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Notes

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Surface Organometallic Chemistry: Synthesis and Characterization of a Tris(neopentyl)zirconium(IV) Complex Grafted to the Surface of a Partially Dehydroxylated Silica

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Introduction

The objectives of surface organometallic chemistry are multiple:[1] synthesis of new catalysts, grafting of complexes or clusters of predetermined coordination sphere,[2] and modification of molecular sieves.[3] For most of these applications, the deposition of only one surface molecular complex is preferred, and thus the occurrence of any secondary reaction should be kept at a low level.

A number of studies have shown that tetrakis(alkyl)-, tetrakis(π-allyl)-, or tetrakis(σ-benzyl)zirconium complexes react easily with the surface OH groups of inorganic oxides such as silica and alumina.[4] The surface reaction has been evidenced by the evolution of the corresponding alkane or alkene (reaction 1).

$$ZrR_4 + xHOSi\lessdot \rightarrow R_{4-x}Zr(OSi\lessdot)_x + xRH \qquad (1)$$

$$R = CH_2C_6H_5,\ C_3H_5,\ Np\ (\text{neopentyl})$$

However, the overall stoichiometry of the surface reaction is dependent, inter alia, upon the degree of hydroxylation of the silica,[4–9] so that mixtures of surface species, corresponding to different values of x, are probably present on the surface in some systems. We wish to report here the synthesis of a well-defined d^0 Zr(IV) surface complex, $\gtrdot Si-O-ZrNp_3$, by reaction between tetrakis(neopentyl)zirconium, $ZrNp_4$, and the surface of a silica partially dehydroxylated at 500 °C, $SiO_2(500)$.

Experimental Section

Physical Measurements. CP-MAS NMR spectra were recorded on a MSL-300 Bruker spectrometer operating at 75.470 MHz for ^{13}C and equipped with a double-bearing probe allowing spinning frequencies of 3–4 kHz. The rotors were made of zirconia. The contact time for cross polarization was 5 ms (90° for ^1H: 6 μs). Before Fourier transformation, a line broadening of 50 Hz was applied. The chemical shifts are given relative to external TMS.

IR spectra were recorded on a Nicolet 10MX-FT instrument, equipped with a special cell designed for in situ preparations under controlled atmosphere.[10]

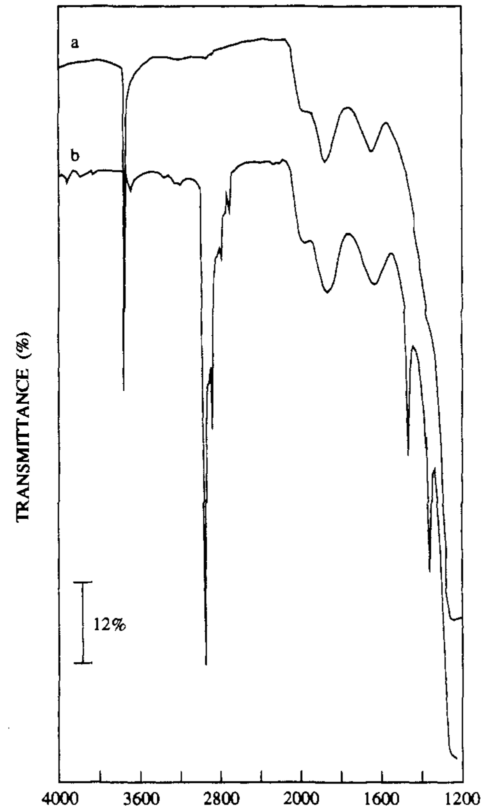

Figure 1. IR spectra: (a) silica dehydroxylated at 500 °C under vacuum; (b) sample a after sublimation of $ZrNp_4$ at 60 °C, followed by vacuum treatment (10^{-5} Torr) at 60 °C and 2 h.

Table I

wt % Zr	mol of NpH/mol of Zr[a]	% NpD[b]	wt % C
0.82	0.97 ± 0.05	93	1.73 ± 0.05
1.49	0.93 ± 0.05	91	*c*
3.12 ± 0.05	*c*	*c*	5.40 ± 0.05

[a] Gas evolved during the reaction of $ZrNp_4$ with $SiO_2(500)$. Neopentane is the only detectable hydrocarbon. [b] Analyzed by MS. [c] Not determined.

Gas-phase analysis was performed by a combination of volumetric and mass spectral measurements. Pressures were accurately determined using a precision gauge (Texas Instruments). Mass spectra were recorded on a quadrupole analyzer (Supravac VG), connected to a vacuum system able to maintain a residual pressure of 10^{-10} Torr.

Preparation of $\gtrdot Si-O-ZrNp_3$. Silica (Aerosil from Degussa, 200 m^2/g) was treated at 500 °C for 16 h, under vacuum (10^{-5} Torr). After this treatment, the number of surface OH groups was ca. 2 OH/nm^2, as determined by titration with $LiAlH_4$.[11] Deuterated silica was prepared by contacting $SiO_2(500)$ with D_2O (22 Torr) at 500 °C for 2 h and subsequent vacuum evacuation at the same temperature for 2 h; this procedure was repeated three times before evacuation at 500 °C for 16 h. The resulting silica was more than 90% deuterated, as determined by quantitative IR data (relative intensities of the bands at 3747 cm^{-1} ($\gtrdot SiOH$) and 2735 cm^{-1} ($\gtrdot SiOD$)).

$ZrNp_4$, prepared according to published procedures,[12] was sublimed in situ on $SiO_2(500)$ at 60 °C. Elimination of unreacted complex was

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achieved by treatment under vacuum at the same temperature for 1–3 h. The efficiency of this procedure was checked by monitoring the experiment by IR spectroscopy until no significant variation of the intensity of the ν(C–H) bands could be detected.

Elemental analysis was performed by the Mikroanalytisches Labor Pascher, Remagen, Germany.

Results and Discussion

When $ZrNp_4$ is sublimed on a disk of $SiO_2(500)$ (Figure 1a), the resulting spectrum presents the ν(C–H) and $\delta(CH_2)$ vibrational bands, typical of neopentyl ligands at 2953 ($\nu_{as}(CH_3)$), 2864 ($\nu_s(CH_2)$), 1464 ($\delta_{as}(CH_3)$), and 1359 cm^{-1} ($\delta_s(CH_3)$) (Figure 1b). Analysis of the gases evolved under the same experimental conditions on a larger sample (ca. 0.5 g) reveals the liberation of ca. 1 mol of NpH/mol of Zr (Table I). But, as partial decomposition of $ZrNp_4$ may occur under sublimation conditions and lead also to the liberation of neopentane,[12] we performed the same experiment with deuterated silica: in this case, the evolved neopentane was at least 90% monodeuterated (NpD), confirming that the observed reaction was mainly a true surface reaction. (The evolution of ca. 10% nondeuterated NpH can be related to the fact that the silica surface was not 100% deuterated.)

Elemental analysis of the solid (Table I) confirms the presence of three neopentyl ligands per surface Zr atom (obtained C/Zr ratio 15 ± 2; expected ratio 15).

Finally, hydrolysis, at room temperature, of the zirconium surface species by an excess of water (22 Torr) liberates ca. 3 mol of NpH/mol of Zr (exp: 3.1 ± 0.3). Simultaneously, the IR spectrum in the 4000–3000-cm^{-1} region shows the bands typical of $Zr(O-H)_x$, at 3784 and 3679 cm^{-1},[13] in agreement with the known reactivity of the Zr–alkyl bond with water.[14]

All these results taken together suggest that the main reaction which occurs between $ZrNp_4$ and the surface of $SiO_2(500)$ is the formation of the surface complex (>Si–O)$ZrNp_3$ (II):

$$\underset{\text{I}}{ZrNp_4} + {>}Si{-}OH(D) \rightarrow \underset{\text{II}}{({>}Si{-}O)ZrNp_3} + NpH(D) \quad (2)$$

It is worth mentioning here that the observed value ($x = 3$) cannot be taken as the mean number of neopentyl ligands per surface zirconium atom for the following reasons. First, all unreacted $ZrNp_4$ has been removed. Second, the experimental x value is independent of the Zr content, i.e. of the number of available surface silanol groups per Zr atom (Table I).

Further characterization of II was achieved by ^{13}C MAS NMR spectroscopy. The spectrum of II shows only one signal at 33.9 ppm (Figure 2b), attributed to the methyl group ($Zr-CH_2-C(CH_3)_3$) by comparison with the solid-state NMR spectrum of a pure sample of $ZrNp_4$ (Figure 2a). The methylene carbon atom is not detected on the supported complex. This is not surprising, since the corresponding signal is also very weak for the pure $ZrNp_4$ solid sample: this is related to a long T_1 relaxation time for CH_2. The peak corresponding to the quaternary C atoms, and expected at ca. 30 ppm,[15] cannot be observed due to line broadness of the solid-state spectra.

The surface complex (>Si–O)$ZrNp_3$ is very sensitive to trace amounts of O_2. Reaction of II with dry O_2 (30 Torr, 24 h, room temperature) is evidenced by IR spectroscopy (appearance of new bands at 1482 and 1446 cm^{-1} ($\delta(CH_2)$) and ^{13}C NMR data (δ 24.4 ppm ($O-CH_2-C(CH_3)_3$), 32 ppm ($O-CH_2-C(CH_3)_3$), and 82 ppm ($O-CH_2-C(CH_3)_3$))[16] (Figure 2c). Reaction of this surface neopentoxy complex (0.5 g; 1.35 wt % Zr) with HCl (1 M solution in Et_2O) gives neopentanol (2.5 mol/mol of Zr).[17] All

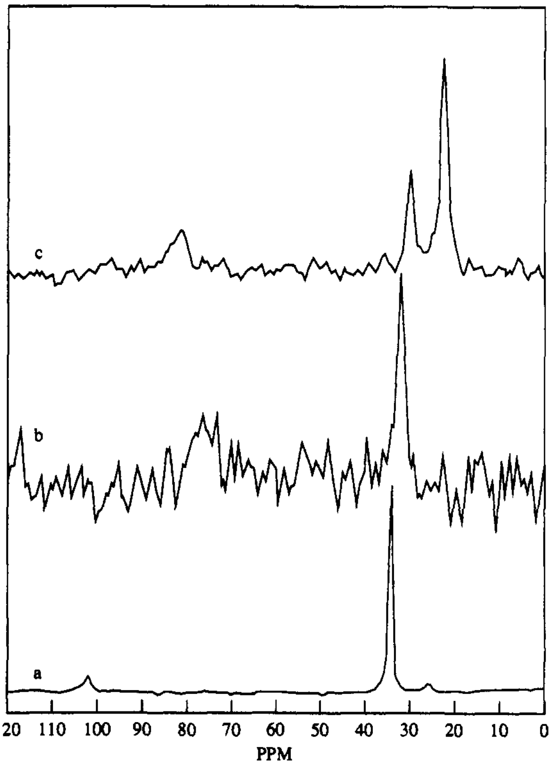

Figure 2. ^{13}C MAS NMR spectra: (a) pure $ZrNp_4$; (b) $ZrNp_4/SiO_2(500)$; (c) sample b after 24 h in the presence of dry O_2.

the neopentyl ligands of I are transformed under O_2 into an alkoxide, since hydrolysis by water does not liberate any detectable amount of neopentane. The following reaction is therefore occurring:

$${>}Si{-}O{-}ZrNp_3 + \tfrac{3}{2}O_2 \rightarrow {>}Si{-}O{-}Zr(ONp)_3 \quad (3)$$

parallel to the known reactivity of molecular analogues.[18] The mechanism of oxidation of this surface complex is not yet clear: the last step of the radical pathway generally accepted[19] involves a bimolecular reaction between two Zr centers. Such a mechanism may be invoked only when the metal centers are sufficiently close for this step to occur on the surface.

In conclusion, this study shows that it is possible to synthesize a given surface complex with a predetermined coordination sphere on a well-chosen surface, with a reasonably high degree of selectivity (>90%). In the case of a silica dehydroxylated at 500 °C, IR,[20] ^1H CRAMPS NMR,[21] and ^{29}Si MAS NMR[22] analyses suggest that the surface presents mainly free, non-hydrogen-bonded silanol groups (>90%), i.e. functional groups of the same chemical nature. Moreover, a computer-modeling study of the surface of silica,[23] taking into account these results, suggests that no steric effects should prevent the reaction of these silanol groups with $ZrNp_4$ with formation of (>SiO)$ZrNp_3$. One cannot however exclude the complete absence of some $({>}SiO)_2ZrNp_2$, if one relies

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(15) See for reference the solution ^{13}C NMR spectra of neopentanol (δ (ppm): 26.3 (CH_3), 32.6 ($C(CH_3)_3$), 72.6 (CH_2)) and neopentane (δ (ppm): 31.7 (CH_3), 28.1 ($C(CH_3)_3$)).

(16) In the presence of molecular oxygen, a paramagnetic molecule, the relaxation times are significantly reduced, so that observation of the peaks corresponding to quaternary and methylene carbon atoms becomes possible.

(17) Some neopentanol probably physisorbs on the surface of silica. Quantitative analysis has thus been performed with reference to NpOH/silica systems of known NpOH concentration.

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on the analytical data, as well as on modeling studies.

Another interesting result is the stabilization by the surface of a tris(neopentyl)zirconium(IV) complex. This tetracoordinated (siloxy)tris(neopentyl)zirconium complex is a highly electron-deficient d^0 complex; stabilization is probably related to steric crowding at the Zr center, even if one considers that some $p\pi$–$d\pi$ donation by siloxy oxygens could eventually participate in this stabilization. Studies on stoichiometric or catalytic reactions of such systems are now under investigation.

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The Product of the Reaction of *trans*-Diamminedichloroplatinum(II) with Diamines Is Dependent on Chain Length. Example of a Bridging Ethylenediamine and Formation of a Novel Trans-Chelated Structure with 1,5-Pentanediamine

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Bis(platinum) complexes containing two platinum–amine coordination spheres linked by a variable length diamine chain are of interest for their chemical and biological properties.[1-3] The most general formula for bis(platinum) complexes with chloride and amine ligands is $[\{PtCl_m(NH_3)_{3-m}\}_2(\text{diamine})]^{2(2-m)+}$ (m = 0–3, and the diamine is usually $H_2N(CH_2)_nNH_2$), and our studies include the design of synthetic pathways to all possible isomers of these complexes. Recently we reported the properties of a complex containing monodentate coordination spheres (m = 1, above) of specific formula $[\{trans\text{-}PtCl(NH_3)_2\}_2(NH_2(CH_2)_4NH_2)]Cl_2$.[4] This complex is of particular interest for its DNA interstrand cross-linking ability and antitumor activity in cell lines resistant to cisplatin. We wished to examine this series of complexes further to study how these properties are affected by varying diamine chain length. The synthesis involves reaction of 1 equiv of diamine with 2 equiv of *trans*-$[PtCl_2(NH_3)_2]$:[1,5]

$$2\,trans\text{-}[PtCl_2(NH_3)_2] + H_2N(CH_2)_nNH_2 \rightarrow [\{trans\text{-}PtCl(NH_3)_2\}_2H_2N(CH_2)_nNH_2]Cl_2$$

The starting material (0.3 g, 0.001 mol) is suspended in H_2O (40 mL) with stirring at 60 °C. A half-equivalent of the appropriate diamine is slowly added dropwise, and stirring is maintained at 60 °C for 3 h, during which time all the *trans*-$[PtCl_2(NH_3)_2]$ dissolves. Upon cooling, the solution is filtered and evaporated in volume to approximately 2 mL and MeOH (50 mL) added. The white precipitate is then filtered off and recrystallized consecutively in H_2O/MeOH until pure. In this contribution we show that the products obtained are dependent on diamine chain length, and with 1,5-pentanediamine we describe the characterization of a novel trans-chelated monomeric species where the amine groups of the pentanediamine bind in mutually trans positions to the same platinum center.

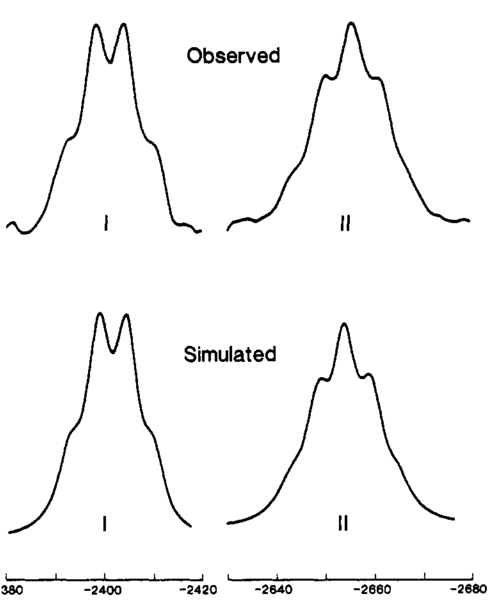
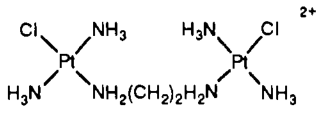


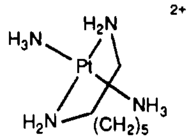
Figure 1. Observed and simulated ^{195}Pt NMR spectra of $[\{trans\text{-}PtCl(^{15}NH_3)_2\}_2H_2{}^{15}N(CH_2)_2{}^{15}NH_2]Cl_2$ (I) containing bridging ethylenediamine and *trans*-$[Pt(^{15}NH_3)_2(H_2{}^{15}N(CH_2)_5{}^{15}NH_2)]Cl_2$ (II) with trans-chelating 1,5-pentanediamine. See the text for structures.

The characterization and analytical data for the n = 2–4 diamines are consistent with the formation of the proposed bis(platinum) product.[6] In contrast the n = 5 derivative showed a ^{195}Pt NMR chemical shift at −2679 ppm (relative to $PtCl_6{}^{2-}$) more characteristic of a PtN_4 core, no ν(Pt–Cl) in the IR spectrum, and an elemental analysis indicating the presence of only 1 Pt per diamine.[6] These results are consistent with a platinum–tetraamine complex $[Pt(NH_3)_2(H_2N(CH_2)_5NH_2)]Cl_2$, but in this case the 1,5-pentanediamine must chelate trans positions. Diamines with longer chain lengths (n = 6–8) gave a mixture of products as indicated by two peaks in the ^{195}Pt NMR spectrum corresponding to PtN_3Cl and PtN_4 coordination spheres.[7]

To confirm the structural assignments, we prepared ^{15}N-substituted complexes for n = 2 (complex I) and n = 5 (complex II).



I



II

For both complexes, a plot of conductivity versus equivalent concentration[8,9] showed that both complexes behave as 1:2 electrolytes in comparison to standards such as $[Pt(NH_3)_4]^{2+}$, $[Pt(NH_3)_2(en)]^{2+}$ (complex III), $[Co(NH_3)_6]^{3+}$, and $[\{Pt(NH_3)_3\}_2(H_2N(CH_2)_nNH_2)]^{4+}$ (n = 4, 5).[10] Table I summarizes the spectral data. The ^{15}N NMR spectrum of the ethylenediamine

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(6) Analytical data for n = 2 are as follows. Anal. Calcd for $C_2H_{20}N_6Cl_4Pt_2$: C, 3.64; H, 3.05; N, 12.73; Cl, 21.48. Found: C, 3.62; H, 3.04; N, 12.63; Cl, 21.16. $\delta(^{195}Pt)$ −2415 ppm, $\delta(^1H)$ 3.07 ppm. ν(NH) = 3300, 3190, 3120 cm^{-1}, ν(Pt–Cl) = 344 cm^{-1}. Analytical data for n = 3 are as follows. Anal. Calcd for $C_3H_{22}N_6Cl_4Pt_2$: C, 5.34; H, 3.29; N, 12.46; Cl, 21.03. Found: C, 5.50; H, 3.28; N, 12.46; Cl, 20.53. $\delta(^{195}Pt)$ −2421 ppm, $\delta(^1H)$ 2.78, 2.11 ppm. ν(NH) = 3100 (br), 3170 cm^{-1}, ν(Pt–Cl) = 330 cm^{-1}. The properties of the n = 4 complex were as reported.[4,5] Analytical data for n = 5 are as follows. Anal. Calcd for $C_5H_{20}N_4Cl_2Pt$: C, 14.93; H, 5.01; N, 13.93; Cl, 17.63. Found: C, 14.99; H, 5.25; N, 13.79; Cl, 17.94. $\delta(^{195}Pt)$ −2679 ppm, $\delta(^1H)$ 2.68, 1.66, 1.38 ppm. ν(NH) = 3160, 3080 cm^{-1}. Spectral conditions are as per Table I.

(7) For n = 6, −2425 and −2678 ppm, for n = 7, −2418 and −2673 ppm, and for n = 8, −2431 and −2682 ppm. Spectral conditions are as per Table I.

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