Letter

N, N-Dialkylcarbamato complexes as precursors for the chemical implantation of metal cations on a silica support. Part I. Tin

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Abstract

Chemical implantation of tin on a commercial silica has been carried out by using the hydrocarbon soluble $Sn(O_2CN^iPr_2)_4$ as precursor, the N,N-dialkylcarbamato group is chemically displaced by the silanol groups of the support under mild conditions.

1. Introduction

One of the current interests in inorganic chemistry is the rational synthesis of oxide matrices appropriately doped or functionalized, to be used, for example, as highly selective heterogeneous catalysts.

Chemical implantation of catalytically active metal centres on oxide surfaces can be carried out by several methods: (a) reaction of organometallic precursors with the Lewis acidic sites of the support, e.g. zirconium(IV) alkyls with dehydroxylated alumina [1] resulting in a heterogeneous polymerization catalyst; (b) reaction of organometallic precursors such as rhodium(III) allyls [2], zirconium(IV) alkyls [3], or alkyls of Group 14, namely germanium(IV) [4] and tin(IV) [5], with the Brønsted acidic sites of silica or other oxide supports; (c) nucleophilic attack of surface hydroxyl groups (especially on magnesia) on metal carbonyl clusters [6]; (d) oxidative addition of surface hydroxyls to metal carbonyls [7]; (e) proton transfer from a metal hydride to a basic oxide [8], whose molecular model is the proton transfer from $CoH(CO)_4$ to a tertiary amine [9]; (f) reaction of an organometallic hydroxo derivative with the silanol groups [10]; (g) thermolysis of

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organometallic or coordination compounds [11], such as metal alkoxides [11](c). Work on model compounds has been carried out to clarify the nature of the metal sites on oxide surfaces [12].

2. Results and discussion

N,N-Dialkylcarbamato complexes of main Group and transition elements [13] of formula $[M(O_2CNR_2)_n]_m$ are reactive towards even weak acids such as MeCOOH [14](a) or acetylacetone [14](b), yielding carbon dioxide evolution and formation of the corresponding metal complex. Moreover, N,N-dialkylcarbamates undergo controlled hydrolysis, forming μ-oxo-carbamato complexes [15]. We have found that N,N-dialkylcarbamates react with the silanol groups of silica, whose Brønsted acidity has been determined by several methods [16]. This paper reports our work on the reaction of commercial amorphous silica with N,N-dialkylcarbamato complexes of tin(IV): the choice of tin is justified by the possibility in the case of tin ($Z = 50$) to carry out large-angle X-ray scattering (LAXS) measurements of expectedly satisfactory accuracy on the product of the surface reaction [17].

The tin(IV) N,N-dialkylcarbamato complexes were prepared in good yields (90–95%) by the well-established procedure [12] consisting of treating the anhydrous metal chloride with the R_2NH/CO_2 system in toluene as medium, according to Eq. 1.

$$SnCl_4 + 8R_2NH + 4CO_2 \rightarrow Sn(O_2CNR_2)_4$$
$$+ 4[R_2NH_2]Cl$$
$$(1)$$
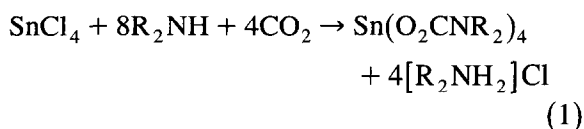
$(R = Et, {}^iPr)$

The colourless compounds were characterized analytically, spectroscopically and by X-ray single crystal diffractometry in the case of $Sn(O_2CN^iPr_2)_4$. This is a mononuclear compound with octacoordinate tin(IV) in a slightly distorted dodecahedral geometry.

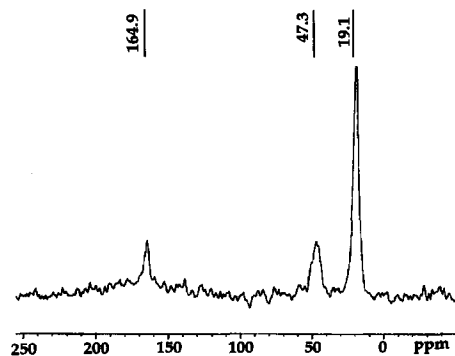Treatment of a toluene solution of the iso-

Fig. 1. CP/MAS ^{13}C NMR spectrum of the product of the reaction of $Sn(O_2CN^iPr_2)_4$ with the silica surface. See text for experimental conditions.

propyl tin(IV) derivative with commercial silica led to carbon dioxide evolution in a CO_2/Sn molar ratio of about 1.5, thus suggesting that residual carbamato groups are present around the surface-bound tin; the tin-containing silica, after filtration and drying in vacuo at room temperature, was characterized analytically, spectroscopically (IR) and by XPS, LAXS and CP/MAS ^{13}C NMR measurements. Treatment of the tin-containing silica, suspended in the mother liquid, with acetic acid led to the evolution of additional 2.4 mol of CO_2 per mol of tin. The presence of tin-bonded carbamato groups has been confirmed by CP/MAS ^{13}C NMR spectroscopy, showing resonances at 19.1, 47.3 and 164.9 ppm, due to methyl, methine and carbamato carbons, respectively (Fig. 1). The ^{13}C NMR data for the parent molecular complex in $CDCl_3$ are similar, see Experimental. As $[NH_2^iPr_2]$ Cl shows ^{13}C NMR peaks in CD_2Cl_2 solution at 19.4 and 47.7 ppm, the CP/MAS spectra are not able to distinguish the contribution of silica-bonded iso-propyl groups in $=SiO^-$ $[NH_2^iPr_2]^+$ from carbamato iso-propyl groups. XPS spectra gave a binding energy for Sn of 487.0 eV, to be compared with a value of 486.4 eV for SnO_2, thus confirming the oxidation state IV, and the oxygen ligand environment for tin. Furthermore, LAXS measurements gave the results summarized in Fig. 2, showing the difference radial distribution function for a sample of tin containing silica: the
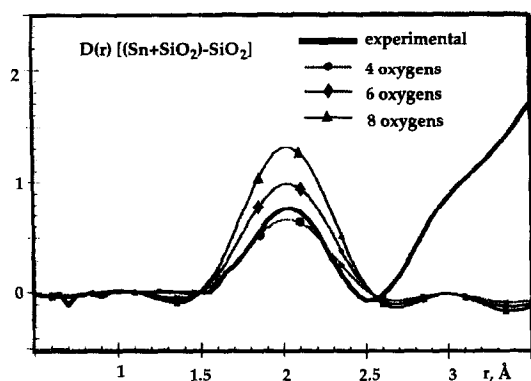
Fig. 2. LAXS spectra of tin(IV) on amorphous silica (3.2% of tin by weight). Difference radial distribution function (el^2 Å^{-1} 10^4) vs. bond distance (Å): expansion of the peak at about 2 Å with the fitting for coordination numbers from 4 to 8.

best fit of the data is for a model with four-co-ordinate tetrahedral tin.

The tin implantation on silica can therefore be represented as shown in the idealized model of Fig. 3 for a tin atom coordinated to a surface silanolato group, the amine occupying a second silanol site. This is believed to represent the bonding situation in the primary reaction of a single silanol site with the tin complex, the amine produced in the reaction being trapped by another silanol group. As the gas-volumetric data show that 2.5 [O$_2$CN^{i}Pr$_2$] groups are retained on tin, the availability of a second silanol group to carry out further electrophilic attack has about 50% probability. Of course, further

exposure of the surface to moisture, as it unavoidably occurs during XPS and LAXS measurements, may further alter the tin coordination environment converting it to Sn–OH or Sn–O–Sn groups, due to hydrolysis of at least part of the residual carbamato groups.

In view of these results, a new alternative method has become available for the chemical implantation of main Group- and transition-metal cations on oxide supports under mild conditions, the thermodynamic driving force for the reaction being largely provided by the evolution of carbon dioxide. Work is in progress to verify the generality of this new method to other metal cations. Application of these systems to heterogeneous catalysis is anticipated.

3. Experimental section

All the operations were carried out by the conventional Schlenk tube technique under a dinitrogen or carbon dioxide atmosphere. Solvents and reagents were carefully dried before use by conventional methods. Silica (Crosfield EP17, surface area 320 m^2 g^{-1}, pore volume 1.6 cm^3 g^{-1}) was pretreated at 160°C in vacuo for 16 h before use and sealed in vials under an atmosphere of carbon dioxide. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were measured with a Bruker WP
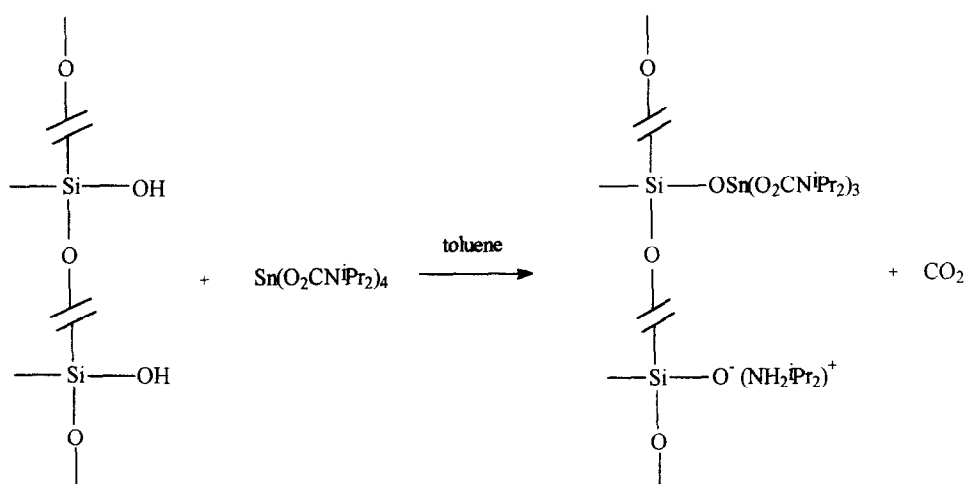

Fig. 3. A simplified model of the primary reaction of Sn(O$_2$CN^{i}Pr$_2$)$_4$, Sn(cbm)$_4$, with the surface silanol groups.

200 instrument on solution of the tin precursor. The XPS measurements have been carried out with a Perkin Elmer PHI 5500 ESCA system; the instrument was equipped with a monochromatic X-ray source (Al-Kα radiation, $h\nu = 1486.7$ eV) on powdered samples pressed between polished indium foils; the diameter of the sample area explored was about 400 μm and the residual pressure inside the analysis chamber was 10^{-8} Pa. The LAXS data were collected with a non-commercial instrument [18], consisting of a white X-ray beam source and a germanium solid-state detector connected to a multichannel analyzer. The cross-polarization/magic angle spinning (CP/MAS) ^{13}C NMR spectra were measured at room temperature on a MSL 200 Bruker instrument, operating at 50.321 MHz. The following conditions were adopted. Irradiating field, 50 kHz; spinning rate, 5 kHz; contact time, 5 ms; sequence recycle time, 4 s; number of transients, 12800; spectral width, 20 kHz; time domain points, 512. Chemical shifts are referred to external TMS.

The iso-propyl complex $Sn(O_2CN^iPr_2)_4$ was prepared by the following procedure. Anhydrous tin(IV) chloride (4.0 ml, 8.9 g, 34.2 mmol) and di-iso-propylamine (50.0 ml, 35.8 g, 354 mmol) in toluene (400 ml) were treated with carbon dioxide at atmospheric pressure at room temperature and the resulting mixture was stirred for about 12 h. After elimination of di-iso-propyl ammonium chloride by filtration, the solution was evaporated to dryness and the resulting colourless solid was recrystallized from heptane (78% yield). ^{1}H NMR (CDCl$_3$; δ, ppm, TMS): 1.2 (doublet), 3.9 (septet); ^{13}C NMR (CDCl$_3$; δ, ppm, TMS): 20.6, 46.9, 164.4, attributed to the methyl, methine and carbamato carbons, respectively, on the basis of the earlier findings on the isostructural compounds of Group 4 metals [13](d), and on the silicon derivative [13](e). ^{119}Sn NMR (CDCl$_3$; δ, ppm, TMSn): -920.8. The X-ray crystal structure determination of $Sn(O_2CN^iPr_2)_4$ was carried out at room temperature with a Siemens AED single-crystal

diffractometer with Mo-Kα radiation ($\lambda = 0.71069$ Å). Crystal data: $C_{28}H_{56}N_4O_8Sn$, MW $= 695.5$, monoclinic, space group $P2_1/c$; $a = 12.671(2)$, $b = 22.080(5)$, $c = 14.681(3)$ Å, $\beta = 113.29(1)°$, $Z = 4$. $D_c = 1.224$ g cm^{-3}, $F(000) = 1464$, μ(Mo-Kα) $= 7.21$ cm^{-1}. The unit cell parameters were determined on the basis of a least-squares analysis of the angular settings of 28 intense reflections. Intensities in the range ϑ–2ϑ scan mode for one quadrant ($+h$, $+k$, $\pm l$) of data. The 3315 unique reflections ($I \geq 2\sigma(I)$) were retained out of a total of 7205 measured reflections. The structure was solved by a combination of Patterson and Fourier techniques [19]. Refinement was by full-matrix least-squares techniques based on F, assuming anisotropic thermal parameters for all non-hydrogen atoms and isotropic ones for hydrogens ($R = 0.0361$, $R_w = 0.0457$ for 504 variables). The eight oxygen donor atoms form an elongated tetrahedron (Sn–O, 2.193(4)–2.218(4) Å) and a flattened (Sn–O, 2.123(4)–2.139(5) Å) one. The Sn–O distances are to be compared with the 2.13–2.29 Å range found in the acetate $Sn(O_2CMe)_4$ [20] and with the Sn–O distance (av.) of 2.053 Å in SnO_2 [21].

The corresponding diethyl derivative was prepared similarly (96% yield). Tin implantation on silica was carried out by the following procedure. Commercial silica (4.57 g, corresponding to 2.78 mmol of silanol groups per gram) was added to a toluene (100 ml) solution of the di-iso-propyl tin(IV) derivative (1.07 g, 1.54 mmol) in a 500 ml flask and the mixture was stirred at room temperature for 2 h, occasionally reducing the partial pressure of carbon dioxide inside the reactor. After being recovered by filtration, the tin-containing silica was dried in vacuo for 24 h (4.88 g) and gave the following analytical results (%): Sn, 3.2, CO$_2$, 1.8, corresponding to a CO$_2$/Sn molar ratio of 1.5, and to an implantation yield of 84%, based on the tin content. In a gas-volumetric experiment, a toluene suspension of the silica, presaturated with carbon dioxide, was treated with the tin(IV) complex at $20 \pm 0.1°$C: the carbon dioxide evo-

lution corresponded to a CO_2/Sn molar ratio of 1.5.

Acknowledgements

References

[1] T.J. Marks, Acc. Chem. Res., 25 (1992) 57.

[2] (a) J. Schwartz, Acc. Chem. Res., 18 (1985) 302; (b) P. Dufour, C.C. Santini, C. Houtman and J.M. Basset, J. Mol. Catalysis, 66 (1991) L23; (c) P. Dufour, C. Houtman, C.C. Santini, C. Nédez, J.M. Basset, L.Y. Hsu and S.G. Shore, J. Am. Chem. Soc., 114 (1992) 4248; (d) P. Dufour, S.L. Scott, C.C. Santini, F. Lefebvre and J.M. Basset, Inorg. Chem., 33 (1994) 2509.

[3] F. Quignard, C. Lecuyer, C. Bougault, F. Lefebvre, A. Choplin, D. Olivier and J.M. Basset, Inorg. Chem., 31 (1992) 928.

[4] C. Nédez, A. Choplin, J.M. Basset and E. Benazzi, Inorg. Chem., 33 (1994) 1094.

[5] (a) C. Nédez, A. Choplin, J.M. Basset and E. Benazzi, Inorg. Chem., 33 (1994) 1575; (b) C. Nédez, F. Lefebvre, A. Choplin, J.M. Basset and E. Benazzi, J. Am. Chem. Soc., 116 (1994) 3039.

[6] F. Hughes, J.M. Basset, Y. Ben Taarit, A. Choplin, M. Primet, D. Rojas and A.K. Smith, J. Am. Chem. Soc., 104 (1982) 7020.

[7] (a) B. Besson, B. Moraweck, A.K. Smith, J.M. Basset, R. Psaro, A. Fusi and R. Ugo, J. Chem. Soc., Chem. Commun., (1980) 569; (b) R. Psaro, R. Ugo, G.M. Zanderighi, B. Besson, A.K. Smith and J.M. Basset, J. Organomet. Chem., 213 (1981) 215; (c) M. Deeba and B.C. Gates, J. Catal., 67 (1981) 303; (d) H. Knözinger, E.W. Thornton and M. Wolf, J. Chem. Soc., Faraday Trans. 1, (1979) 1888; (e) S.L. Cook, J. Evans, G.S. McNulty and G. Neville Greaves, J. Chem. Soc., Dalton Trans., (1986) 7.

[8] (a) H.H. Lamb and B.C. Gates, J. Am. Chem. Soc., 108 (1986) 81; (b) A. Choplin, L. Huang, J.M. Basset, R. Mathieu, U. Siriwardane and S.G. Shore, Organometallics, 5 (1986) 1547.

[9] (a) F. Calderazzo, G. Fachinetti, F. Marchetti and P.F. Zanazzi, J. Chem. Soc., Chem. Commun., (1981) 181; (b) L. Brammer, M.C. McCann, R.M. Bullock, R. K McMullan and P. Sherwood, Organometallics, 11 (1992) 2339.

[10] T.Y. Meyer, K.A. Woerpel, B.M. Novak and R.G. Bergman, J. Am. Chem. Soc., 116 (1994) 10290.

[11] (a) Q. Zhuang, A. Fukuoka, T. Fujimoto, K. Tanaka and M. Ichikawa, J. Chem. Soc., Chem. Commun., (1991) 745; (b) W. Lin, T.H. Warren, R.G. Nuzzo and G.S. Girolami, J. Am.

Chem. Soc., 115 (1993) 11644; (c) D.C. Bradley, Chem. Rev., 89 (1989) 1317.

[12] (a) B. Breitscheidel, J. Zieder and U. Schubert, Chem. Mater., 3 (1991) 559; (b) F.T. Edelmann, Angew. Chem., Int. Ed. Engl., 31 (1992) 586; (c) N. Winkhofer, H.W. Roesky, M. Noltemeyer and W.T. Robinson, Angew. Chem., Int. Ed. Engl., 31 (1992) 599; (d) A. Vizi-Orosz, R. Ugo, R. Psaro, A. Sironi, M. Moret, C. Zucchi, F. Ghelfi and G. Pályi, Inorg. Chem., 33 (1994) 4600.

[13] (a) D. Belli Dell'Amico and F. Calderazzo, in, S. Daolio, M. Fabrizio, P. Guerriero, E. Tondello and P.A. Vigato (Eds.), N,N-Dialkylcarbamates of Transition and Non-transition Elements, Syntheses and Methodologies in Inorganic Chemistry, Proceedings of the Meeting, Bressanone, Italy, 2–7 December 1991; (b) F. Calderazzo, S. Ianelli, G. Pampaloni, G. Pelizzi and M. Sperrle, J. Chem. Soc., Dalton Trans., (1991) 693; (c) D. Belli Dell'Amico, F. Calderazzo, M. Dell'Innocenti, B. Güldenpfennig, S. Ianelli, G. Pelizzi and P. Robino, Gazz. Chim. Ital., 123 (1993) 283; (d) D. Belli Dell'Amico, F. Calderazzo, F. Gingl, L. Labella and J. Strähle, Gazz. Chim. Ital., 124 (1994) 375, and references therein; (e) D. Belli Dell'Amico, F. Calderazzo and G. Pampaloni, Chem. Rev., in preparation.

[14] (a) D. Belli Dell'Amico, F. Calderazzo, F. Marchetti and G. Perego, J. Chem. Soc., Dalton Trans., (1983) 483; (b) A. Belforte, D. Belli Dell'Amico, F. Calderazzo, M. Devillers and U. Englert, Inorg. Chem., 32 (1993) 2282.

[15] (a) D. Belli Dell'Amico, F. Calderazzo, L. Labella, C. Maichle-Mössmer and J. Strähle, J. Chem. Soc., Chem. Commun., (1994) 1555, and references therein.

[16] Kirk–Othmer Encyclopedia of Chemical Technology, Vol. 20, J. Wiley, New York, 1982, p. 766; H.H. Kung, Stud. Surf. Sci. Catal., 45 (1989) p. 1 ff; Y. Morikawa, Adv. Catal., 39 (1993) 303.

[17] A preliminary account of this work has been communicated: (a) D. Belli Dell'Amico, F. Calderazzo, F. Marchetti and G. Pampaloni, in, I. Horváth and F. Joó, (Eds.), Stoichiometric and Exhaustive Hydrolysis of N,N-Dialkylcarbamates, NATO Workshop on Aqueous Organometallic Chemistry and Catalysis, Debrecen, Hungary, 28 Aug.–2 Sept. 1994; (b) D. Belli Dell'Amico, F. Calderazzo, R. Caminiti, F. Garbassi, G. Pelizzi, P. Robino and A. Tomei, Meeting on Perspectives in Inorganic Chemistry, Bressanone, Italy, 2–7 October 1994, abstracts of the papers.

[18] (a) R. Caminiti, C. Sadun, V. Rossi, F. Cilloco and R. Felici, 25th National Meeting of Physical Chemistry, Chia, Cagliari, Italy, 17–21 June 1991; (b) Ital. Pat. Appl. RM/93 A 000410, 23 June 1993.

[19] (a) International Tables for X-Ray Crystallography, Vol IV, Kynoch Press, Birmingham, 1974; (b) G.M. Sheldrick, SHELX76, Program for Crystal Structure Determination, University of Cambridge, 1976; (c) G.M. Sheldrick, SHELX86, Program for Structure Solution, University of Göttingen, 1986; (d) D. Delledonne, G. Pelizzi and C. Pelizzi, Acta Crystallogr., C43 (1987) 1052.

[20] N.W. Alcock and V.L. Tracy, Acta Crystallogr., B35 (1979) 80.

[21] D.B. Rogers, R.D. Shannon, A.W. Sleight and J.L. Gillson, Inorg. Chem., 8 (1969) 841; A.F. Wells, Structural Inorganic Chemistry, Clarendon Press, Oxford, 5th Ed., 1986, p. 540.