-z}C_{x+z}$ and $CrSi_2$ in the case of **X5**.

To characterize the inorganic residue obtained after CO evolution, the pyrolysis at 400 °C was carried out on a preparative scale. The gels **X1**, **X2**, and **X4** were heated at 400 °C under an argon flow for **1** and ¹/₂ h (eq 5).

$$\left[X-\!\!\left\langle \bigcirc \right\rangle\!\!-X' \right]_n \xrightarrow[\text{1h30}]{400°C/Ar} \left[X-\!\!\left\langle \bigcirc \right\rangle\!\!-X' ; Cr \right]_n + 3n \overset{\nearrow}{CO} \quad (5)$$

X1 X = H, X' = $SiO_{1.5}$ **P1** X = H, X' = $SiO_{1.5}$

X2 X = X' = $SiO_{1.5}$ **P2** X = X' = $SiO_{1.5}$

X4 X = X' = $CH_2CH_2SiO_{1.5}$ **P4** X = X' = $CH_2CH_2SiO_{1.5}$

The obtained residues **P1**, **P2**, and **P4** corresponded to weight losses, $\Delta m/m$(%), respectively, of 32.5, 24.7, and 23.2 in good agreement for carbon monoxide loss with the calculated ones based on the ideal stoichiometry (Table 4). The complete elimination of CO ligands was confirmed by both IR and ¹³C NMR spectroscopies: the strong bands at ∼1900 and 1970 cm⁻¹ and the ¹³C NMR signal at $\delta \sim 233$ ppm corresponding to CO ligands had completely disappeared. Interestingly the resonances corresponding to the aromatic carbons appeared as broad signals centered respectively at $\delta = 135$ ppm for **P1**, $\delta = 133$ ppm for **P2**, and $\delta = 147$ ppm for **P4**; these values correspond to noncomplexed aromatic carbons. ²⁹Si solid-state CP MAS NMR revealed the presence of the T units of silsesquioxanes; however, the signals that appear at the same chemical shifts as the starting gels (Table 3) are broad and not very well defined. The chromium-to-silicon ratio was determined by EDS (energy-dispersive spectrometry) in all cases. The ratios found for **P1**, Cr/Si = 1.04; **P2**, Cr/Si = 0.53; **P4**, Cr/Si = 0.48, clearly show that neither silicon nor chromium are lost in this reaction. The X-ray powder diffraction pattern of the black solids showed no crystallinity in all cases.

To further characterize the chromium phases obtained after pyrolysis, XPS spectra (X-ray photoelectron spectrometry) of samples **P2** and **P4** have been recorded. The preliminary results obtained from the crude solids show that the chromium is present at the surface as chromium oxide. After stripping of the surface by Ar⁺ at 4 kV during 30 min, a shift of the binding energies to lower values is observed. These results show that after stripping of the surface chromium is present either as elemental chromium or in a low oxidation state. Thus the presence of chromium oxide at the surface can be attributed to an oxidation of the chromium by air, and we can conclude that chromium might be mainly as Cr^0 in the bulk of the material. This result is in agreement with the observation made by Shea on materials containing a lower ratio of chromium.[14d,26]

(24) Cerveau, G.; Corriu, R. J. P.; Lepeytre, C., to be published.
(25) (a) Cerveau, G.; Corriu, R. J. P.; Lepeytre, C., unpublished results. (b) Belot, V.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *J. Non-Cryst. Solids* **1994**, *176*, 33 and references therein.

Conclusion

The use of polysilylated organic molecules allows a general and easy preparation of monophasic hybrid organic–inorganic gels. The hydrolytic sol–gel process appears to be of general applicability. Even with bulky precursors, it leads to a wide variety of hybrid gels where the molecular structure of the organic molecule is always retained. In the cases described here the Cr-$(CO)_3$ ligand does not change either the texture of the solid or the degree of polycondensation of silicon atoms with disubstituted organic units. Only the trisubstituted one exhibits several differences.

Experimental Section

All reactions were carried out under nitrogen using a vacuum line and Schlenk tube techniques.[27] Solvents were dried and distilled before use. The reported yields refer to pure isolated materials. Melting points were determined with a Gallenkamp apparatus and are uncorrected. IR spectra were recorded using a Perkin-Elmer 1600 FT IR spectrophotometer using KBr pellets or by the DRIFT method. ^{1}H NMR spectra were recorded on a Bruker AW 80 or a Bruker DPX 200 spectrometer, ^{13}C and ^{29}Si NMR spectra were obtained in solution on another spectrometer (Bruker AC 250), and in the solid state, cross polarization/magic angle spinning (CP/MAS) ^{29}Si and ^{13}C spectra, with a Bruker FT-AM 300 spectrometer. Solvents and chemical shifts (δ relative to Me$_4$Si) are indicated. The specific surface areas were determined by analyzing the N$_2$ adsorption/desorption isotherms according to the BET method using a Micromeritics Gemini 2360 apparatus. Analyses were carried out by the Service Central de Micro-Analyse du CNRS. Thermogravimetric analyses (TGA) were performed under flowing argon (50 mL min^{-1}) with a Netzsch STA 409 thermobalance. About 40 mg of the sample in an alumina crucible was heated from room temperature to 1500 °C at a heating rate of 10 °C min^{-1}. X-ray powder diffraction measurements were performed using a Seifert MZ 4 apparatus. The pyrolysis experiments, performed with an Eurotherm furnace, were carried out by pouring weighed samples of solids into an aluminum oxide boat placed in a aluminum oxide tube connected to a vacuum line. The argon flow was maintained around 50 mL min^{-1} during pyrolysis, the samples were heated from room temperature to 400 °C at a heating rate of 10 °C min^{-1} and were allowed to stand at 400 °C for 1 h 30. XPS measurements were performed with a photoelectron spectrometer ESCALAB MK II VG.

Preparation of the Precursor. *[η^6-(Trimethoxysilyl)-benzene]tricarbonylchromium] (1).* This compound was prepared according to the procedure previously described.[28] Yellow crystals were isolated upon crystallization in hexane at −25 °C.

{η^6-[1,4-Bis(trimethoxysilyl)benzene]}tricarbonylchromium (2). Chromium hexacarbonyl (5.5 g, 25 × 10^{-3} mol) was converted to (CH$_3$CN)$_3$Cr(CO)$_3$ in refluxing CH$_3$CN for 24 h according to ref 29. The mixture was allowed to cool and the solvent was removed under reduced pressure. Recently prepared (CH$_3$CN)$_3$Cr(CO)$_3$ (5.83 g, 22.5 × 10^{-3} mol) was treated with 7.15 g (22.5 × 10^{-3} mol) of 1,4-bis(trimethoxysilyl)benzene[12a] at 115 °C under nitrogen. The course of the reaction was monitored by IR spectroscopy. The heating was stopped when the ν(CO) bands due to (CH$_3$CN)$_3$Cr(CO)$_3$ had disappeared and the new ν(CO) bands at ≈1904 and 1975 cm^{-1} stopped increasing. The mixture was then cooled to room temperature and taken up with hexane. The solution was filtered and the yellow filtrate was cooled at −25 °C for several

days. Yellow crystals of pure **2** were isolated (3.6 g; 30% yield); mp = 50–55 °C, IR ν(CO) 1904, 1975 cm^{-1}; ^{1}H NMR (CDCl$_3$, δ) 3.69 (s, 18H, OCH$_3$), 5.33 (s, 4H, C$_6$H$_4$); ^{13}C NMR (CDCl$_3$, δ) 51.8 (OCH$_3$), 91.1 (C$_{ar}$–Si), 97.3 (C$_{ar}$–H) 232.5 (CO); ^{29}Si NMR (CDCl$_3$, δ) −57.9. Anal. Calcd for C$_{15}$H$_{22}$CrO$_9$Si$_2$: C, 39.65; H, 4.85; Cr, 11.45; Si, 12.33. Found: C, 39.42; H, 4.85; Cr, 9.65; Si, 12.0.

{η^6-[1,4-Bis(trimethoxysilylmethyl)benzene]}tricarbonylchromium (3). 1,4-Bis(trimethoxysilylmethyl)benzene was prepared by methanolysis of 1,4-bis(trichlorosilylmethyl)benzene. To a suspension of 19.06 g (51.1 × 10^{-3} mol) of 1,4-bis-(trichlorosilylmethyl)benzene[30] in 400 mL of hexane was added 64 mL (0.460 mol) of freshly distilled Et$_3$N. Then 18.6 mL (0.460 mol) of dried methanol was added dropwise to the above suspension cooled at 0 °C. After the addition was complete, the mixture was stirred at room temperature for 15 h and then filtered. The solvent was evaporated in vacuo and distillation of the residue (115–120 °C/0.1 mbar) afforded 15.58 g (88% yield) of 1,4-bis(trimethoxysilylmethyl)benzene. ^{1}H NMR (CDCl$_3$, δ) 2.2 (4H, s), 3.52 (18H, s), 7.08 (4H, s); ^{13}C NMR (CDCl$_3$, δ) 18.8, 51.17, 129.2, 133.4; ^{29}Si NMR (CDCl$_3$, δ) −47.58. Anal. Calcd for C$_{14}$H$_{26}$O$_6$Si$_2$: C, 48.52; H, 7.56; O, 27.7; Si, 16.21. Found: C, 48.70; H, 7.36; O, 27.84; Si, 16.10.

Compound **3** was prepared according to the procedure described for **2** from 5.83 g (22.5 × 10^{-3} mol) of (CH$_3$CN)$_3$Cr-(CO)$_3$ and 6.99 g (20.2 × 10^{-3} mol) of 1,4-bis(trimethoxysilylmethyl)benzene. After usual workup, 3.85 g (40% yield) of **3** were obtained by crystallization in hexane at room temperature; mp = 95–97 °C; IR ν(CO) 1887, 1962 cm^{-1}; ^{1}H NMR (CDCl$_3$, δ) 1.85 (s, 4H, CH$_2$), 3.53 (s, 18H, OCH$_3$), 5.24 (s, 4H, C$_6$H$_4$); ^{13}C NMR (CDCl$_3$, δ) 18.6 (CH$_2$), 51.3 (OCH$_3$), 94.4 (C$_{ar}$–Si), 107.9 (C$_{ar}$–H), 234.5 (CO); ^{29}Si NMR (CDCl$_3$, δ) −50.4. Anal. Calcd for C$_{17}$H$_{26}$CrO$_9$Si$_2$: C, 42.32; H, 5.39; Cr, 10.79; Si, 11.62. Found: C, 42.25; H, 5.47; Cr, 12.60; Si, 12.40.

{η^6-[1,4-Bis(trimethoxysilylethyl)benzene]}tricarbonylchromium (4). This compound was prepared according to a literature procedure.[20] *{η^6-[1,3,5-Tris(trimethoxysilyl)benzene]}-tricarbonylchromium (5).* As described previously, **5** was obtained using 6.47 g (25 × 10^{-3} mol) of (CH$_3$CN)$_3$Cr(CO)$_3$ and 10.95 g (25 × 10^{-3} mol) of 1,3,5-(trimethoxysilyl)benzene.[12a] After usual workup, 4.3 g (30% yield) of **5** was obtained upon crystallization in hexane at −25 °C; mp 72–77 °C (decomp); IR ν(CO) 1912, 1978 cm^{-1}; ^{1}H NMR (CDCl$_3$, δ) 3.67 (s, 27H, OCH$_3$), 5.79 (s, 3H C$_6$H$_3$); ^{13}C NMR (CDCl$_3$, δ), 51.7 (OCH$_3$), 86.8 (C$_{ar}$–Si), 105.5 (C$_{ar}$–H), 232 (CO); ^{29}Si NMR (CDCl$_3$, δ) −57.7. Anal. Calcd for C$_{18}$H$_{30}$CrO$_{12}$Si$_3$: C, 37.63; H 5.23; Cr, 9.06; Si, 14.63. Found: C, 37.39; H, 5.2, Cr, 7.1; Si, 14.4.

Hydrolysis–Polycondensation of Precursors (1–5). The preparation of the gels were carried out according to the following general procedure. All the hydrolysis–polycondensation reactions were performed in Schlenk tubes, using vacuum line techniques under an inert atmosphere of nitrogen or argon. The solvent was methanol, the concentration of the precursor was 0.5 M, and of the catalyst (NH$_4$F) was 10^{-2} mol equiv.

Hydrolysis and Polycondensation of [η^6-(Trimethoxysilyl)-benzene]tricarbonylchromium (1). To 1.97 g (5.9 × 10^{-3} mol) of **1** in methanol were added 3 mol equiv of water and the catalyst. The homogeneous yellow solution was allowed to stand at 20 °C. A yellow precipitate formed within 2 min. After standing at 20 °C for 8 days, the solid was collected, washed with acetone and ether, and then dried in vacuo at 100 °C, yielding 1.56 g of a yellow powder **X1** (quantitative yield based on C$_9$H$_5$CrO$_{4.5}$Si). FT IR (KBr) 3415 (weak), 1968, 1880 cm^{-1}; ^{13}C CP MAS NMR 94, 233 ppm; ^{29}Si CP MAS NMR −77, −79 ppm. Anal. Calcd for C$_9$H$_5$CrO$_{4.5}$Si: C, 40.75; H, 1.89; Cr, 19.62; Si, 10.57. Found: C, 40.55; H, 1.99; Cr, 19.05; Si, 10.85. The carbon-to-silicon ratio was 8.72 (calculated C/Si = 9) and chromium-to-silicon ratio was 0.95 (calculated Cr/Si = 1). The N$_2$ BET surface area was less than 10 m^2 g^{-1}.

Hydrolysis and Polycondensation of {η^6-[1,4-Bis(trimethoxysilyl)benzene]}tricarbonylchromium (2). Following the above

(26) Choi, K. M.; Hemminger, J. C.; Shea, K. J. *J. Phys. Chem.* **1995**, *99*, 4720.

(27) Schriver, D. F. *The Manipulation of Air-Sensitive Compounds*; MacGraw-Hill; New York, 1969.

(28) Harrod, J. F.; Shaver, A.; Tucka, A. *Organometallics* **1985**, *4*, 2166.

(29) Wright, M. E. *Organometallics* **1989**, *8*, 407.

(30) Motevalli, M.; Li Ou, D.; Sullivan, A. C. *J. Organomet. Chem.* **1993**, *445*, 35.

procedure 3.7×10^{-5} mol (1%) of NH_4F and 11.2×10^{-3} mol (3 equiv) of water were added to a solution of 1.7 g (3.7×10^{-3} mol) of **2** in 7.4 mL of MeOH. Gelation occurred within 1 min, and the gel was allowed to stand for 8 days. The above workup gave 1.18 g of yellow solid **X2** (quantitative yield based on $C_9H_4CrO_6Si_2$). FT IR (KBr) 3420 (broad), 1971, 1896 cm^{-1}; ^{13}C MAS NMR 51.8, 94, 231 ppm; ^{29}Si CP MAS NMR broad signal centered at -70 ppm. Anal. Calcd for $C_9H_4CrO_6Si_2$: C, 34.18; H, 1.27; Cr, 16.46; Si, 17.72. Found: C, 31.74; H, 2.45; Cr, 14.45; Si, 16.10. The carbon-to-silicon ratio was 4.6 (calculated C/Si = 4.5), and the chromium-to-silicon ratio was 0.48 (calculated Cr/Si = 0.5). The N_2 BET surface area was 588 m^2 g^{-1}.

Hydrolysis and Polycondensation of {η^6-[1,4-Bis(trimethoxysilylmethyl)benzene]}tricarbonylchromium (3). As above, to 1.58 g (3.3×10^{-3} mol) of **3** in 6.6 mL of methanol heated at ~30 °C (because of the low solubility of **3** in methanol) were added 3.3×10^{-5} mol (1%) of NH_4F and 9.9×10^{-3} mol (3 equiv) of water. A transparent yellow gel formed instantaneously. The above workup gave 1.13 g of a yellow powder **X3** (quantitative yield based on $C_{11}H_8CrO_6Si_2$). FT IR (KBr) 3415 (strong), 1960, 1874 cm^{-1}; ^{13}C CP MAS NMR 21, 51.4, 93, 106, 234 ppm; ^{29}Si CP MAS NMR -56, -63, -71 ppm. Anal. Calcd for $C_{11}H_8CrO_6Si_2$: C, 38.37; H, 2.32; Cr, 15.12; Si, 16.28. Found: C, 38.73; H, 3.66; Cr, 9.75; Si, 14.70. The carbon-to-silicon ratio was 6.15 (calculated C/Si = 5.5), and the chromium-to-silicon ratio was 0.35 (calculated Cr/Si = 0.5). The N_2 BET surface area was 18 m^2 g^{-1}.

Hydrolysis and Polycondensation of {η^6-[1,4-Bis(trimethoxysilylethyl)benzene]}tricarbonylchromium (4). As above, 3.6×10^{-5} mol (1%) of NH_4F and 10.8×10^{-3} mol (3 equiv) of water were added to a solution of 1.84 g (3.6×10^{-3} mol) of **4** in 7.2 mL of methanol. Gelation occurred within 5 min. Usual workup gave 1.34 g of a yellow solid **X4** (quantitative yield based on $C_{13}H_{12}CrO_6Si_2$). FT IR (KBr) 3415 (broad), 1960, 1857 cm^{-1}; ^{13}C CP MAS NMR 15, 29, 51, 93, 115, 234 ppm; ^{29}Si CP MAS NMR -50, -58, -67 ppm. Anal. Calcd for $C_{13}H_{12}CrO_6Si_2$: C, 41.93; H, 3.23, Cr, 13.9; Si, 15.05. Found: C, 41.91; H, 3.83; Cr, 14.10; Si, 14.20. The carbon-to-silicon ratio was 6.8 (calculated C/Si = 6.5), and the chromium-to-silicon ratio was 0.5 (calculated Cr/Si = 0.5). The N_2 BET surface area was less than 10 m^2 g^{-1}.

Hydrolysis and Polycondensation of {η^6-[1,3,5-Tris(trimethoxysilyl)benzene]}tricarbonylchromium (5). As above 3.7×10^{-5} mol (1%) of NH_4F and 16.9×10^{-3} mol (4.5 equiv) of water were added to a solution of 2.16 g (3.7×10^{-3} mol) of **5** in 7.5 mL of methanol. A gel formed after 31 days. Usual workup gave 1.35 g of a yellow powder **X5** (quantitative yield based on $C_9H_3CrO_{7.5}Si_3$). FT IR (KBr) 3450 (broad), 2952, 2850, 1978,

1910 cm^{-1}; ^{13}C CP MAS NMR 51, 88, 103, 230 ppm; ^{29}Si CP MAS NMR -63, -70 ppm. Anal. Calcd for $C_9H_3CrO_{7.5}Si_3$: C, 29.43; H, 0.8; Cr, 14.17; Si, 22.89. Found: C, 30.89; H, 3.27; Cr, 10.10; Si, 19.05. The carbon-to-silicon ratio was 3.78 (calculated C/Si = 3), and the chromium-to-silicon ratio was 0.28 (calculated Cr/Si = 0.33). The N_2 BET surface area was less than 10 m^2 g^{-1}.

Thermal Treatment of Xerogels X1−X5. *Pyrolysis of Xerogel X1*. The solid **X1** (0.247 g, 0.93×10^{-3} mol) was calcined under an argon flow at 400 °C for 1.5 h. A weight loss of 32.5% was observed, and 0.167 g of dark powder **P1** was obtained. ^{13}C CP MAS NMR 135 ppm; ^{29}Si CP MAS NMR impossible to detect the signal because of the background noise. In an additional experiment, **X1** was calcined at 1500 °C under argon flow. X-ray powder diffraction of the solid obtained after carbothermal reduction: *d* spacing 1.32, 1.54 and 2.52 Å, SiC: 1.87, 2.24, and 2.31 Å, Cr_3C_2.

Pyrolysis of Xerogel X2. As above, the solid **X2** (0.558 g, 1.77×10^{-3} mol) was calcined, yield 0.420 g of a black solid **P2** (weight loss of 24.7%). ^{13}C CP MAS NMR 133 ppm; ^{29}Si CP MAS NMR: broad signal centered at -70 ppm. As above, **X2** was heated at 1500 °C under argon. X-ray powder diffraction of the solid obtained after carbothermal reduction of **X2**: *d* spacing 1.32, 1.54, and 2.52 Å, SiC; 1.96, 2.02 and 2.06 Å, $Cr_{5-x}Si_{3-z}C_{x+z}$.

Pyrolysis of Xerogel X3. As above **X3** was calcined at 1500 °C under argon flow. X-ray powder diffraction of the solid obtained after carbothermal reduction: *d* spacing 1.32, 1.54, and 2.52 Å, SiC; 1.87, 2.24, and 2.31 Å, Cr_3C_2.

Pyrolysis of Xerogel X4. As above gel **X4** (0.280 g, 0.75×10^{-3} mol) gave a weight loss of 23.2%, yield 0.215 g of a black powder **P4**. ^{13}C CP MAS NMR 147 ppm; ^{29}Si CP MAS NMR broad signal between -50 and -70 ppm. As above **X4** was heated at 1500 °C. X-ray powder diffraction of the solid obtained after carbothermal reduction: *d* spacing 1.32, 1.54, and 2.52 Å, SiC; 1.87, 2.24, and 2.31 Å, Cr_3C_2.

Pyrolysis of Xerogel X5. As above, **X5** was calcined at 1500 °C under argon. X-ray powder diffraction of the solid obtained after carbothermal reduction: *d* spacing 1.32, 1.54, and 2.52 Å, SiC; 1.96, 2.02, and 2.06 Å, $Cr_{5-x}Si_{3-z}C_{x+z}$; 1.82, 2.09, and 2.12 Å, $CrSi_2$.

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