DALTON
FULL PAPER

Cyclopentadienyl–diethylcarbamato derivatives of zirconium(IV) and hafnium(IV), $[M(C_5H_5)(O_2CNEt_2)_3]$: synthesis and use as precursors for chemical implantation on a silica surface

Luigi Abis,[a] **Fausto Calderazzo,**[b] **Cäcilia Maichle-Mössmer,**[c] **Guido Pampaloni,***[,b] **Joachim Strähle**[c] **and Giovanna Tripepi**[b]

[a] *Istituto Guido Donegani-Enichem, Via G. Fauser 4, I-28100 Novara, Italy*
[b] *Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, I-56126 Pisa, Italy*
[c] *Institut für Anorganishe Chemie der Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany*

Reaction of $Mg(C_5H_5)_2$ with the homoleptic diethylcarbamato derivatives of zirconium(IV) or hafnium(IV), $M(O_2CNEt_2)_4$, gave the mixed cyclopentadienyl–diethylcarbamato complexes $[M(C_5H_5)(O_2CNEt_2)_3]$. These derivatives have also been obtained by reaction of $Fe(O_2CNEt_2)_2$ with $M(C_5H_5)_4$ in the appropriate stoichiometric ratio. The compound $[Zr(C_5H_5)(O_2CNEt_2)_3]$ crystallizes in the space group $P\bar{1}$, $Z = 2$, $a = 9.734(4)$, $b = 10.234(2)$, $c = 12.948(6)$ Å; $\alpha = 83.41(4)$, $\beta = 86.13(4)$ and $\gamma = 67.43(3)°$. On reaction of $[Zr(C_5H_5)(O_2CNEt_2)_3]$ with dehydrated silica, 1 mol of CO_2 per zirconium was evolved. The organometallic fragment $Zr(C_5H_5)(O_2CNEt_2)_2$ grafted on silica has been characterized by analytical methods and by CP MAS ^{13}C NMR spectroscopy.

Recently, some of us reported that dialkylcarbamato derivatives of tin(IV), $Sn(O_2CNR_2)_4$, are appropriate precursors for the implantation of this cation on a silica surface.[1] This general method, see equation (1), which has also been applied for the

$$M(O_2CNR_2)_n + m\,{\equiv}Si(OH) \longrightarrow (\equiv SiO)_mM(O_2CNR_2)_{n-m} + m\,CO_2 + m\,NHR_2 \quad (1)$$

implantation of platinum(II) on a commercial silica under mild conditions,[2] represents a new route for supporting a metal cation on a silica surface.[3]

In the framework of this research project, we became interested in diamagnetic systems containing both organic and dialkylcarbamato ligands on general composition $M(C_5H_5)_x(O_2CNR_2)_y$. These systems could be useful starting materials because, in principle, they can undergo attack by the silanol groups at two sites, namely, the C_5H_5 ligand [equation (2)] and the dialkylcarbamato group [equation (3)]. The reaction of

$$M(C_5H_5)_x(O_2CNR_2)_y + {\equiv}Si(OH) \longrightarrow (\equiv SiO)M(C_5H_5)_{x-1}(O_2CNR_2)_y + C_5H_6 \quad (2)$$

$$M(C_5H_5)_x(O_2CNR_2)_y + {\equiv}Si(OH) \longrightarrow (\equiv SiO)M(C_5H_5)_x(O_2CNR_2)_{y-1} + CO_2 + NHR_2 \quad (3)$$

both ligands was considered to be an unlikely possibility, see below.

Reactions (2) and (3) would thus represent new entries into surface organometallic chemistry,[4] if the dialkylcarbamato groups were the preferential site of attack by the silanols. In order to drive the reaction toward the maintainance of the C_5H_5 ligand on the silica-bonded zirconium, the most appropriate starting materials were anticipated to be derivatives of general formula $M(C_5H_5)(O_2CNEt_2)_3$, *i.e.* compounds with a high diethylcarbamato : C_5H_5 ratio.

The present paper reports the synthesis and full characterization of zirconium(IV) and hafnium(IV) derivatives of general formula $M(C_5H_5)(O_2CNEt_2)_3$, and the use of the zirconium derivative $[Zr(C_5H_5)(O_2CNEt_2)_3]$ for the implantation of a cyclopentadienyl–diethylcarbamato fragment on a dehydrated silica surface.[5]

Experimental

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified nitrogen or argon. Solvents were dried by conventional methods prior to use.

The IR spectra were measured with a Perkin-Elmer FT-1725X instrument on solutions or Nujol and/or poly(chlorotrifluoroethylene) (pctfe) mulls prepared under rigorous exclusion of moisture and air. Diffuse reflectance infrared Fourier transform (DRIFT) spectra were measured with the same instrument by mixing the sample with dry KBr and by transfer to the cell (Spectra Tech) under an inert atmosphere. Proton and ^{13}C NMR spectra were measured on solutions with a Varian Gemini 200 BB instrument. The cross polarization magic angle spinning (CP MAS) ^{13}C NMR spectra were measured at room temperature with a MSL 200 Bruker instrument operating at 50.321 MHz. The following conditions were used: irradiating field, 50 KHz; spinning rate, 5400 Hz; contact time, 5 ms; recycle time, 4 s; number of transients, 12 000; time domain points, 1024. The chemical shifts are referred to $SiMe_4$.

The zirconium and hafnium content of the complexes was determined as MO_2 after decomposition of the sample with diluted nitric acid and calcination in a platinum crucible at *ca.* 1000 °C. The zirconium content of the samples resulting from the anchoring of $[Zr(C_5H_5)(O_2CNEt_2)_3]$ on silica was determined by inductively coupled plasma atomic emission spectroscopy (ICP AES).

Commercial silica (Grace, SD 3217/50; surface area, 318 $m^2\,g^{-1}$; pore volume, 2.22 $cm^3\,g^{-1}$) was treated at 160 °C for 12 h *in vacuo* (*ca.* 10^{-2} mmHg, *ca.* 1.33 Pa) in order to eliminate most of the physi- and chemi-sorbed water and then stored in flame-sealed vials under an atmosphere of argon. The total silanol content (2.4 mmol g^{-1}) was assumed to correspond to the weight loss (water) by calcination at 850 °C.

The compounds $M(O_2CNEt_2)_4$ (M = Zr or Hf) were prepared according to the literature[6] and recrystallized from heptane.

δ_H(200 MHz, solvent C_6D_6; standard $SiMe_4$) M = Zr, 3.02 (16 H, q, 8 CH_2) and 0.83 (24 H, t, 8 CH_3); M = Hf, 3.01 (16 H, q, 8 CH_2) and 0.83 (24 H, t, 8 CH_3). The compounds $M(C_5H_5)_4$ (M = Zr or Hf)[7] and $Mg(C_5H_5)_2$[8] were prepared according to the literature.

Reaction of $M(O_2CNEt_2)_4$ (M = Zr or Hf) with $Mg(C_5H_5)_2$

Only the reaction for M = Zr is described in detail, that with $Hf(O_2CNEt_2)_4$ being carried out in a similar way. A solution of $Zr(O_2CNEt_2)_4$ (2.59 g, 4.7 mmol) in toluene (25 cm^3) was treated with solid $Mg(C_5H_5)_2$ (0.37 g, 2.4 mmol). After *ca.* 4 h of stirring at room temperature the colourless solid was filtered off and dried *in vacuo* at room temperature (0.98 g); this was shown spectroscopically to be a mixture of $Mg(O_2CNEt_2)_2$† and $[Zr(C_5H_5)(O_2CNEt_2)_3]$. $\tilde{\nu}_{max}/cm^{-1}$ (pctfe) 3087mw, 2960ms, 2932ms, 2872w, 1635s, 1582vs, 1541vs, 1505s, 1484vs, 1461s, 1428s, 1378ms, 1349m and 1309vs. δ_H(200 MHz, solvent CD_3CN; standard $SiMe_4$) 6.1 (s, C_5H_5), 3.2 (m, CH_2), 2.6 (m, CH_2) and 1.1 (m, CH_3).

The filtrate was evaporated to dryness under reduced pressure at room temperature and the residue treated with heptane (8 cm^3), yielding a suspension of a colourless solid in a pale yellow solution. After cooling at *ca.* 4 °C for 12 h the solid was filtered off and dried *in vacuo* at room temperature (0.67 g) (Found: C, 47.4; H, 7.2; N, 8.2; Zr, 18.2; CO_2, 25.8. $C_{20}H_{35}N_3O_6Zr$ requires C, 47.5; H, 7.0; N, 8.3; Zr, 18.1; CO_2, 26.1%). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol and pctfe) 3087mw, 2976s, 2934s, 2874s, 1541vs, 1538vs, 1500vs, 1485s, 1462s, 1437s, 1378s, 1318s, 1211ms, 1155s, 1099mw, 1085s, 1075ms, 1019mw, 973m, 938m, 895m, 837s, 822s, 797s, 643s, 612s and 442m. δ_H(200 MHz, solvent C_6D_6; standard $SiMe_4$) 6.55 (5 H, s, C_5H_5), 3.05 (12 H, m, 6 CH_2) and 0.90 (18 H, t, 6 CH_3). δ_C(50.3 MHz, solvent C_6D_6; standard $SiMe_4$) 169.37 (1 C, s, CO_2), 166.61 (2 C, s, CO_2), 114.73 (s, C_5H_5), 39.75 (s, CH_2) and 14.09 (s, CH_3). The filtrate was evaporated to dryness under reduced pressure at room temperature, giving additional $[Zr(C_5H_5)(O_2CNEt_2)_3]$ (0.56 g, total yield 52%).

$[Hf(C_5H_5)(O_2CNEt_2)_3]$: reaction time: 48 h; 48% yield; colourless crystalline solid (Found: C, 40.5; H, 5.7; Hf, 30.6; N, 7.2; CO_2, 22.7. $C_{20}H_{35}HfN_3O_6$ requires C, 40.6; H, 5.9; Hf, 30.3; N, 7.1; CO_2, 22.3%). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol and pctfe); 3088mw, 2977s, 2965s, 2935s, 2874s, 1553vs, 1505vs, 1489s, 1462s, 1440s, 1378s, 1319s, 1211ms, 1126s, 1099mw, 1085s, 1075ms, 1019mw, 973m, 938m, 895m, 840s, 823s, 797s, 645s, 612s and 488m. δ_H(200 MHz, solvent C_6D_6; standard $SiMe_4$) 6.47 (5 H, s, C_5H_5), 3.03 (12 H, m, 6 CH_2) and 0.89 (18 H, t, 6 CH_3). δ_C(50.3 MHz, solvent C_6D_6; standard $SiMe_4$) 169.10 (1 C, s, CO_2), 166.28 (2 C, s, CO_2), 114.40 (s, C_5H_5), 39.42 (s, CH_2) and 13.77 (s, CH_3).

Reaction of $Fe(O_2CNEt_2)_2$ with $M(C_5H_5)_4$ (M = Zr or Hf)

Only the reaction of $Hf(C_5H_5)_4$ is described in detail, that with $Zr(C_5H_5)_4$ being performed in a similar way. A solution of $Fe(O_2CNEt_2)_2$ (0.216 g, 0.75 mmol) in toluene (25 cm^3) was treated with solid $Hf(C_5H_5)_4$ (0.22 g, 0.49 mmol). After 16 h of stirring at room temperature, the orange solution was evaporated to dryness, the residue warmed at *ca.* 40 °C *in vacuo* and $Fe(C_5H_5)_2$ (^1H NMR spectroscopy) was sublimed off. The residue was washed with heptane (2 x 5 cm^3) and dried *in vacuo* at room temperature affording 0.143 g (49%) of $[Hf(C_5H_5)(O_2CNEt_2)_3]$ (^1H NMR and IR spectra). The zirconium derivative $[Zr(C_5H_5)(O_2CNEt_2)_3]$ was similarly obtained (41%).

Crystallography

Colourless crystals of $[Zr(C_5H_5)(O_2CNEt_2)_3]$ suitable for X-ray diffractometric study were obtained by slow cooling at *ca.* 0 °C of a dilute solution of the complex in toluene. Intensity data were collected at 213 K with Mo-Kα radiation (λ = 0.710 73 Å) on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator and the ω-scan mode.

Crystal data and data collection parameters. $C_{20}H_{35}N_3O_6Zr$, $M = 504.73$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.734(4)$, $b = 10.234(2)$, $c = 12.948(6)$ Å, $\alpha = 83.41(4)$, $\beta = 86.13(4)$, $\gamma = 67.43(3)°$, $U = 1182.9(7)$ Å^3, $Z = 2$, $D_c = 1.417$ Mg m^{-3}, $\mu = 0.503$ cm^{-1}, $F(000) = 528$. 6064 Reflections were measured in the range $3.0 < \theta < 27.0°$; 3977 unique reflections with $I > 2.0\ \sigma(I)$ were used for further computations. No significant variation in intensities of three standard reflections was observed during the data collection.

Structure solution and refinement. The structure was solved by direct methods using the SHELXS 86 program,[9] and refined with SHELXL 93.[10] Some of the hydrogen atoms were located in the Fourier-difference synthesis, the others were calculated geometrically. After completion of the isotropic structural model, an empirical absorption correction was applied with the DIFABS program[11] before averaging over symmetrically equivalent reflections. Anisotropic thermal parameters and the calculated positions of the hydrogen atoms which were not located in the Fourier synthesis were used in the refinement. With 291 parameters and by using a statistical weighting scheme $w = 1/[\sigma^2|F_o|]$, the refinement converged at values of $R = 0.046$ $\{R = \Sigma|\Delta F|/\Sigma|F_o|\}$ and $R' = 0.098$ $\{R' = [\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w = 1/[\sigma^2(F_o^2) + (0.3152P)^2 + 3.39P]\}$ with goodness of fit = 1.119.

CCDC reference number 186/844.

Reaction of $[Zr(C_5H_5)(O_2CNEt_2)_3]$ with dehydrated silica

A suspension of dehydrated silica (8.55 g, 20.52 mmol of silanol groups) in toluene (100 cm^3) was treated with solid $[Zr(C_5H_5)(O_2CNEt_2)_3]$ (1.72 g, 3.4 mmol) to give a OH : Zr molar ratio of 6.0 : 1. Evolution of gas was observed upon mixing the reagents. After 48 h of stirring at room temperature the suspension was filtered, washed with toluene (5 × 10 cm^3) and dried *in vacuo* affording 9.74 g of a colourless solid containing 88% of the zirconium introduced (Found: C, 5.7; H, 0.77; N, 0.84; Zr, 2.8%). $\tilde{\nu}/cm^{-1}$ (DRIFT) 3114w, 2984m, 2944mw, 1631m, 1529s, 1463s and 1332ms. δ_C(CP MAS) 167.9 (CO_2), 160.8 (CO_2), 113.8 (C_5H_5), 40.2 (CH_2) and 11.5 (CH_3).

A suspension of dehydrated silica (1.32 g, 3.17 mmol of silanol groups) in toluene (25 cm^3) was saturated with CO_2 at 22.9 °C and treated with solid $[Zr(C_5H_5)(O_2CNEt_2)_3]$ (0.233 g, 0.46 mmol), OH : Zr molar ratio = 6.9 : 1. Evolution of 0.44 mmol of CO_2 corresponding to a CO_2 : Zr molar ratio of 0.95 : 1 was obtained. The addition of CO_2-saturated $MeCO_2H$ to the suspension caused evolution of CO_2 corresponding to a CO_2 : Zr molar ratio of 2.02 : 1.

Results and Discussion

The zirconium(IV) and the hafnium(IV) derivatives $[M(C_5H_5)(O_2CNEt_2)_3]$ can be obtained by two synthetic procedures, namely by the exchange reaction of $Mg(C_5H_5)_2$ with $M(O_2CNEt_2)_4$ and that of $M(C_5H_5)_2$ with $Fe(O_2CNEt_2)_2$ in toluene, equations (4) and (5). The sparingly soluble magnesium

$$Mg(C_5H_5)_2 + 2\,M(O_2CNEt_2)_4 \longrightarrow Mg(O_2CNEt_2)_2 + 2\,[M(C_5H_5)(O_2CNEt_2)_3] \quad (4)$$

$$2\,M(C_5H_5)_4 + 3\,Fe(O_2CNEt_2)_2 \longrightarrow 2\,[M(C_5H_5)(O_2CNEt_2)_3] + 3\,Fe(C_5H_5)_2 \quad (5)$$

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† $Mg(O_2CNEt_2)_2$ in CD_3CN shows resonances at δ 2.55 (q, 8 H) and 1.12 (t, 12 H).

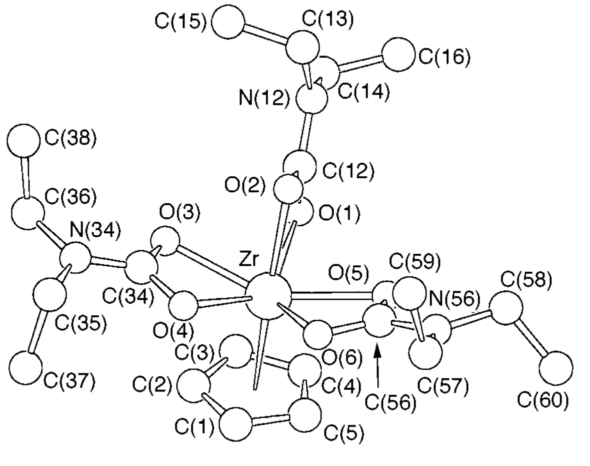

Fig. 1 A SCHAKAL[14] plot of the molecular structure of [Zr$(C_5H_5)(O_2CNEt_2)_3$] with the atom numbering used

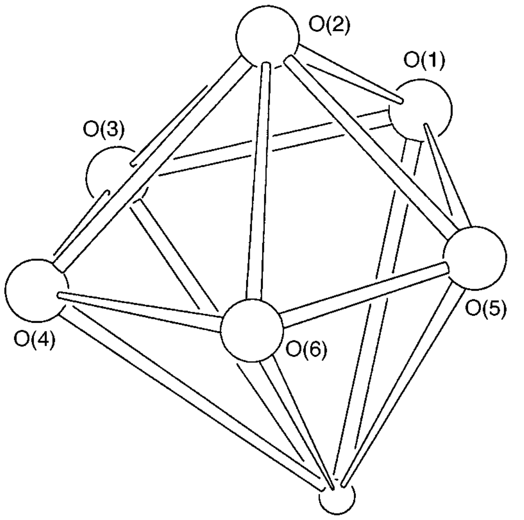

Fig. 2 Co-ordination polyhedron of zirconium in [Zr$(C_5H_5)(O_2CNEt_2)_3$]

diethylcarbamate was separated by filtration in admixture with some [M$(C_5H_5)(O_2CNEt_2)_3$]. Pure [M$(C_5H_5)(O_2CNEt_2)_3$] was recrystallized from the filtrate by cooling. In the case of the reaction (5), ferrocene can be easily separated from the diethylcarbamato compound by sublimation.

The cyclopentadienyl(diethylcarbamato) compounds have been characterized by spectroscopic and analytical methods. The infrared spectrum in the solid state shows absorptions typical of the cyclopentadienyl ring and strong absorptions in the 1540–1318 cm^{-1} region typical[12] of bidentate diethylcarbamate ligands. Therefore, if the cyclopentadienyl ligand is assumed to occupy a single co-ordination site, [M$(C_5H_5)(O_2CNEt_2)_3$] were predicted to be seven-co-ordinate derivatives of zirconium(IV) or hafnium(IV). As structurally characterized organometallic compounds containing dialkylcarbamate ligands are not common,[6,13] we decided to carry out an X-ray structural analysis of the zirconium compound.

The crystal structure consists of discrete molecules separated by normal intermolecular contacts. In each molecule the zirconium atom is surrounded by six oxygen atoms of the three bidentate diethylcarbamato groups and by the cyclopentadienyl ring (Fig. 1). The co-ordination geometry at the zirconium atom is that of a distorted pentagonal bipyramid with the apical positions occupied by one of the bites of the diethylcarbamate and by the C_5H_5. Fig. 2 shows the co-ordination polyhedron of the zirconium cation and Table 1 lists a selection of bond distances and angles. A similar co-ordination geometry is observed in [ZrCl(acac)$_3$],[15] [ZrCl(tmhd)$_3$] (tmhd = 2,2,6,6-tetramethylheptane-3,5-dionate),[16] [Zr(C_5H_5)(hfacac)$_3$] (hfacac = 1,1,1,5,5,5-hexafluoropentane-2,5-dionate)[17] and in [Zr(C_5H_5)(trop)$_3$] (Htrop = 2-hydroxycyclohepta-2,4,6-trienone).[18] If reference is made to the structure of the cyclopentadienyl derivatives, the deviation from a regular pentagonal bipyramid is more severe for the diethylcarbamato compound, due to the smaller bite[19] of the O_2CN group, than for the acetylacetonato or tropolonato complexes. In fact in [Zr(C_5H_5)(hfacac)$_3$] the angles at zirconium between the oxygen atoms which define the pentagonal plane and the apical oxygen atom are similar, between 78.8(2) and 80.5(2)°, while in [Zr$(C_5H_5)(O_2CNEt_2)_3$] four of the oxygen atoms which define the pentagonal plane [O(3) to O(6)] show angles at zirconium with apical O(2) between 76.82(10) and 88.21(10)°, and the O(1)–Zr–O(2) angle is 59.50(10)°. This smaller angle is in agreement with the shorter O(1)···O(2) contact of 2.20 Å, with respect to the corresponding distance in [Zr(C_5H_5)(hfacac)$_3$][17] [2.81(1) Å] and in [Zr(C_5H_5)(trop)$_3$][18] (2.52 Å).

Table 1 Selected bond distances (Å) and angles (°) of [Zr$(C_5H_5)(O_2CNEt_2)_3$]. Estimated standard deviations given in parentheses refer to the least significant digit

Zr–O(4)	2.180(3)	O(1)–C(12)	1.281(4)
Zr–O(1)	2.194(3)	O(2)–C(12)	1.279(4)
Zr–O(6)	2.196(3)	O(3)–C(34)	1.280(4)
Zr–O(2)	2.234(3)	O(4)–C(34)	1.297(4)
Zr–O(3)	2.276(3)	O(5)–C(56)	1.283(4)
Zr–O(5)	2.276(3)	O(6)–C(56)	1.278(5)
O(4)–Zr–O(1)	131.61(9)	O(4)–Zr–O(5)	132.26(9)
O(4)–Zr–O(6)	75.45(10)	O(1)–Zr–O(5)	78.61(10)
O(1)–Zr–O(6)	130.59(10)	O(6)–Zr–O(5)	58.51(10)
O(4)–Zr–O(2)	88.21(10)	O(2)–Zr–O(5)	77.84(10)
O(1)–Zr–O(2)	59.50(10)	O(3)–Zr–O(5)	151.78(10)
O(6)–Zr–O(2)	86.59(10)	O(2)–C(12)–O(1)	118.2(3)
O(4)–Zr–O(3)	58.94(9)	O(2)–C(12)–N(12)	120.9(3)
O(1)–Zr–O(3)	77.97(10)	O(1)–C(12)–N(12)	120.9(3)
O(6)–Zr–O(3)	131.43(10)	O(3)–C(34)–O(4)	116.7(3)
O(2)–Zr–O(3)	76.82(10)	O(3)–C(34)–N(34)	122.8(3)
		O(4)–C(34)–N(34)	120.5(3)

As far as the diethylcarbamate ligands are concerned, both the bond distances and angles are in agreement with values generally reported for this type of ligand. The O_2CN groups are substantially planar with very small deviations (0.001–0.004 Å) from planarity. The angles between the planes of the carbamates in the pseudo-*cis* positions [as defined by O(1) to O(6)] are 71.16 and 78.61°. The angle between the planes defined by the two pseudo-*trans* carbamates [as defined by O(3), O(4) and O(5), O(6)] is 25.15°, to be compared with 0° for a regular pentagonal bipyramid. This confirms the distortion of the pentagonal plane which is directed away from the cyclopentadienyl ligand. The C_5H_5 ligand is substantially planar with a zirconium-ring centroid distance of 2.241(6) Å {2.23(1) Å is the corresponding distance in [Zr(C_5H_5)(hfacac)$_3$]}. The mean equatorial Zr–O distance is 2.224(3) Å comparable with those observed in [Zr(C_5H_5)(hfacac)$_3$] [2.225(1) Å (mean)], [ZrCl(acac)$_3$] [2.145(13) Å (mean)], [Zr(C_5H_5)(tmhd)$_3$] [2.134(3) Å (mean)] and [Zr(C_5H_5)(trop)$_3$] [2.21(1) Å (mean)].[15–18]

The availability of [Zr$(C_5H_5)(O_2CNEt_2)_3$] prompted us to investigate the reaction of this mixed cyclopentadienyl–diethylcarbamato compound with the silanol groups of a silica surface. The complex promptly reacts with silica with evolution of 1 mol of CO_2 per mol of zirconium, no C_5H_6 being released {as established by ^1H NMR monitoring of the solution after the reaction of [Zr$(C_5H_5)(O_2CNEt_2)_3$] with ≡Si(OH) in C_6D_6}, equation (6). Steric hindrance and the unavailability of reactive

$$[Zr(C_5H_5)(O_2CNEt_2)_3] + {\equiv}Si(OH) \longrightarrow (\equiv SiO)Zr(C_5H_5)(O_2CNEt_2)_2 + CO_2 + NHEt_2 \quad (6)$$

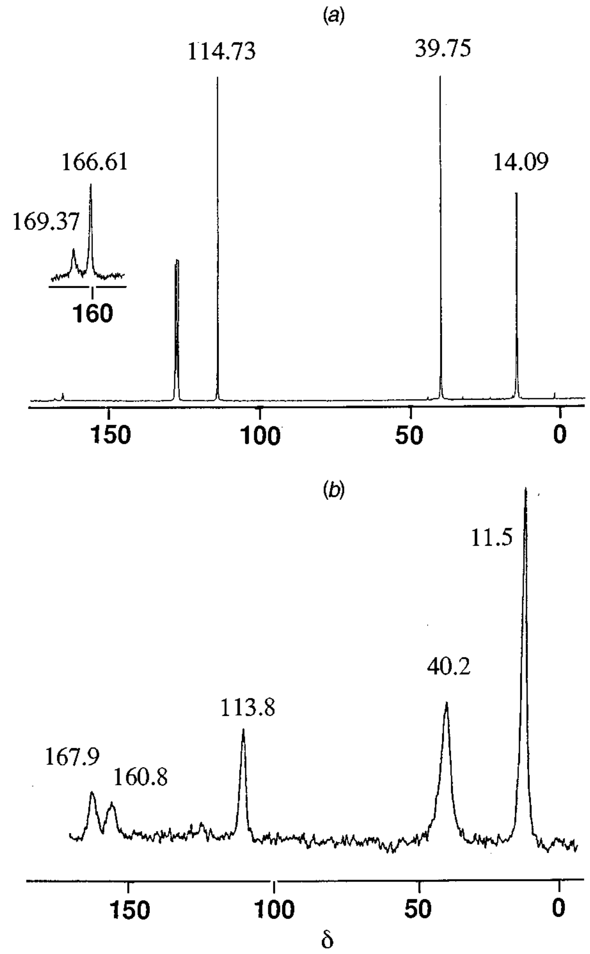

Fig. 3 (*a*) Carbon-13 NMR spectrum of $[Zr(C_5H_5)(O_2CNEt_2)_3]$ in C_6D_6; the inset shows an expanded view of the 160 ppm region, typical of the carboxylic carbon atoms of the carbamate ligand. (*b*) The CP MAS ^{13}C NMR spectrum of $(\equiv SiO)Zr(C_5H_5)(O_2CNEt_2)_2$

adjacent silanol groups explain the failure to observe higher ratios than 1 : 1 for the evolution of carbon dioxide.

The DRIFT spectrum of the solid shows absorptions typical of cyclopentadienyl, alkyl and dialkylcarbamato groups. The presence of these functional groups has been confirmed by the CP MAS ^{13}C NMR spectrum which shows resonances due to the carbon atoms of the cyclopentadienyl ring, the methylene and the methyl groups of the diethylcarbamate ligand (δ 113.8, 40.2 and 11.5, respectively); moreover, two resonances of approximately equal intensity are observed at δ 167.9 and 160.8 which have been assigned to the carboxylic carbon atoms of the diethylcarbamato fragment.

These experimental facts, together with the evolution of 2 mol of carbon dioxide per mol of zirconium on treatment of the solid with $MeCO_2H$ in toluene, confirm the stoichiometry (6).

The solid-state and the solution (C_6D_6) ^{13}C NMR spectra of the silica-supported $\equiv(SiO)Zr(C_5H_5)(O_2CNEt_2)_2$ and of the zirconium(IV) precursor $[Zr(C_5H_5)(O_2CNEt_2)_3]$, respectively, need some comment. The solution spectrum of the complex shows two resonances due to the carboxylic carbon atoms of unequal intensity [Fig. 3(*a*)]. By taking into consideration that its solid-state structure shows two O_2CNEt_2 ligands [identified by O(3), O(4) and O(5), O(6) in Fig. 2] lying in the equatorial plane of the pentagonal bipyramid and a third bonded to the zirconium through equatorial [O(1)] and axial [O(2)] positions, the solution ^{13}C NMR spectrum clearly indicates the absence of fluxionality within the non-equivalent O_2CNEt_2 groups of the molecule.

On the other hand the solid-state spectrum of the compound implanted on silica shows two resonances attributed to carboxylic carbon atoms. The non-equivalence of the diethylcarbamato groups [see Fig. 3(*b*)] suggests that during the reaction of the zirconium(IV) compound with the silica surface, the O_2CNEt_2 group which has undergone degradation to CO_2 and $NHEt_2$ is preferentially one of the two equatorial ligands. The reason may be either statistic (two equatorial *vs.* one equatorial/axial group are present in the starting material) or mechanistic {molecular recognition of one of the two different sites of the $[Zr(C_5H_5)(O_2CNEt_2)_3]$ molecule by the silica surface}.

Conclusion

Mixed cyclopentadienyl–diethylcarbamato compounds of zirconium(IV) and hafnium(IV) containing the highest diethylcarbamate : C_5H_5 ratio, $[M(C_5H_5)(O_2CNEt_2)_3]$, have been prepared and characterized. The possibility of implanting zirconium(IV) organometallic fragments on a commercially available silica support starting from mixed cyclopentadienyl–diethylcarbamato precursors is demonstrated, through electrophilic reaction of the silanol groups on the reactive diethylcarbamate ligand. The resulting silica is a functionalized one, statistically containing one residual $Zr(C_5H_5)(O_2CNEt_2)_2$ fragment. This implantation method is highly selective as deduced from the ^{13}C NMR spectra of $[Zr(C_5H_5)(O_2CNEt_2)_3]$ implanted on silica. Also, provided a high OH : Zr molar ratio is used, the yield of the liquid–solid reaction is almost quantitative; moreover, the activity of the silanol groups is kept to a maximum, since solvents of low polarity can be used.

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