Notes

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Registry No. (2-Aminopyrimidine)Co^{III}...

Registry No. (2-Aminopyrimidine)Co

Registry No. (2-Aminopyrimidine)Co^{III}(acac)$_2$(NO$_2$), 64457-12-1; Na[Co(acac)$_2$(NO$_2$)$_2$], 14024-47-6.

Supplementary Material Available: Hydrogen parameters, complete intramolecular dimensions, and a listing of structure factors (11 pages). Ordering information is given on any current masthead page.

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Structural Feature in TiCl₃, a Component in the Ziegler–Natta Catalyst, by X-Ray Absorption Studies

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The dependence of catalytic activity on the bonding and structure in catalysts has been proposed by several investigators.[2] The Ziegler–Natta type catalysts[3-5] used in the polymerization of olefins continue to be an active field of investigation. Many questions relating to the constitution of these catalysts, the nature of the active sites, and the mechanism of their action remain to be resolved.[6] Titanium trichloride, TiCl₃, is the typical solid component of the Ziegler–Natta type catalyst for stereospecific polymerization of α olefins; hence, a great interest in the knowledge of its crystal structure arises. Fiber-shaped (β form) and layered forms (α, γ, and σ) of TiCl₃ were studied using the powder x-ray technique.[7] Optical microscopy[8] linked polymerization at the surface of a TiCl₄–AlR₃ crystal face to localization of the active site, and single-crystal x-ray diffraction[9] work with (C₂H₅)₂TiCl₂Al(C₂H₅)₂ confirmed the bimetallic nature of the catalyst. Despite these efforts, however, the Ti–Cl distance remains unknown.

We report the interatomic bond distance of TiCl₃ by the analysis of the extended x-ray absorption fine structure (EXAFS). This technique does not rely on single crystals and has been used previously to determine interatomic distances in iron–sulfur proteins,[10] in copper salts in aqueous solutions,[11] and in polymer-bound rhodium(I) catalysts.[12]

Experimental Section

The photoabsorption K edge of Ti in TiCl₃ was measured using the tunable x-ray synchrotron source at the Stanford Synchrotron Radiation Project at Stanford University. The instrumentation has been previously described.[13]

The measurement of the intensity, I_0, of the incident x-ray radiation passing through one ionization chamber (He + N₂) and the transmitted

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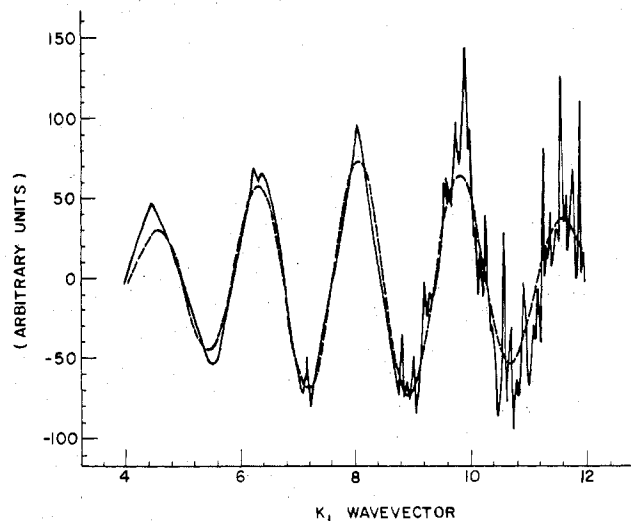
Figure 1. The Ti EXAFS of TiCl₃ where the raw data (——) and Fourier-filtered data (- - -) have had the background removed.
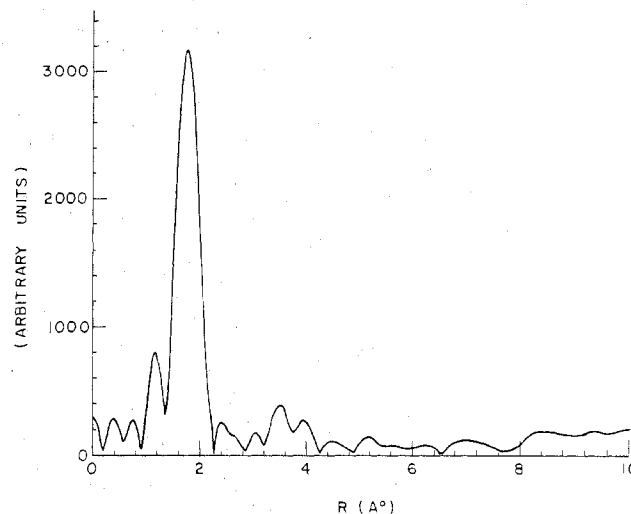
Figure 2. Fourier transform of the raw data.

intensity, I, through the sample and finally to a second ionization chamber (N₂) allows the relationship $\mu x = \ln (I_0/I)$, where μ is the linear absorption coefficient and x is the absorber thickness, to be plotted against the photon energy.

The data were taken on violet γ-TiCl₃ purchased from Alfa-Ventron. The sample was sealed between two thin layers of Kapton tape which is transparent to the x rays and protects the moisture- and air-sensitive TiCl₃ sample.

The current theoretical view of EXAFS[15,16] is that the modulation of the x-ray absorption, $\chi = (\mu - \mu_0)/\mu_0$, is due to the interference between the backscattered and outgoing photoelectrons in the photoabsorption matrix element, where μ_0 is the absorption coefficient of an isolated atom. Thus, the modulation of $\Delta\mu/\mu$ of the x-ray absorption coefficient of an atom is given by eq 1, where N_j is the

$$\frac{\Delta\mu}{\mu} = \sum_j \frac{-N_j |f_j(k, \pi)| e^{-2\sigma j^2 k^2}}{R_j^2 k} \sin (2kR_j + \phi_j(k)) \qquad (1)$$

number of scattering atoms j at a distance R_j to the absorbing atom with a Debye–Waller like factor $e^{-2\sigma j^2 k^2}$. The ϕ_j and f_j are energy-dependent phase shifts and amplitude functions for the scatterers, respectively, and k is the wavevector of the emitted photoelectron.

The raw data for TiCl₃ where Ti is the absorber is given in Figure 1, showing a single frequency, indicative of a single distance. The Fourier transform of the data is given in Figure 2.

Two methods were used to determine the Ti–Cl interatomic distance. One method[17] used theoretical phase shifts, ϕ_j, and amplitudes, f_j, to fit the data to eq 1. An empirical method[13a] with
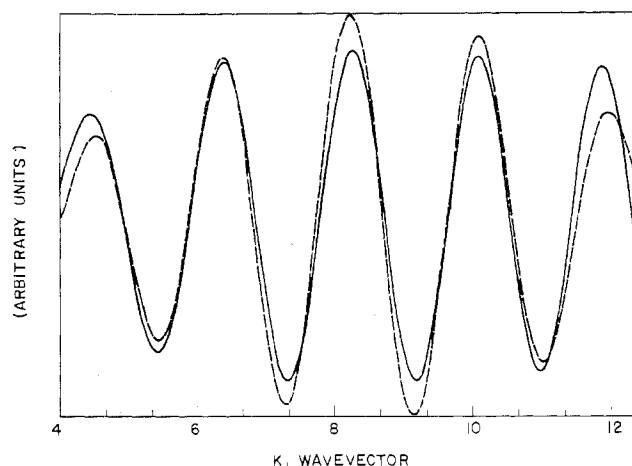
Figure 3. The fit (- - -) of the EXAFS data (—) for TiCl₃.

theoretical phase shifts was also used.

Results and Discussion

The results of the fitting technique (Figure 3) gave a Ti–Cl bond distance of 2.22 (1) Å. The empirical method gave a Ti–Cl interatomic distance of 2.21 (2) Å. The data support the argument that all the Ti–Cl bonds are equal in distance from the Ti atom. It has previously been shown that theoretical phase shifts and amplitudes can be used to accurately predict interatomic distances by EXAFS to ±0.01 Å in known structures.[16b,17] The measured distance of 2.21 Å is considerably shorter than the 2.40-Å bond distance that would result from a Ti^{3+}–Cl^- ionic bond, indicating the strong covalent nature of the bonding in TiCl₃. The techniques and results reported herein demonstrate the practical application of EXAFS to the solution of structural problems. This analysis technique supplements single-crystal x-ray diffraction as another tool for the resolution of structural problems for which x-ray crystallography could not or has not been applied.

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Base Strengths of (ω-Methoxyalkyl)triphenyl- and (ω-Methoxyalkyl)diphenylmethylsilanes

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It has been suggested that the nature of the substituents directly bound to the silicon atom will determine to a large extent which resonance interactions will be of prime importance.[1-3] We had previously examined the base strengths of $CH_3O(CH_2)_nSiR_3$ (R = H, Cl, and CH₃) compounds and suggested that lowered basicity (R = H and Cl) and the lack of such an effect when R = CH₃ is consistent with a trend that lowered basicities result when the substituent is able to induce a positive charge on the silicon.[4,5] In order to test this hypothesis we prepared the analogous compounds in which R = C₆H₅.

Experimental Section

$CH_3OCH_2Si(C_6H_5)_2CH_3$. This new compound was prepared from the addition of chloromethyl methyl ether to diphenylmethylsilyllithium. In a typical reaction, a solution of 48.0 g (0.198 mol) of $(C_6H_5)_2CH_3SiCl$ in 75 mL of anhydrous THF was added dropwise to 3.1 g (0.45 mol) of Li clippings in 75 mL of THF. After the reaction mixture was stirred for 3.5 h, the dark red lithium reagent was filtered from excess Li and cooled to –15 °C, and a solution of 17 g (0.21 mol) of CH_3OCH_2Cl in 50 mL of THF was added dropwise. After 15 min, the reaction mixture turned yellow-brown, and a white precipitate was observed. The solution was then allowed to slowly warm to 20 °C and stirred for an additional 1.5 h. The reaction mixture was hydrolyzed with a saturated NH₄Cl solution, extracted with diethyl ether, and dried over CaCl₂. Removal of the solvent in vacuo yielded a mixture consisting of a yellow oil and a white solid $[(C_6H_5)_4(CH_3)_2Si_2]$. The oil was distilled under reduced pressure and chromatographed on a 2 ft × 1 in alumina (Brockman activity II) column. Petroleum ether (bp 40–60 °C) was used as the elutant. The yield based on $(C_6H_5)CH_3SiCl$ was 40%.

Proton chemical shifts for this and the compounds listed below are given in Table I.

Major peaks in the IR spectrum occur at 3071, 3050, 2975, 2925, 2843, 2810 (m), 1430 (s), 1251 (m), 1107 (vs), 985 (m), 820, 788, 733, 700, 487 (s), and 470 (m) cm⁻¹. Mass spectral peaks in >10% relative abundance occur at m/e values of 44 (15.9%), 105 (11.1%, $C_6H_5Si^+$), 151 (47.7%, $(C_6H_5)CH_3SiOCH_3^+$ (R)), 197 (100%, $(C_6H_5)_2SiCH_3^+$), and 198 (19.1%, $(C_6H_5)_2SiO^+$ (R)). Anal. Calcd: C, 74.32; H, 7.49. Found: C, 74.55; H, 7.35.

$CH_3O(CH_2)_2Si(C_6H_5)_2CH_3$. This new compound was obtained in 40% yield from the addition of 2-chloro-1-methoxyethane in THF to a –10 °C solution of diphenylmethylsilyllithium in THF. The product was purified in a manner similar to that for CH_3OCH_2-$Si(C_6H_5)_2CH_3$. Major peaks in the IR spectrum occur at 3072, 3051, 3020, 2925, 2896, 2870, 2823, 1485, 1456 (m), 1425 (s), 1380, 1255, 1205, 1187, and 1157 (m) cm⁻¹. Mass spectral peaks at >10% relative abundance occur at m/e values of 32 (66.1%), 105 (16.0%), 121 (12.3%), 151 (100%), 152 (13.2%), 179 (15.9%), 183 (13.4%), 197 (52.8%), 198 (12.3%), 213 (59.2%), and 214 (11.7%). Anal. Calcd: C, 74.94; H, 7.86. Found: C, 74.94; H, 7.66.

$CH_3O(CH_2)_3Si(C_6H_5)_2CH_3$. This new compound was obtained in 45% yield by reacting 3-chloro-1-methoxypropane with diphenylmethylsilyllithium in THF. The product was purified in a manner similar to that for $CH_3OCH_2Si(C_6H_5)_2CH_3$. Major peaks in the IR spectrum occur at 3070, 3052, 3015 (m), 2927 (s), 2825, 1480, 1456 (m), 1431, 1423 (s), 1380, 1256, 1210, 1180, 1150 (m), 1111 (s), 1059 (m), 787, 730, 701 (s), 485, 475, and 434 (m) cm⁻¹. Mass spectral peaks at >10% relative abundance occur at m/e values of 28 (14.3%), 44 (10.8%), 105 (19.4%), 121 (10.4%), 151 (56.2%), 181 (11.6%), 183 (11.1%), 193 (100%), 194 (16.9%), 195 (13.2%), 197 (82.5%), 198 (17.7%), and 213 (27.8%). Anal. Calcd: C, 75.50; H, 8.20. Found: C, 75.53; H, 8.46.

$CH_3O(CH_2)_4Si(C_6H_5)_2CH_3$. This new compound was obtained in ca. 10% yield from the dropwise addition of 4-bromo-1-methoxybutane