Synthesis and Characterization of Titanium Complexes Containing Potentially Tridentate Amido-Cyclopentadienyl Ligands

Jun Okuda*[+], Karen E. du Plooy, Werner Massa, Hak-Chul Kang, and Ulrich Rose

Fachbereich Chemie der Universität Marburg,
Hans-Meerwein-Straße, D-35032 Marburg, Germany

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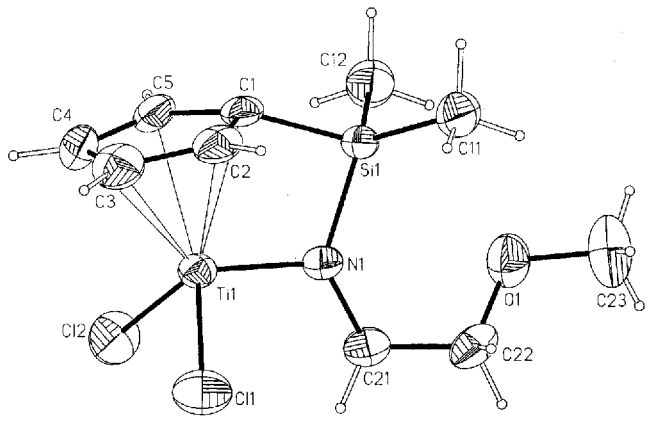
Two new titanium complexes of the general type Ti(η^5:η^1-$C_5H_4SiMe_2NCH_2CH_2X)Cl_2$ (X = NMe_2, OMe), containing a tridentate ligand, were prepared by reaction of Ti(η^5-$C_5H_4SiMe_2Cl)Cl_3$ with the lithium amide Li($NHCH_2CH_2X$) (X = NMe_2, OMe). The ^{1}H-NMR chemical shifts for the protons of the ethylene link were found to vary considerably as a function of the temperature, indicating the presence of an equilibrium between the tri- and bidentate bonding mode of the ligand. A single-crystal X-ray structural analysis of Ti(η^5:η^1-$C_5H_4SiMe_2NCH_2CH_2OMe)Cl_2$ revealed that the methoxy function is not intramolecularly coordinated in the solid state.

Functionalized cyclopentadienyl ligands[1] allow the synthesis of a wide variety of transition metal complexes with novel coordination spheres, which may be used in the control of the catalytic behavior of the metal center. In the context of designing new metallocene catalysts for olefin polymerization, amido-functionalized cyclopentadienyl ligands in particular have been of considerable recent interest[2]. Not only do they allow variation of the ring substituents and the nature of the bridge, which constitute common tools for the manipulation of Brintzinger-type ansa-metallocenes, but modification of the amido substituent[3] is also possible. In order to modulate the Lewis acidic group-4 metal center, we are studying potentially tridentate ligands by introducing an additional donor group[4].

Results and Discussion

Previously we noted that the reaction of the dilithium derivatives $Li_2(C_5H_4SiMe_2NCH_2CH_2X)$ (X = NMe_2, OMe) with $TiCl_4(THF)_2$, or with $TiCl_3(THF)_3$ followed by oxidation, unexpectedly led to the formation of the stable C_2-symmetric bis(ligand) complexes of the type Ti(η^5:η^1-$C_5H_4SiMe_2NCH_2CH_2X)_2$[5,7a] rather than to the mono(ligand) complexes Ti(η^5:η^1-$C_5H_4SiMe_2NCH_2CH_2X)Cl_2$. In contrast, Ti($\eta^5$:$\eta^1$-$C_5H_4SiMe_2NCH_2CH_2NMe_2)Cl_2$ could be obtained as orange crystals in good yield by the reaction of the easily prepared Ti(η^5-$C_5H_4SiMe_2Cl)Cl_3$[6] with 1.33 equivalents of Li($NHCH_2CH_2NMe_2$) in toluene, followed by work-up of the reaction mixture by filtering off LiCl and the ammonium salt $[NH_3CH_2CH_2NHMe_2]Cl_2$. ^{1}H-, ^{13}C-NMR-spectroscopic as well as mass-spectral and analytical data confirm the structure of a mono(ligand) complex. However, the nature of the additional bonding site remains undefined. Variable temperature ^{1}H-NMR spectra show a fairly strong shift of the signals due to the bridge methylene protons, compatible with fluxional behavior in solution. Thus, the triplet-like resonances due to the $NCH_2CH_2NMe_2$ group at δ = 3.31 and 3.68 at 25 °C are shifted to δ = 2.82 and ca. 2.59 upon cooling to −80 °C with concomitant line broadening. Likewise, the sharp singlet for the NMe_2 protons is significantly broadened at low temperatures. Despite the presumably higher Lewis acidity of the titanium center compared with that of the tetramethyl analog Ti(η^5:η^1-$C_5Me_4SiMe_2NCH_2CH_2NMe_2)Cl_2$[7], the dimethylamino group is apparently not more strongly coordinated[8]. On the other hand, a single-crystal structure analysis revealed that the additional donor site is unambiguously interacting with the titanium center, although considerable disorder in the $CH_2CH_2NMe_2$ chain precluded an accurate solution of the structure[9].

Figure 1. ORTEP diagram of the molecular structure of Ti(η^5:η^1-$C_5H_4SiMe_2NCH_2CH_2OMe)Cl_2$. Thermal ellipsoids are drawn at the 50% probability level



Selected bond distances (pm) and angles (°): Ti−N 187.4(3), Ti−C1 230.2(3), Ti−C2 231.3(3), Ti−C3 237.8(3), Ti−C4 239.2(3), Ti−C5 233.3(3), Ti−Cl1 226.2(1), Ti−Cl2 225.9(1); Cl1−Ti−Cl2 103.30(4), Ti1−N−Si1 108.76(14), C21−N−Ti 120.2(2), Si−N−C21 130.1(2).

Treatment of Ti(η^5-$C_5H_4SiMe_2Cl)Cl_3$ with Li($NHCH_2CH_2OMe$) resulted in the isolation of orange yellow crystals of Ti(η^5:η^1-$C_5H_4SiMe_2NCH_2CH_2OMe)Cl_2$ in good yield. ^{1}H-, ^{13}C-NMR-spectroscopic as well as mass spectral and analytical data are consistent with the desired constitution, whilst the bonding nature of the methoxy function again remained obscure. The low-temperature spectra show only a slight shift which indicate that the equilibrium between the intramolecularly coordinated structure and the

[+] New address: Institut für Anorganische Chemie und Analytische Chemie, Universität Mainz, J.-J.-Becher-Weg 24, D-55099 Mainz, Germany.

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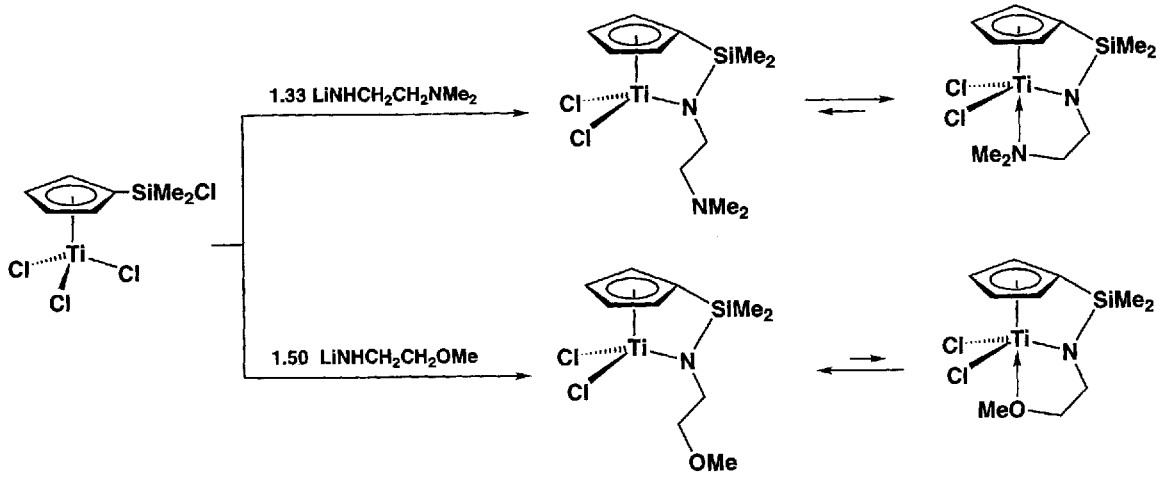
Scheme 1



"open" complex lies on the side of the latter. Further corroboration of this assumption came from the X-ray structural analysis of this complex, which unambiguously showed the absence of any bonding interaction between the methoxo group and the titanium center. Pertinent structure parameters of the molecule are comparable with those of similar complexes containing the amido-cyclopentadienyl ligand (Figure 1).

Thus, the amido nitrogen is planar and the short nitrogen–titanium bond length of 187.4(3) pm is due to a metal–ligand double-bond character[10]. Similar bond parameters were found in other half-sandwich titanium amido complexes, e.g., in $Ti(\eta^5\text{-}C_5H_5)Cl_2(NiPr_2)$[10b] and $Ti(\eta^5\text{-}C_5H_5)Cl_2(NHtBu)$[10c]. It is interesting to note that the OMe group, which is clearly less sterically demanding than the NMe_2 function, is not favored by the titanium center in an otherwise almost identical coordination sphere.

In conclusion, we have extended the method developed by Royo et al. for the preparation of linked amido-cyclopentadienyl titanium complexes to potentially tridentate ligand systems and characterized two examples of the type $Ti(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2NCH_2CH_2X)Cl_2$ (X = NMe_2, OMe). We are continuing to utilize this simple access with other ligand types.

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Experimental

All experiments were carried out under dry argon by using standard Schlenk techniques. Solvents were purified, dried, and distilled under argon. – ^1H and ^{13}C NMR: Bruker ARX 200, AC 300, AM 400, or AMX 500. – IR: Nicolet FT-5-DX. – Mass spectra: Varian CH 7. – Elemental analyses: Microanalytical laboratory of this department.

Dichloro[$\eta^5{:}\eta^1$-cyclopentadienyldimethylsilyl(N,N'-dimethylaminoethylamido)]titanium: A solution of $Ti(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2Cl)Cl_3$ (880 mg, 2.80 mmol) in 40 ml of THF was treated at 0 °C with $Li(NHCH_2CH_2NMe_2)$ (400 mg, 4.25 mmol) in small portions. The dark mixture was stirred for 1 h at 0 °C and for 2 h at room temp. All volatile compounds were removed under vacuum and the residue was extracted with 45 ml of a 1:2 mixture of dichloromethane/hexane. After filtration the extracts were first cooled to −18 °C whereupon a black oily material precipitated. Decantation and reduction of the volume gave brown crystals at −78 °C. Recrystallization from a mixture of dichloromethane and hexane (1:4) afforded 420 mg (1.28 mmol) of orange crystals; yield 45%; m.p. 103 °C. – ^1H NMR ($CDCl_3$, 25 °C): δ = 0.42 (s, 6H, $SiCH_3$), 2.60 [s, 6H, $N(CH_3)_2$], 3.14 ("t", 2H, CH_2NMe_2), 3.68 ("t", 2H, CH_2NSi), 6.30 (m, 2H, ring H), 7.08 (m, 2H, ring H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = −3.3 ($SiCH_3$), 47.5 [$N(CH_3)_2$], 54.6 ($SiNCH_2$), 60.8 (CH_2NMe_2), 112.1 (ring C attached to $SiMe_2$), 122.0, 129.0 (ring C). – EI-MS, *m/z* (%): 326 (1) [M^+], 240 (1) [$M^+ - NMe_2C_2H_4N$], 122 (5) [$C_5H_4SiMe_2^+$], 58 (100) [$NMe_2CH_2^+$]. – $C_{11}H_{20}Cl_2N_2SiTi$ (327.2): calcd. C 40.38, H 6.16, N 8.56; found C 40.16, H 5.92, N 8.52.

Dichloro[$\eta^5{:}\eta^1$-cyclopentadienyldimethylsilyl(2-methoxoethylamido)]titanium: To a solution of $Ti(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2Cl)Cl_3$ (780 mg, 2.50 mmol) in 40 ml of THF was added $Li(NHCH_2CH_2OMe)$ (320 mg, 3.95 mmol) at 0 °C. The brown mixture was stirred for 1 h at 0 °C and for 2 h at room temp. All volatile compounds were removed under vacuum and the residue stirred with 60 ml of hexane. After filtration the volume of the filtrate was reduced under vacuum until the crude product precipitated. Recrystallization from hexane afforded 430 mg (1.37 mmol) of yellow-brown crystals; 55% yield; m.p. 93 °C. – ^1H NMR ($CDCl_3$, 25 °C): δ = 0.49 (s, 6H, $SiCH_3$), 3.30 (s, 3H, OCH_3), 3.41 ("t", 2H, OCH_2), 4.46 ("t", 2H, NCH_2), 6.46 (m, 2H, ring H), 6.98 (m, 2H, ring H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 2.6 ($SiCH_3$), 56.9 (NCH_2), 58.3 (OCH_3), 71.8 (OCH_2), 111.3 (ring C at $SiMe_2$), 124.0, 126.1 (ring C). – EI-MS, *m/z* (%): 313 (4) [M^+], 268 (100) [$M^+ - CH_2OMe$], 241 (4) [$M^+ - 2$ HCl], 45 (21) [CH_2OMe^+]. – $C_{10}H_{17}Cl_2NOSiTi$ (314.1): calcd. C 38.23, H 5.45, N 4.46; found C 37.97, H 5.40, N 4.31.

X-ray Crystal Structure Analysis of Ti($\eta^5{:}\eta^1$-$C_5H_4SiMe_2NCH_2CH_2OMe$)Cl_2: Yellow cubes of $Ti(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2NCH_2CH_2OMe)Cl_2$ were obtained by slow cooling in hexane. Cell dimensions and intensity data were obtained with an Enraf-Nonius CAD-4 diffractometer: $C_{10}H_{17}Cl_2NOSiTi$, M = 314.14, a = 1107.3(1), b = 793.1(1), c = 1723.9(2) pm, β = 103.69(1)°, Z = 4, $d_{calc.}$ = 1.419 Mgm^{-3}, monoclinic, $P2_1/n$, Cu-K_α (λ = 154.178 pm), graphite monochromator, 0.50 × 0.40 × 0.25 mm, T = 193(2) K, 4.00° < Θ < 60.00°, $F(000)$ = 648. Number of reflections measured 2346, 2188 independent reflections [R(int) = 0.0356] of which 1993 were assigned observed [$I > 2\sigma(I)$], absorption coefficient 4.384 mm^{-1}. The structure was solved by direct methods and difference Fourier synthesis and refined against all F^2 data (SHELX-86[11a],

SHELXL-93[11b]). All non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were calculated at their idealized positions. The refinement converged at residuals $wR2 = 0.1258$ for all reflections, corresponding to a conventional $R = 0.0435$ for the observed F_0 data. The maxima and minimum electron density was 0.483 and $-0.794 \cdot 10^{30}$ em^{-3}, respectively[12].

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