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TRICHLORO-(2,6-DITERTBUTYLPHENOXO)-TITANIUM(IV): SYNTHESIS AND X-RAY STRUCTURE

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Abstract—The reaction of Na(2,6-^{t}Bu$_2$-C_6H_3O) with $TiCl_4$ in toluene gave $TiCl_3$(2,6-^{t}Bu-C_6H_3O) (compound **1**). Dark red crystals suitable for X-ray diffraction analysis were obtained by sublimation or cooling the product in hydrocarbon solvent to −20°C. Structural analysis showed that compound **1** is monomeric and titanium atom occupies the distorted tetrahedral environment surrounded by three chlorides and one bulky phenoxo group. The Ti—OAr bond of complex is very short which indicates that there is a Ti—O multiple bond.

Bulky aryloxide and alkoxide complexes of transition metals are of continuing interest in organometallic chemistry.[1–3] Aryloxide compounds of group 4 metals can be used as an alternative to cyclopentadienyl compounds to provide a coordinatively unsaturated d^0 metal complexes with reducible Cl-ligands.[4,5] These are of special interest in olefin polymerization reactions.

The steric properties of the alkoxo ligands is an important aspect in metal alkoxide chemistry. Simple alkoxo and phenoxo ligands tend to act as bridging groups causing the oligomerization of metal complexes.[6,7] This can be prevented by using a sterically crowded alkoxo group, e.g. 2,6-dialkyl substituted phenoxo ligand. The 2,6-dialkyl substitution of phenols in many cases prevents the formation of oxygen bridges, and the transition metal complexes of these ligands are usually monomeric.[8–10]

In the present study we replaced one Cl-ligand in $TiCl_4$ with a sterically bulky aryloxide ligand to obtain a monomeric d^0 titanium(IV) complex with three halide ligands. We present the synthesis and the crystal structure of trichloro-(2,6-ditertbutylphenoxo)-titanium(IV). The complex has been shown to be active in olefin polymerization reactions.

EXPERIMENTAL

All manipulations were carried out under argon using standard Schlenk techniques. 2,6-Ditertbutylphenol (>98%, Fluka Chemica) was purified by distillation under reduced pressure. The *n*-butyl lithium used was a 1.6 M solution in hexane (Merck) and metallic Na was pro analysis grade (Merck). Toluene (pro analysis grade, R. P. Normapur), THF (Rathburn, HPLC grade) and pentane (analytical grade, Lab-Scan) were dried and purified by refluxing on $LiAlH_4$ followed by distillation under argon. The purity of $TiCl_4$ (Aldrich) was 99.9%. NMR data was recorded with a Varian Gemini-200 spectrometer (200 MHz).

Synthesis of sodium compound of 2,6-ditertbutylphenol (NaOAr′)

2,6-Ditertbutylphenol (5 g; 0.024 mol) was dissolved in toluene and metallic Na (0.4 g; 0.017 mol) was added. The reaction mixture was refluxed for 6 h. When the sodium melted, the white solid began to form rapidly. The white precipitation was recrystallized from THF. The yield of the THF solvate of NaOAr′ was 10 g (80%).

Synthesis of the trichloro-(2,6-ditertbutyl)phenoxo-titanium(IV) (**1**)

$TiCl_4$ (0.52 cm^3; 0.0047 mol) was added dropwise to a stirred toluene suspension of NaOAr′ (3.5 g,

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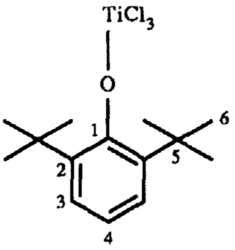
0.0047 mol) at $-78^\circ C$. The reaction mixture was allowed to warm to room temperature and it was stirred overnight. Toluene was then evaporated under reduced pressure and the resulting mixture of the Ti-complex and NaCl was extracted with pentane. The extract was filtered through Celite to remove the NaCl. Pentane was evaporated *in vacuo*. The product was sublimed and transferred to $-20^\circ C$. The yield of the deep red crystals which formed was 1.1 g (65%).

^1H-NMR shifts (ppm, in $CDCl_3$, TMS = 0) : δ 7.15 (d, 2H), δ 6.82 (t, 1H), δ 1.45 (s, 18H). ^{13}C-NMR shifts (ppm, in $CDCl_3$, TMS = 0) : δ 150.17 (C1), δ 141.04 (C2), δ 126.22 (C3), δ 121.93 (C4), δ 39.95 (C5), δ 32.25 (C6).



X-Ray data collection and structure determination

One crystal was transferred from the mother liquid to an inert oil and cooled down to $-120^\circ C$. The manipulation of the air sensitive crystal was according to the method of Hope.[11] The ω–2θ data collection was carried out with a Rigaku AFC-7S diffractometer using Mo K_α ($\lambda = 0.71073$) radiation. The data for structure determination were corrected for absorption and decay. The structure was solved and refined using the SHELXTL[12] program. In the refinements hydrogen atoms were placed on calculated positions (Structure 1). The details for crystal analysis, data collection and structure determination and refinement are given in Table 1. Selected bond lengths and angles are listed in Table 2.

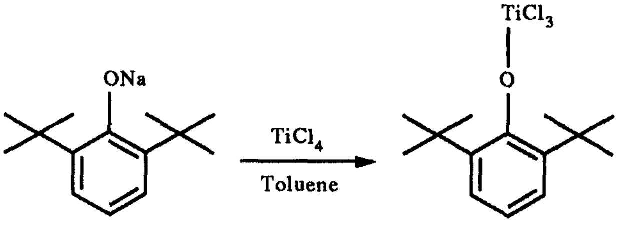
Table 1. Summary of crystal data, intensity collection and structure refinement for **1**

Formula	$C_{14}H_{21}Cl_3O_1Ti_1$
Fw	359.6
Space group	P2(1)/c
a (Å)	16.201(4)
b (Å)	9.549(4)
c (Å)	11.111(5)
β (°)	93.89(3)
Z	4
V (Å^3)	1714.9(9)
d(calc) (Mg m^{-3})	1.393
Cryst. size (mm)	0.40 × 0.30 × 0.30
Cryst. colour	deep red
Temp. (°C)	−120
Rad. wavelength (Å)	MoαK (0.71073)
Linear abs. coeff. (cm^{-1})	9.56
Abs. correction	psi-scan
Trans. factor range	0.93–1.00
Diffractometer	Rigaku AFC-7S
Scan method	ω–2θ
Scan rate (° min^{-1})	8–32
2θ range (°)	3–53
No. of unique data	2730
No. of data with $F_0 > 5.0\sigma(F)$	1871
No. of parameters	193
$R(F)$	0.050
$wR(F)$	0.057
Weighting scheme	$w = 1[\sigma^2(F)+0.0005F^2]$
Goodness of fit	1.19
Largest Δ/σ	0.00

RESULTS AND DISCUSSION

2,6-Ditertbutylphenoxo ligand was introduced to titanium(IV) halide as a sodium compound (NaOAr′) in hydrocarbon solvent (Scheme 1).

The treatment of $TiCl_4$ with 1 equiv. of NaOAr′



(1)

Scheme 1. Derivation of $TiCl_3(2,6\text{-}^tBu_2C_6H_3O)$ **1** from NaOAr′.

Table 2. Selected bond distances (Å) and angles (°) for **1**

Ti(1)—Cl(1)	2.196(2)	Ti(1)—Cl(2)	2.190(2)
Ti(1)—Cl(3)	2.188(2)	Ti(1)—O(1)	1.748(4)
Cl(1)—Ti(1)—Cl(2)	106.8(1)	Cl(1)—Ti(1)—Cl(3)	107.4(1)
Cl(2)—Ti(1)—Cl(3)	107.8(1)	Cl(1)—Ti(1)—O(1)	111.7(1)
Cl(2)—Ti(1)—O(1)	114.3(1)	Cl(3)—Ti(1)—O(1)	108.5(1)
Ti(1)—O(1)—C(1)	166.5(3)		

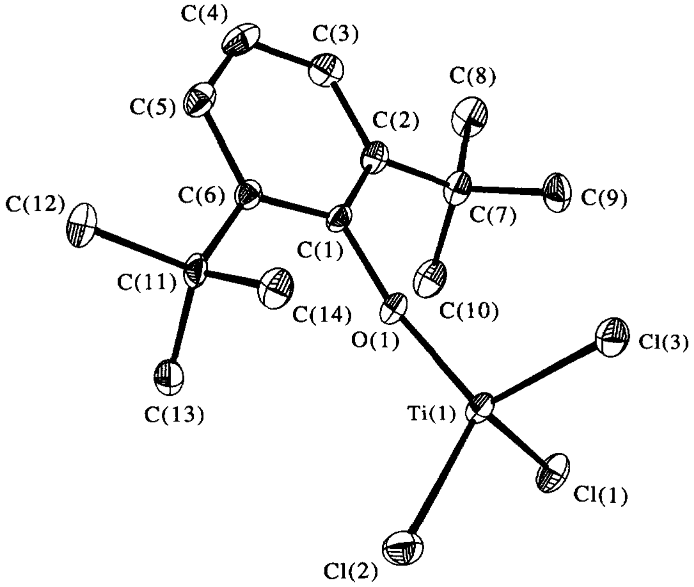


Fig. 1. The atom numbering scheme of ORTEP-view of $TiCl_3(2,6\text{-}^tBu_2C_6H_3)$ **1** (hydrogen atoms omitted for clarity).

yielded an air sensitive, deep red compound **1**. The use of toluene as reaction medium prevented the coordination of additional ligands (solvent molecules) to the titanium atom. Compound **1** has three reducible chloride ligands and shows high coordinative unsaturation. The complex can be crystallized at low temperatures in hydrocarbon solvents. It is very soluble in any hydrocarbon solvent. The compound sublimes at 150°C, 8 mmHg without decomposition. Figure 1 shows the ORTEP-view of compound **1**.

Compound **1** is monomeric, the 2,6-ditertbutyl substitution of phenol prevents the formation of oxygen bridges between the metal atoms. Monomeric form is a common feature of group 4 metal complexes containing bulky phenoxo ligands.

In the compound **1** the coordination sphere of titanium is a distorted tetrahedron. The titanium atom is surrounded by three chlorides and one bulky phenoxo group. The X—M—O angles vary between 108.5(1) and 114.3(1)° and X—M—X angles vary from 106.8(1)° to 107.8(1)°, due to steric bulk of the phenoxo ligand. The M—OAr′ distance is very short, 1.748(4) Å, significantly shorter than in titanium(III) monophenoxo complex [1.807(8) Å].[1] That bond is also considerably shorter than the calculated covalent bond length (2.01 Å) for a Ti—O single bond,[9] which supports the fact that there is a Ti—O multiple bond. Also the bent M—O—Ar′ angle, 166.5(3)° can be taken as indicative of π bonding between oxygen and Ti.

The reactivity of compound **1** as an active species in polymerization of olefins have been studied in the copolymerization of styrene and ethylene. The complex produced a homogeneous mixture of polyethylene and atactic polystyrene.[13]

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