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# Group 4 Metal Alkoxo Complexes as Catalysts for Olefin Polymerization: Synthesis and Crystal Structure of Bis(dibenzoylmethanate)dichlorotitanium(IV)

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Two equivalents of lithiated 1,3-diphenyl-1,3-propanedione react with $TiCl_4$ to produce a bis-β-diketonate complex, *cis*-dichlorobis(1,3-diphenyl-1,3-propanedionato)titanium(IV) [*cis*-$(bzbz)_2TiCl_2$] in good yield. The deep red crystalline complex was characterized by X-ray diffraction. *Cis*-$(bzbz)_2TiCl_2$ crystallizes in the orthorhombic space group *Pbca* (no. 61) with $a=16.214(3)$, $b=17.300(3)$, $c=18.967(4)$ Å and $Z=4$. The octahedral complex adopt the *cis*-configuration which is typical for (β-diketonate)$_2M^{IV}X_2$ complexes.

Group 4 metal complexes of β-diketonate ligands have been a subject of considerable interest since the 1960s.[1–6] The mechanism of rearrangement of stereochemically nonrigid octahedral bis-chelate complexes, (β-diketonate)$_2M^{IV}X_2$ (M = Group 4 metal, X = halide, alkoxide etc.), have been studied by many researchers.[7–10] The mechanism for rearrangement is proposed to be a torsional twist that produces a six-coordinate trigonal prismatic transition state.[8] Rearrangement has also been proposed to occur via reversible dissociation of the X ligand (or one end of the chelate ligand) to produce a five-coordinate cationic intermediate.[7] Harrod and Taylor have proposed that the reactive intermediate resembles a tightly bound ion-pair.[9]

Most of the (β-diketonate)$_2M^{IV}X_2$ complexes adopt the *cis*-configuration, although steric factors favour the *trans*-configuration. Electronic factors obviously stabilize the *cis*-configuration. The existence of a π-electron interaction between the metal and chelate ligand is believed to be the *cis*-stabilizing electronic factor.[8]

The properties of most (β-diketonate)$_2M^{IV}X_2$ complexes have been studied by variable-temperature NMR and IR methods in solution in the 1960s and 1970s.[7–10] Surprisingly, there are few solid-state structural data available of *bis*-chelate complexes of the titanium(IV) ion.[11] It is now possible to study structures of easily hydrolyzable complexes through improvements in crystal handling at low temperatures and the availability of stable low temperature devices in X-ray diffractometers.

In the present paper we report the synthesis and structural characterization of a (β-diketonate)$_2M^{IV}X_2$ complex, *cis*-dichlorobis(1,3-diphenyl-1,3-propanedionato) titanium(IV).

The motive behind this study is to synthesize early transition metal alkoxo complexes which could be used as soluble catalysts in the polymerization of olefins.[12] The complex reported here is shown to be highly active in the polymerization of ethylene, when MAO (methylaluminiumoxane) is used as cocatalyst.[13]

## Experimental

All manipulations were performed under an argon atmosphere by using standard Schlenk techniques. Dibenzoylmethane (Fluka Chemica, >98%) was recrystallized twice from diethyl ether before use. Methyllithium (Merck) used was a 5% solution in diethyl ether. The purity of $TiCl_4$ (Aldrich) was 99.9%. Diethyl ether (Merck, pro analysis grade) and toluene (R.P. Normapur, pro analysis grade) were dried and purified by refluxing on $LiAlH_4$ followed by distillation under an argon atmosphere. Dichloromethane (Merck, pro analysis grade) was dried by refluxing on phosphorus pentoxide followed by distillation under an argon atmosphere.

*Synthesis of* cis-*dichloro-bis(1,3-diphenyl-1,3-propanedionato) titanium(IV).* 3.0 g (0.0134 mol) of 1,3-diphenyl-1,3-propanedione was dissolved into diethyl ether. The solution was cooled to −78 °C and 8.5 cm$^3$ (0.0136 mol) of methyllithium were added dropwise. The reaction mixture was allowed to warm to room temperature and

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was stirred for 2 h. Diethyl ether was then evaporated under reduced pressure. The resulting white solid was redissolved into dichloromethane and cooled to −78 °C. 0.74 $cm^3$ (0.0067 mol) of $TiCl_4$ were added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 2 h. The resulting deep red mixture was filtered through Celite, and dichloromethane was evaporated. The product was recrystallized twice from toluene–dichloromethane (1:6). The yield of deep red crystalline [*cis*-(bzbz)$_2$TiCl$_2$] was 3.3 g (86%).

*X-Ray data collection and structure determination.* Information concerning the crystal data and structure refinement of [*cis*-(bzbz)$_2$TiCl$_2$] is given in Table 1. Owing to their high air and moisture sensitivity, the crystals were transferred from a Schlenk bottle under an argon atmosphere into polyfluoropolyether oil (RS 3000, Riedel-de Haen, Seelze, Germany) and mounted on the tip of a glass fiber using the oil-drop technique.[14,15] The quality of the crystals was poor, which is typical for many titanium alkoxo(β-diketonato) complexes, and thus the number of observed reflections is low and the resolution quite limited. Intensities were collected by ω–2θ scan mode with a Rigaku AFC-7S diffractometer using graphite monochromatized Mo Kα radiation (λ = 0.710 73 Å) at 193 K. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was made.[16,17] The structure was solved and refined using SHELXTL[18] and SHELXL-93[19] programs. The non-hydrogen atoms were refined as anisotropic, and the hydrogen atoms of the phenyl groups were situated at calculated positions. Other hydrogen atoms were found from difference Fourier maps and refined with an isotropic temperature factor 1.5 times $U_{eq}$ of the atom to which they are connected.

## Results and discussion

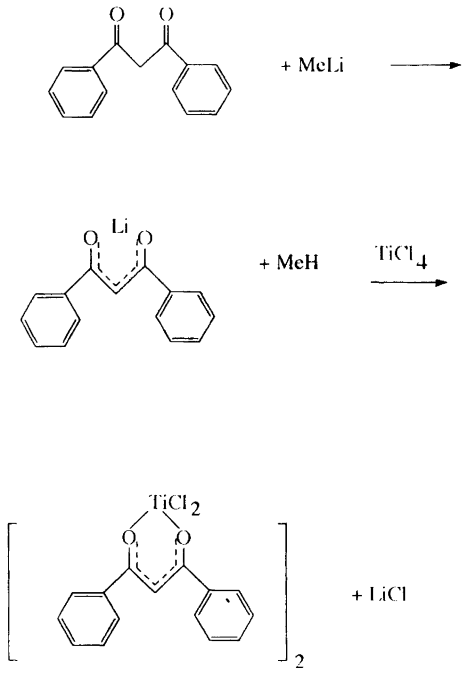
A straightforward route to Group 4 metal alkoxo complexes is the displacement of the halide from metal chlorides to the alkoxo ligand by an alkali-metallated alkoxo complex. 1,3-Diphenyl-1,3-propanedione was first alkali-metallated with methyllithium and then introduced to 0.5 equiv. of $TiCl_4$ (Scheme 1).

*cis*-(bzbz)$_2$TiCl$_2$ is relatively air sensitive. However, the observable decomposition did not start before exposure for several hours in air. The complex hydrolyzed immediately in moist solvents. *cis*-(bzbz)$_2$TiCl$_2$ is readily soluble in ethers and chlorinated solvents and aromatics. It is insoluble or slightly soluble in alkanes. The complex is a deep red crystalline solid at room temperature.

The molecular structure and atom numbering of *cis*-(bzbz)$_2$TiCl$_2$ is given in Fig. 1. Selected interatomic distances and angles are given in Table 2. The title complex is monomeric, having a distorted octahedral coordination geometry. The two Cl ions coordinating to titanium and both of the dibenzoylmethanate groups adopt the *cis*-configuration. The interesting feature of the coordination

*Table 1.* Crystal data and structure refinement parameters.

| | |
|---|---|
| Empirical formula | $C_{30}H_{22}Cl_2O_4Ti$ |
| Formula weight | 565.29 |
| Temperature/K | 193(2) |
| Wavelength/Å | 0.71073 |
| Crystal system | Orthorhombic |
| Space group | *Pbca* (no. 61) |
| Unit-cell dimensions | *a* = 16.214(3) Å α = 90° |
| | *b* = 17.300(3) Å β = 90° |
| | *c* = 18.967(4) Å γ = 90° |
| Volume/Å$^3$ | 5320(2) |
| *Z* | 8 |
| Density (calcd.)/Mg m$^{-3}$ | 1.411 |
| Absorption coefficient/mm$^{-1}$ | 0.557 |
| Absorption correction | ψ-scan |
| Transmission factor | 0.720–1.000 |
| *F*(000) | 2320 |
| Crystal size/mm | 0.30 × 0.30 × 0.20 |
| θ-range for data collection/° | 2.49 to 24.02 |
| Index ranges | $-17 \leqslant h \leqslant 0$, $0 \leqslant k \leqslant 19$, $0 \leqslant l \leqslant 18$ |
| Diffractometer | Rigaku AFC-7S |
| Scan method | ω–2θ |
| Scan rate/° min$^{-1}$ | 2–8 |
| Reflections collected | 2578 |
| Independent reflections | 2578 [*R*(int) = 0.0000] |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 2554/24/334 |
| Goodness-of-fit on $F^2$ | 0.918 |
| Final *R*-indices [$I > 2\sigma(I)$] | $R_1 = 0.0889$, $wR_2 = 0.1821$ |
| *R*-indices (all data) | $R_1 = 0.1742$, $wR_2 = 0.2394$ |
| Weights | $[\sigma^2(F_o^2) + (0.0889*P)^2 + 15.40*P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ |
| Largest difference peak and hole/e A$^{-3}$ | 0.431 and −0.427 |




*Scheme 1.* Preparation of the title compound from 1,3-diphenyl-1,3-propanedione and $TiCl_4$.

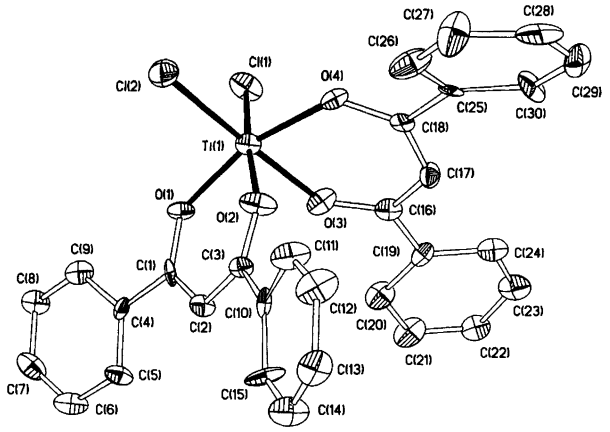



*Fig. 1.* Molecular structure of the title compound. The thermal ellipsoids are drawn at 30% probability level.

*Table 2.* Selected bond lengths (in Å) and angles (in °).

| | | | |
|---|---|---|---|
| Ti(1)–O(2) | 1.884(8) | Ti(1)–O(3) | 2.050(10) |
| Ti(1)–O(1) | 1.983(9) | Ti(1)–Cl(1) | 2.163(4) |
| Ti(1)–O(4) | 2.030(9) | Ti(1)–Cl(2) | 2.326(5) |
| O(2)–Ti(1)–O(1) | 81.7(4) | O(2)–Ti(1)–Cl(2) | 95.8(3) |
| O(2)–Ti(1)–O(4) | 83.6(4) | O(1)–Ti(1)–Cl(2) | 90.9(3) |
| O(1)–Ti(1)–O(4) | 162.0(3) | O(4)–Ti(1)–Cl(2) | 100.8(3) |
| O(2)–Ti(1)–O(3) | 81.9(4) | O(3)–Ti(1)–Cl(2) | 176.6(3) |
| O(1)–Ti(1)–O(3) | 91.3(4) | Cl(1)–Ti(1)–Cl(2) | 90.2(2) |
| O(4)–Ti(1)–O(3) | 76.5(4) | C(1)–O(1)–Ti(1) | 133.6(8) |
| O(2)–Ti(1)–Cl(1) | 174.0(3) | C(3)–O(2)–Ti(1) | 132.7(8) |
| O(1)–Ti(1)–Cl(1) | 98.8(3) | C(16)–O(3)–Ti(1) | 138.9(8) |
| O(4)–Ti(1)–Cl(1) | 94.9(3) | C(18)–O(4)–Ti(1) | 134.0(7) |
| O(3)–Ti(1)–Cl(1) | 92.1(3) | | |

sphere is the unexpected *trans*-effect. The shortest bonds, Ti–O = 1884(8) Å, and Ti–Cl = 2.163(4) Å, and the longest bonds, Ti–O = 2.050(19) Å and Ti–Cl, 2.326(5) Å, are opposite each other. This goes against the general behaviour. Otherwise the bond distances and angles are typical for *cis*-β-diketonate complex.[20–23] The deviations of the titanium, 0.43(1) and 0.33(1) Å, from the least-squares planes through the Ti(1)–O(1)–C(1)–C(2)–C(3)–O(2)–Ti(1) and Ti(1)–O(3)–C(16)–C(17)–C(18)–O(4)–Ti(1) metallocycles are typical for β-diketonate complexes.[1]

The polymerization activity of the title compound can be explained by its *cis*-conformation. One of the chloride anions is easily removed, and a reaction center of suitable size for the ethylene molecule to enter is exposed in the titanium coordination sphere (Fig. 2). The other Cl ligand can be changed to an alkyl group, which is necessary for the migration insertion step of polymerization.

*Table 3.* Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (in $Å^2 \times 10^3$).

| Atom | x | y | z | $U_{eq}$[a] |
|---|---|---|---|---|
| Ti(1) | 6925(1) | 104(1) | 7325(1) | 35(1) |
| Cl(1) | 7725(2) | −895(2) | 7278(2) | 59(1) |
| Cl(2) | 7719(2) | 716(2) | 6469(2) | 59(1) |
| O(1) | 6106(5) | −212(5) | 6604(5) | 32(2) |
| O(2) | 6170(5) | 922(4) | 7444(5) | 46(3) |
| O(3) | 6229(6) | −377(5) | 8114(6) | 45(3) |
| O(4) | 7437(5) | 538(4) | 8218(5) | 33(2) |
| C(1) | 5324(8) | −51(7) | 6502(6) | 28(3) |
| C(2) | 4943(8) | 520(7) | 6868(7) | 32(4) |
| C(3) | 5417(8) | 1003(7) | 7277(7) | 29(3) |
| C(4) | 4859(8) | −496(7) | 5941(7) | 29(4) |
| C(5) | 4010(8) | −504(8) | 5912(8) | 41(4) |
| C(6) | 3607(9) | −892(8) | 5344(9) | 50(5) |
| C(7) | 4051(10) | −1298(8) | 4846(9) | 53(5) |
| C(8) | 4898(9) | −1321(7) | 4890(9) | 41(4) |
| C(9) | 5304(8) | −921(7) | 5431(8) | 40(4) |
| C(10) | 5034(8) | 1702(6) | 7513(6) | 24(3) |
| C(11) | 5566(9) | 2229(7) | 7764(8) | 53(5) |
| C(12) | 5251(9) | 2876(8) | 7998(9) | 54(5) |
| C(13) | 4411(10) | 2978(8) | 7977(8) | 48(4) |
| C(14) | 3903(9) | 2456(9) | 7748(9) | 57(5) |
| C(15) | 4212(7) | 1793(7) | 7525(8) | 47(5) |
| C(16) | 6128(8) | −311(7) | 8833(9) | 36(4) |
| C(17) | 6541(8) | 240(8) | 9230(8) | 39(4) |
| C(18) | 7152(7) | 643(7) | 8910(8) | 28(4) |
| C(19) | 5550(9) | −792(7) | 9239(8) | 35(4) |
| C(20) | 5002(10) | −1159(8) | 8792(9) | 55(5) |
| C(21) | 4487(10) | −1649(8) | 9161(10) | 63(5) |
| C(22) | 4543(10) | −1780(8) | 9940(9) | 48(4) |
| C(23) | 5109(10) | −1413(10) | 10346(10) | 60(5) |
| C(24) | 5615(9) | −927(8) | 10034(9) | 47(4) |
| C(25) | 7470(7) | 1273(7) | 9346(8) | 27(3) |
| C(26) | 7703(9) | 1861(9) | 8899(10) | 66(6) |
| C(27) | 7948(11) | 2472(10) | 9252(10) | 74(6) |
| C(28) | 7946(8) | 2499(9) | 10039(11) | 60(5) |
| C(29) | 7738(9) | 1913(9) | 10489(8) | 50(4) |
| C(30) | 7515(9) | 1288(8) | 10144(8) | 50(5) |

[a] $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

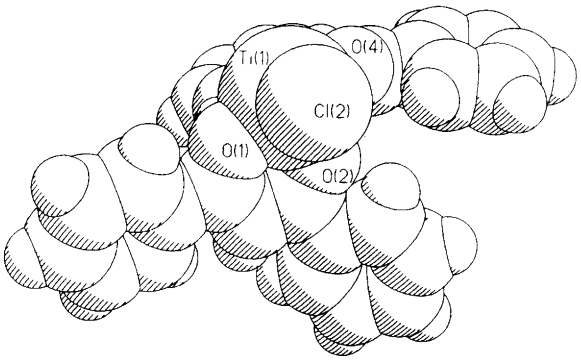



*Fig. 2.* Space filling model of the title compound with Cl1 removed showing the exposed reaction center for the entering ethylene molecule in the tianium coordination sphere.

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