Titanium(III) Compounds with η^2-Pyrazolato Ligands

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The reduction of $[L_2TiCl_2]$ (**1**) (L = 3,5-*tert*-butylpyrazolate) with 1% Na/Hg in tetrahydrofuran (THF) affords the complex $[L_2TiCl(THF)_2]$ (**2**), which crystallizes from hexane in moderate yield. The analogous reduction carried out in toluene gives dimeric $[(L_2TiCl)_2]$ (**3**) in high yield. If the reduction time is extended to 3 days, the complex $[L_3Ti]$ (**4**) is isolated as light blue crystals in low yield. An alternative procedure for preparing compound **4** requires mixing $[TiCl_3(THF)_3]$ with 3 equivalents of potassium 3,5-*tert*-butylpyrazolate in toluene. Crystallization from hexane affords **4** in high yield. Crystallographic data for **2**, **3** and **4** are presented.

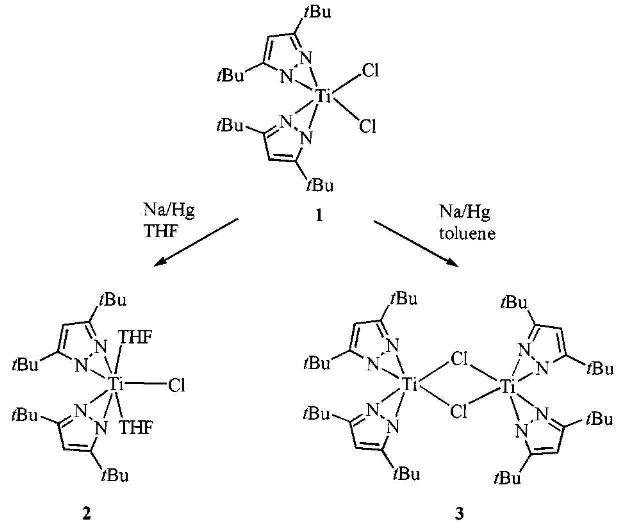
Introduction

In the search for alternatives to the ubiquitous cyclopentadienyl ligand there has been considerable interest in other monoanionic species that may serve as ancillary ligands for early transition metals and that allow a better control of the electronic and steric properties. In particular, nitrogen-based systems have received considerable attention such as trispyrazolylborates,[1] amides,[2][3] amidinates,[4] aminoiminophosphoranates[5] and others.[6−8] A recent example that has caught our attention is the use of 3,5-disubstituted pyrazoles as ancillary ligands in early transition metal chemistry.[9−11] The coordination of pyrazole derivatives to mid- and late transition metals has been thoroughly investigated over many years. Of the four possible modes (bridging, η^1, η^2 and η^5), mainly bridging and η^1 have been observed.[12] The work of two research groups indicates that η^2-coordination towards early transition metals is favorable as they were able to isolate and structurally characterize several Ti^{IV}, Zr^{IV} and Ta^{V} complexes containing η^2-pyrazolato ligands.[10,13−15] According to a theoretical study[10] the presence of empty d-orbitals seems to be an important feature for η^2-coordination and, so far, all of the reported systems are d^0 metal complexes. Very recently, η^5-coordination has been reported for a late transition metal.[16] For a better understanding of the electronic features of these interesting systems we started to investigate the reduction chemistry of $[L_2TiCl_2]$. Our results can be compared to related Ti^{III} systems that contain other N-donor ligands such as amides,[3][17] N_4-macrocycles[18][19] or amidinates.[20][21]

Herein we report the synthesis and the molecular structure of three titanium(III) complexes that contain pyrazolato ligands. In all of these compounds the coordination mode of the pyrazolato ligand is exclusively η^2 and, to our knowledge, these represent the first d^1 metal complexes that contain η^2-pyrazolato ligands.

Results and Discussion

The starting material for our reduction chemistry is $[L_2TiCl_2]$ (L = 3,5-*tert*-butylpyrazolato = 3,5-tBu$_2$pz) **(1)**, first reported by Guzei and Winter.[22] We found that this compound can be conveniently synthesized by the addition of two equivalents of 3,5-tBu$_2$pzH to $TiCl_4(THF)_2$ in the presence of triethylamine in dichloromethane. Removal of the solvent, extraction and crystallization from hexane gave the product as yellow crystals in high yield. This synthetic route represents a slight modification to an improved procedure recently described.[13]



Scheme 1. Reduction of $[L_2TiCl_2]$

A 1% Na/Hg amalgam reduction of compound **1** at 0 °C in THF gave paramagnetic $[L_2TiCl(THF)_2]$ **(2)** after 2 h, in moderate yield, which was isolated as blue crystals from hexane as shown in Scheme 1. The ^1H NMR spectrum shows broad signals in the range 1.55−2.16 ppm for $(CCH_3)_3$ and the β-protons of the coordinated THF molecules, and at 4.8 ppm for the α-protons of THF. Infrared spectroscopy also indicates the presence of THF, since in comparison to $[(L_2TiCl)_2]$ (vide infra) the IR spectrum

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shows two additional absorptions (1029 and 872 cm^{-1}). X-ray crystallography reveals a monomeric species with a pentacoordinated titanium atom in a trigonal bipyramidal environment, considering the pyrazolato ligands as occupying one coordination site each. The metal is further coordinated to two THF molecules and a Cl atom. Figure 1 shows an ORTEP view of the molecule, along with selected bond lengths and angles. The two THF molecules occupy the apical positions with an O1−Ti1−O2 angle of 176.2°. The four nitrogen atoms, the chloride and the titanium atom are in the equatorial plane to within a few degrees. The angles between each of these atoms and O1 or O2 vary within the range 86−93°. As expected, the length of the titanium chloride bond [2.4143(8) Å] is slightly longer than that in the titanium(IV) compound [L_2TiCl_2] [2.247(4) and 2.251(3) Å][22] due both to the larger covalent radius of Ti^{III} vs. Ti^{IV} and the higher coordination number. The structure is similar to the related compound [$(BTBA)_2TiCl(THF)$][20] [BTBA = *N*,*N*′-bis(trimethylsilyl)benzamidinate], where only one THF molecule is coordinated to Ti. In addition, it is noteworthy that the reduction of [Cp_2TiCl_2] in THF yields the base-free [$(Cp_2TiCl)_2$][23] suggesting that not only steric factors are responsible for the structure of compound **2**. The more electrophilic nature of the pyrazolato ligand relative to the cyclopentadienyl ligand leads to a rather electrophilic metal center which is stabilized by the coordination of additional base (two THF molecules).

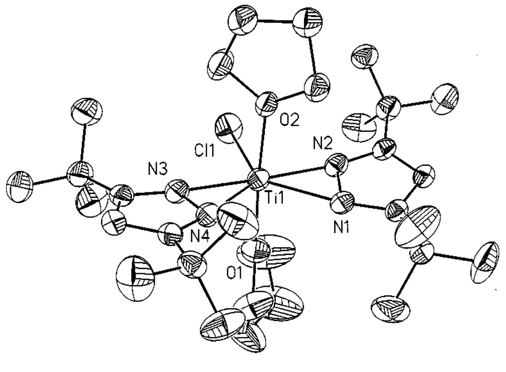


Figure 1. ORTEP view of [$L_2TiCl(THF)_2$] **(2)** drawn with 50% thermal ellipsoids; selected bond lengths (Å) and angles (°): Ti1−Cl1 2.4143(8); N1−Ti1−O1 86.67(8), N2−Ti1−O1 91.91(8), N3−Ti1−O1 89.91(8), N4−Ti1−O1 93.36(8), Cl1−Ti1−O1 91.26(6), N1−Ti1−O2 89.54(7), N2−Ti1−O2 85.50(7), N3−Ti1−O2 92.71(8), N4−Ti1−O2 86.96(8), Cl1−Ti1−O2 91.60(5).

In an analogous reaction, 1% Na/Hg amalgam reduction of compound **1** at 0 °C in toluene followed by workup in hexane gave blue-green crystals in high yield. X-ray crystallography reveals the species to be the base-free dimer [$(L_2TiCl)_2$] **(3)**. Figure 2 shows an ORTEP view of the molecule, along with selected bond lengths and angles. The structure is similar to the related titanocene derivative [$(Cp_2TiCl)_2$], which is also dimeric.[24] The Ti−Cl bonds [2.4265(8) Å and 2.4299(8) Å] are slightly shorter than in [$(Cp_2TiCl)_2$] (average 2.543 Å). However, the bond angles in the Ti_2Cl_2 core [Cl−Ti−Cl 89.59(2)° and Ti−Cl−Ti 90.41(2)°] contrast sharply with those in [$(Cp_2TiCl)_2$] (average Cl−Ti−Cl 77.98°, average Ti−Cl−Ti 101.96°). These trends (the shorter M−Cl bond length and the different angles in the Ti_2Cl_2 core) can be attributed to the smaller steric constraint in the molecule. The bite angle between the two ligands (considering the center of the N−N bond as the coordination site) is in the same range for compound **3** (116.6°) and [L_2TiCl_2] (113°).[22]

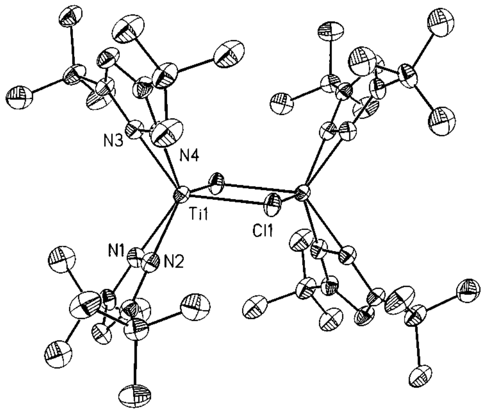
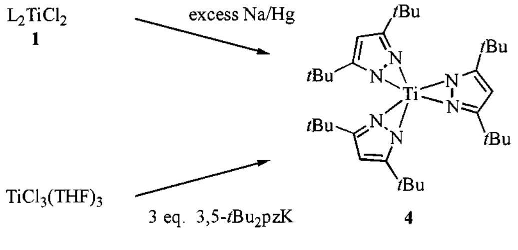


Figure 2. ORTEP view of [$(L_2TiCl)_2$] **(3)** drawn with 50% thermal ellipsoids; selected bond lengths (Å) and angles (°): Ti1−N1 2.027(2), Ti−N2 2.043(2), Ti−N3 2.040(2), Ti−N4 2.029(2), Ti1−Cl1 2.4265(8), Ti1−Cl1a 2.4299(8); Cl1−Ti−Cl1a 89.59(2), Ti1−Cl1−Ti1a 90.41(2); equivalent atoms "a" generated with: $-x + 1, -y, -z - 1$.

Reduction with an excess of Na/Hg over 3 days gave a black reaction mixture, from which, after extraction with hexane, light blue crystals could be isolated in low yield. X-ray crystallography revealed a titanium(III) species [L_3Ti] **(4)** containing three η^2-pyrazolato ligands. Alternatively, complex **4** has been synthesized conveniently and in high yield directly from $TiCl_3(THF)_3$ by the addition of 3 equivalents of *t*Bu_2PzK in toluene. Figure 3 shows an ORTEP view of the molecule, along with selected bond lengths and angles. The molecule has a crystallographic threefold axis running through Ti^{III}. The TiN_6 core is almost perfectly trigonal prismatic with a small deviation of 6° (angle between the projection of N1 and N2 onto a plane perpendicular to the C_3 axis). This is in contrast to the structure of [$(PhNC(H)NPh)_3Ti$], a related Ti^{III} compound with a TiN_6 core.[21] Its structure is best described as distorted trigonal antiprismatic. Due to the constraint imposed by the pyrazolato ring on the 1,2-*N*,*N*-bond length, a further tilting of the ligand cannot achieve an antiprismatic environment of the metal and leads to a higher steric repulsion between neighboring ligands.



Scheme 2. Formation of [L_3Ti]

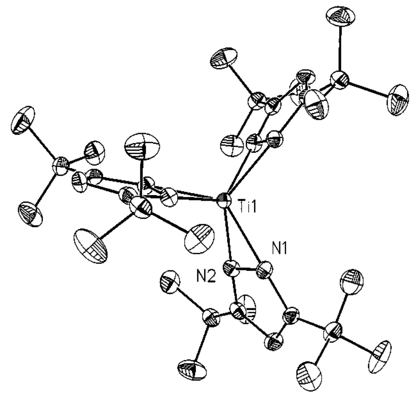


Figure 3. ORTEP view of [L_3Ti] **4** drawn with 50% thermal ellipsoids. Selected bond lengths (Å) and angles (°): Ti1−N1 2.034(3), Ti1−N2 2.038(3), N1−Ti1−N1b 109.37(1), N1−Ti−N1c 109.37(1), N1b−Ti−N1c 109.37(1); equivalent atoms "b" and "c" generated with: b = $-x + 1, -x + y, z$; c = $x - y + 1, -y + 1, z$).

In reactions with other reducing agents such as Mg, Zn or KC_8 the only isolable product was the homoleptic [L_3Ti] (**4**). The mechanism of formation of compound **4** in the reduction reaction is unclear. We assume that, initially, the system is reduced to Ti^{II}, but that bridging η^1-coordination then starts to compete with η^2-coordination at the large and electron-rich metal center. In addition, for steric reasons η^1-coordination is less favorable, although one example of a late transition metal has been reported.[25] Therefore such a bridging η^1 titanium(II) species is presumably not stable and disproportionates to [L_3Ti] and insoluble elemental titanium indicated by the black reaction mixtures. On these grounds it is less surprising that in several reduction reactions of [L_2TiCl_2] under 1 bar of N_2, C_2H_4 or CO the homoleptic titanium(III) species **4** has been isolated exclusively.

We have shown that η^2-coordination of pyrazolato ligands is favored for titanium centers with partially filled d-orbitals. However, very low oxidation states are not favored because, presumably, η^1-coordination starts to compete. So far, no reactivity at the ligands itself (such as C−H bond activation) has been observed. Therefore, as long as oxidation states are high to medium, η^2-pyrazolates may prove to serve as innocent ancillary ligands for a variety of metal centers.

Experimental Section

All reactions were carried out under dry nitrogen using standard Schlenk techniques. Solvents were dried by distillation from sodium/benzophenone or sodium/potassium alloy. [L_2TiCl_2] was prepared according to a literature procedure.[13] NMR spectra were recorded with a Bruker AC 250 spectrometer. IR samples were prepared as mineral oil mull, taken between KBr plates and obtained with a Bio-Rad FTS7 spectrometer. Mass spectra were obtained with a Finnigan MAT 8200 or MAT 95 spectrometer. Elemental analyses were performed in our institute.

[$L_2TiCl(THF)_2$] (2): A solution of **1** (0.71 g, 1.45 mmol) in THF (30 mL) was treated with one equivalent of 1% Na/Hg (0.037 g Na) at 0°C for 2 h. The solvent was removed under reduced pressure, the resulting blue-green mixture extracted with hexane (30 mL) and filtered through Celite. Complex **2** was isolated at −25°C as blue crystals (0.45 g, 53%). − ^1H NMR (C_6D_6): δ = 4.8 (br s, 8 H, α-H of THF), 2.16 (br s, 8 H, THF), 1.55 [br s, 36 H, $C(CH_3)_3$]. − IR (CsI): $\tilde{\nu}$ = 1508, 1361, 1252, 1233, 1029, 1020, 993, 872, 802, 720, 500, 478, 395, 322, 282 cm^{-1}. − MS: m/z = 441 [M^+ − 2THF]. − $C_{30}H_{54}ClN_4O_2Ti$ (586.10): calcd. C 61.48, H 9.29, N 9.56; found C 60.06, H 9.13, N 9.41.

[$L_2TiCl]_2$ (3): A solution of **1** (0.37 g, 0.78 mmol) in toluene (30 mL) was treated with 1% Na/Hg (0.023 g Na) at 0°C for 2 h. The solvent was removed under reduced pressure, the resulting blue-green mixture extracted with hexane (30 mL) and filtered through Celite. Complex **3** was isolated at −25°C as green crystals (0.29 g, 83%). − ^1H NMR (250 MHz, C_6D_6): δ = 6.04 (s, 2 H, C*H*), 1.30 [s, 36 H, $C(CH_3)_3$]. − IR (CsI): $\tilde{\nu}$ = 1506, 1364, 1253, 1233, 1018, 982, 820, 806, 719, 492, 399, 387, 323 cm^{-1}. − MS: m/z = 441 [$M^+/2$]. − $C_{44}H_{76}N_8Cl_2Ti_2$ (883.77): calcd. C 59.80, H 8.67, N 12.68; found C 59.40, H 8.85, N 12.59.

[L_3Ti] (4). Method 1: A solution of **1** (0.47 g, 0.98 mmol) in toluene (30 mL) was treated with an excess of 1% Na/Hg (0.113 g Na) for 3 days. The solvent was removed under reduced pressure, the resulting dark brown mixture extracted with hexane (30 mL) and filtered through Celite. Complex **4** was isolated at −25°C as light blue crystals (0.15 g, 26%).

Method 2: $TiCl_3(THF)_3$ (0.62 g, 1.7 mmol) and tBu_2pzK[26] (1.15 g, 5.3 mmol) were placed in a Schlenk flask and toluene was added. The mixture was stirred at room temperature for 5 h. The volatiles were removed under reduced pressure and the residue was extracted with 30 mL of hexane. Complex **4** was isolated at −25°C as light blue crystals (0.80 g, 82%). − ^1H NMR (250 MHz, C_6D_6): δ = 2.05 [br s, $C(CH_3)_3$]. − IR (CsI): $\tilde{\nu}$ = 1529, 1364, 1252, 1232, 1020, 991, 808, 721, 501, 408 cm^{-1}. − MS: m/z = 585 [M^+]. − $C_{33}H_{57}N_6Ti$ (585.71): calcd. C 67.67, H 9.81, N 14.35; found C 67.53 H 10.39 N 14.29.

X-ray Crystal Structure Analysis

The crystals were mounted on a glass fiber in a rapidly cooled perfluoropolyether.[27] Diffraction data were collected on a Stoe-Siemens-Huber four-circle diffractometer coupled to a Siemens CCD area-detector at 153(2) K for **2** and 133(2) K for **3** and **4**, with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), performing φ- and ω scans. The structures were solved by direct methods using SHELXS-97[28] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[29] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model.

Compound 2: The single-crystal X-ray structure shows **2** to crystallize in the tetragonal space group $P4_2/n$ with one molecule in the asymmetric unit. One of the coordinated THF molecules is heavily disordered and was refined on two positions. Three difference electron density peaks near the inversion center at 0.25, 0.25, 0.25 were refined as a THF molecule with an occupancy of 0.25, using similarity restraints for 1−2 and 1−3 interatomic distances (bond lengths and angles) and displacement parameters.

Compound 3: The asymmetric unit contains half a molecule of compound **3** and a partially occupied molecule of toluene, which is disordered over the inversion center. Two of the four *t*Bu groups are heavily disordered and were refined on three positions.

Compound 4: The data for compound **4** were modeled as merohedrally twinned using the twin matrix (-1,0,0; 0,-1,0; 0,0,1). The twinning parameter refined to a value of 0.457(3). The three highest

Table 1. Crystal data and data collection parameters

Compound	**2**	**3**	**4**
Empirical formula	$C_{30}H_{54}ClN_4O_2Ti{\cdot}0.25THF$	$C_{22}H_{38}ClN_4Ti{\cdot}0.5toluene$	$C_{33}H_{57}N_6Ti$
Formula weight [g/mol]	602.13	487.98	474.78
Crystal size [mm]	0.3 × 0.3 × 0.2	0.4 × 0.4 × 0.3	0.4 × 0.3 × 0.3
Crystal system	tetragonal	triclinic	trigonal
Space group	$P4_2/n$	$P1$bar	$P3$bar
Unit cell	a = 25.577(4) Å b = 25.577(4) Å c = 10.652(2) Å α = 90° β = 90° γ = 90°	a = 10.202(2) Å b = 10.338(2) Å c = 14.686(3) Å α = 70.945(3)° β = 70.738(3)° γ = 84.110(3)°	a = 14.582(3) Å b = 14.582(3) Å c = 10.453(5) Å α = 90° β = 90° γ = 120°
Volume [Å^3]	V = 6968(2)	V = 1382.1(5)	V = 1924.8(11)
Z	8	2	2
Density [Mg/m^3]	1.148	1.173	1.011
Absorption coefficient	0.354 mm^{-1}	0.425 mm^{-1}	0.249 mm^{-1}
F(000)	2600	524	638
Reflections collected	108057	9473	28131
Reflections unique	6139 (R_{int} = 0.0941)	4847 (R_{int} = 0.0289)	2278 (R_{int} = 0.0710)
Data/Restr./Param.	6139 /210/437	4847/176/354	2278/0/122
Data collection range	2.07 ≤ 2Θ ≤ 25.00°	2.17 ≤ 2Θ ≤ 25.18°	2.53 ≤ 2Θ ≤ 25.00°
Final R indices [$I>2\sigma(I)$][a]	$R1$ = 0.0431 $wR2$ = 0.1071	$R1$ = 0.0405 $wR2$ = 0.0981	$R1$ = 0.0566 $wR2$ = 0.1908
Final R indices (all data)	$R1$ = 0.0747 $wR2$ = 0.1219	$R1$ = 0.0644 $wR2$ = 0.1046	$R1$ = 0.0637 $wR2$ = 0.1846
Goodness-of-fit on F^2 [b]	1.008	1.010	1.336
Largest diff. peak and hole	0.390 and −0.242 eÅ^{-3}	0.462 and −0.366 eÅ^{-3}	1.905 and −0.338 eÅ^{-3}

[a] $R1 = \Sigma|F_o - F_c|/\ \Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$. – [b] Goodness of fit $S = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma\ (n\text{-}p)]^{1/2}$).

difference density peaks are located on the threefold axis and result from a disordered hexane molecule.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-129633 (**2**), -129627 (**3**) and -129636 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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