Synthesis of titanium(IV) 3,6-di-*tert*-butylcatecholate complexes

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Two synthetic approaches were used for the synthesis of 3,6-di-*tert*-butylcatecholate derivatives of titanium(IV). These approaches are based on the exchange reaction between sodium catecholate and titanium(IV) chloride and the reaction of 3,6-di-*tert*-butylpyrocatechol with titanium tetrabutoxide. Depending on the reaction conditions, the former method allows the synthesis of the titanium monocatecholate complex 3,6-CatTiCl$_2$(THF)$_2$ (3,6-Cat is doubly deprotonated 3,6-di-*tert*-butylpyrocatechol) or bimetallic sodium titanium catecholate derivatives. Using the latter method, it is possible to synthesize six-coordinate titanium(IV) bis-catecholate complexes in high yields after the introduction of neutral bidentate donor ligands (TMEDA, DME, 2,2′-bipyridyl) to the reaction mixture.

Key words: titanium(IV), 3,6-di-*tert*-butyl-*o*-benzoquinone, 3,6-di-*tert*-butylpyrocatechol, catecholate complexes, redox-active ligands.

In recent literature, there has been a sustained and growing interest in titanium(IV) compounds containing different diolate, in particular catecholate, ligands. This type of compounds has attracted great attention due to prospects of their practical use in different fields, including medicine,[1—3] the design of ceramic materials,[4] coatings,[4] photovoltaic cells,[5—8] and homogeneous and heterogeneous catalysts.[9—14] For instance, titanium(IV) monocatecholate complexes containing different salen and salan ligands exhibit anticancer activity.[1—3] In particular, this is due to the presence of the catecholate moiety displaying antibacterial, antitumor, cytotoxic, anti- and prooxidant activity.[15,16] The introduction of the catecholate functionality into polyoxotitanium and titanium alkoxide clusters not only facilitates the study of the cluster structures but also endows these compounds with important physicochemical properties.[4—11,17,18] In particular, polyoxotitanium catecholate nanoparticles exhibit an intense absorption band in the visible region of electromagnetic radiation assigned to titanium—catechol ligand-to-metal charge transfer (LMCT), which significantly increases the efficiency of these compounds as photocatalysts. The following two methods are described in the literature for the synthesis of such clusters: the reactions of titanium(IV) alkoxides with pyrocatechols under solvothermal conditions and the introduction of the catecholate moiety into the ready polyoxotitanates. It should be noted that even slight changes in the reaction conditions (the ratio of the starting reagents, the solvent, temperature, and so on) lead to changes in the composition and structure of the resulting clusters and, as a consequence, to changes in their chemical and physicochemical properties. A large part of titanium(IV) catecholate complexes characterized by X-ray diffraction are those based on unsubstituted pyrocatechol. Complexes with 4-nitro-, 4-methyl-, 4-*tert*-butyl-, 3-methoxy-, and 3,5-di-*tert*-butylpyrocatechols[3,4,6,7,10—12] are also known. The majority of reliably characterized titanium(IV) complexes contain Ti and Cat (Cat is doubly deprotonated unsubstituted or substituted pyrocatechol) in a ratio higher than 1. The complexes, in which the coordination sphere of the titanium atom includes additional bulky neutral or charged ligands, are rare examples of neutral mononuclear monocatecholate derivatives of Ti^{IV}.[1—3,12,13] The only structurally characterized compound with the ratio Cat : Ti > 1, namely, the titanium(IV) bis-catecholate complex, was synthesized based on unsubstituted pyrocatechol.[11] The use of the close analogs of pyrocatechols, such as substituted *o*-aminophenols[19] and *alpha*-diamines,[20—26] as ligands for the preparation of titanium(IV) complexes allows the synthesis of various mononuclear monoligand or bis(ligand) derivatives. As in the case of the known catecholate derivatives, titanium amidophenoxide and diamide complexes are characterized by reversible intramolecular ligand-to-metal charge transfer.[26] Hence, this class of compounds holds promise in homogeneous or heterogeneous catalysis. The goal of this study is to develop synthetic approaches for the preparation of Ti^{IV} 3,6-di-*tert*-butylcatecholate complexes. The presence of bulky *tert*-butyl groups adjacent to catecholate oxygen atoms in the ligand system should decrease the possibility of the formation of oligomeric structures. Besides, broad opportunities for functionalization of the 3,6-di-*tert*-butylcatecholate ligand[27—29] and the ability of the latter to

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reversibly change the oxidation state in metal complexes (the redox-active ligand) make it possible to significantly modify the chemical properties of coordination and organometallic compounds.[30]

Results and Discussion

One of the most versatile methods for the synthesis of various types of organometallic and coordination compounds based on redox-active ligands involves the exchange reaction between alkali metal catecholates and halides of appropriate elements.[31] Hence, in the first step, we employed this synthetic approach in order to prepare titanium(IV) 3,6-di-*tert*-butylcatecholate complexes. The addition of a solution of titanium(IV) chloride in toluene to a solution of sodium 3,6-di-*tert*-butylcatecholate (3,6-$CatNa_2$) in THF at room temperature leads to the immediate change in the color of the reaction mixture from pale yellow to deep wine-red. Regardless of the stoichiometric ratio of the reagents (3,6-$CatNa_2$: $TiCl_4$ = = 1 : 1 or 2 : 1), we isolated the monocatecholate complex 3,6-$CatTiCl_2(THF)_2$ (**1**), which contains two chlorine atoms and two THF molecules coordinated to the titanium atom, as the major product (Scheme 1).

Therefore, on the experimental time scale, the exchange reaction in this medium occurs only in the first step, and the subsequent reaction of 3,6-$CatTiCl_2(THF)_2$ with 3,6-$CatNa_2$, which would afford the Ti^{IV} bis-catecholate complex, is not observed (see Scheme 1). Apparently, this behavior of the reaction system is attributed to the use of the mixed THF—toluene solvent. Toluene can significantly decrease the rate of exchange reactions of this type.[32] Compound **1** was isolated by recrystallization from diethyl ether as a red-brown finely crystalline powder. The composition and structure of complex **1** were determined by elemental analysis, IR and ^1H NMR spectroscopy, and X-ray diffraction. The highest preparative yields of 3,6-$CatTiCl_2(THF)_2$ were achieved using the reagents in the ratio 3,6-$CatNa_2$: $TiCl_4$ = 1 : 1.

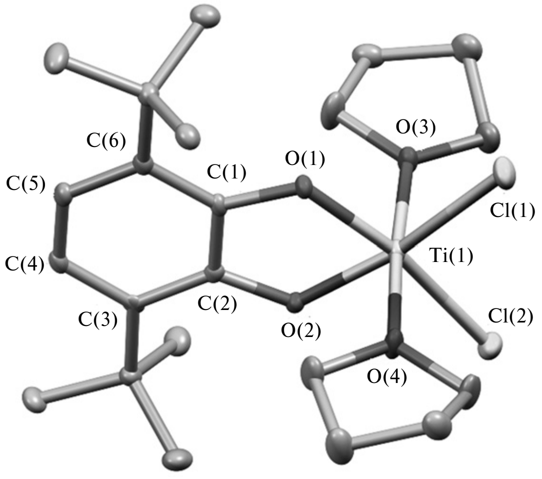
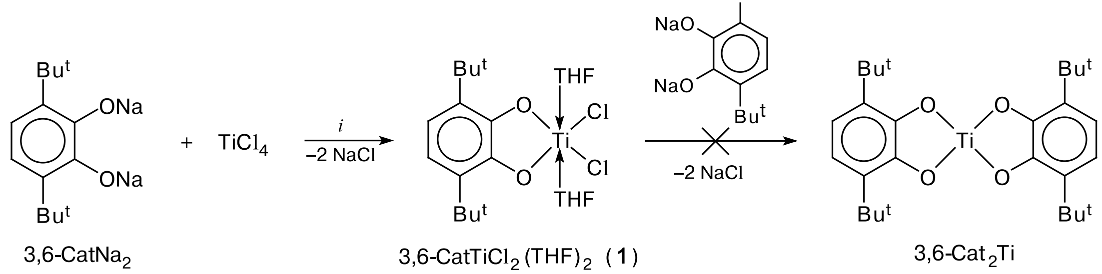


Fig. 1. Molecular structure of complex **1** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

According to the X-ray diffraction data, the complex 3,6-$CatTiCl_2(THF)_2$ (**1**) is isomorphous with the known tin catecholate complex 3,6-$CatSnCl_2(THF)_2$.[33] The molecular structure of **1** is shown in Fig. 1. Selected bond lengths and bond angles of complex **1** are given in Table 1. The titanium atom in complex **1** has a distorted octahedral environment with the oxygen atoms of the chelating ligand and two chlorine atoms in the equatorial plane and the oxygen atoms of THF molecules in apical positions. The deviation of Ti from the O(1)O(2)Cl(1)Cl(2) plane is 0.010(2) Å; the O(3)—Ti(1)—O(4) angle is 176.38(6)° (Table 1). The *tert*-butyl groups of the catecholate ligand are in the eclipsed conformation. The Ti(1)—O(1) (1.905(2) Å) and Ti(1)—O(2) (1.901(2) Å) bond lengths are smaller than the sum of the covalent radii of the corresponding elements (2.03 Å)[34] and are typical of titanium(IV) catecholate complexes.[1—13,17,18] The O(1)—C(1) (1.358(2) Å) and O(2)—C(2) (1.354(2) Å) bond lengths correspond to O—C single bonds in the known catecholate complexes.[33,35] The C—C distances in the six-mem-

Scheme 1



i. THF, toluene.

Table 1. Selected bond lengths (*d*) and bond angles (ω) in complex **1**

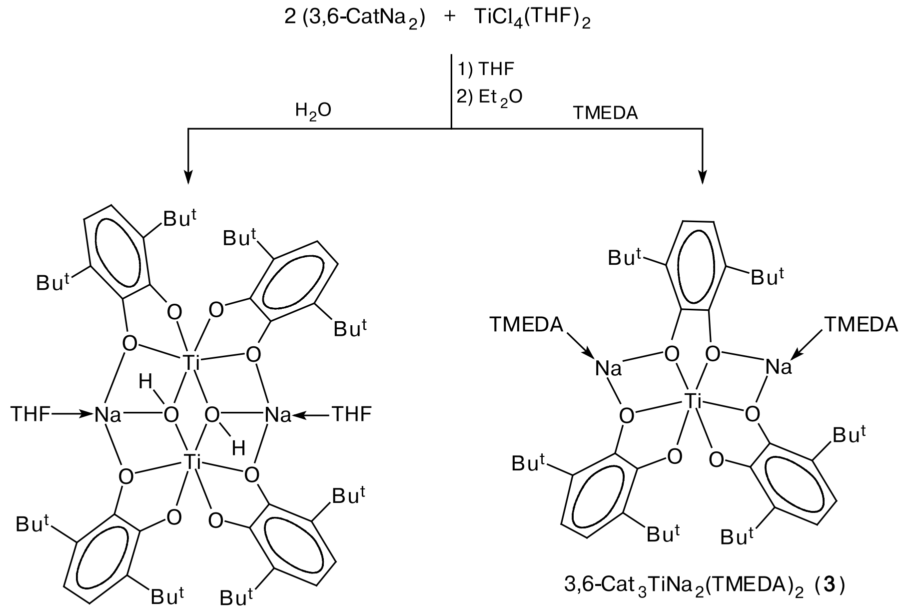
Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Ti(1)—O(1)	1.905(2)	O(2)—Ti(1)—O(1)	78.82(6)	O(3)—Ti(1)—Cl(2)	89.49(4)
Ti(1)—O(2)	1.901(2)	O(2)—Ti(1)—O(3)	91.25(6)	O(4)—Ti(1)—Cl(2)	88.30(5)
Ti(1)—Cl(1)	2.3439(7)	O(1)—Ti(1)—O(3)	92.35(6)	O(2)—Ti(1)—Cl(1)	170.47(4)
Ti(1)—Cl(2)	2.3302(6)	O(2)—Ti(1)—O(4)	91.66(6)	O(1)—Ti(1)—Cl(1)	91.66(4)
Ti(1)—O(3)	2.062(2)	O(1)—Ti(1)—O(4)	90.32(6)	O(3)—Ti(1)—Cl(1)	88.55(5)
Ti(1)—O(4)	2.073(2)	O(3)—Ti(1)—O(4)	176.38(6)	O(4)—Ti(1)—Cl(1)	88.92(5)
O(1)—C(1)	1.358(2)	O(2)—Ti(1)—Cl(2)	91.33(4)	Cl(2)—Ti(1)—Cl(1)	98.19(2)
O(2)—C(2)	1.354(2)	O(1)—Ti(1)—Cl(2)	170.01(5)		

bered catecholate carbon ring vary in a narrow range (1.393(3)—1.408(3) Å). The Ti(1)—O(3) (2.062(2) Å) and Ti(1)—O(4) (2.073(2) Å) bond lengths are comparable with the sum of the covalent radii of the titanium and oxygen atoms (2.03 Å)[**34**] and are significantly smaller than the sum of their van der Waals radii (3.6 Å).[**34**]

The ^{1}H NMR spectrum of a dilute solution of compound **1** in C_6D_6 is in agreement with the expected spectral pattern. The proton signals of THF at δ 1.22 and 4.35 are broadened and shifted with respect to those of free THF (δ 1.40 and 3.57). This is evidence that the coordination of tetrahydrofuran molecules to the titanium atom is retained in solution. The analysis of the ^{1}H NMR spectra of compound **1** revealed the dependence of the spectral pattern on the concentration. An increase in the concentration of complex **1** in solution leads to a broadening of the lines accompanied by the appearance of additional signals. Besides, the line widths and chemical shifts are temperature-dependent. This indicates that in solution, the monomeric complex is present in equilibrium with its oligomeric derivatives. In dilute solutions, this equilibrium is almost completely shifted to the monomeric complex.

The exchange reaction using titanium tetrachloride bis(tetrahydrofuranate) $TiCl_4(THF)_2$ as the starting reagent also did not afford the mononuclear titanium(IV) bis-catecholate complex (Scheme 2). The mixing of solutions of 3,6-$CatNa_2$ and $TiCl_4(THF)_2$ in THF is accompanied by the appearance of a deep dark orange color of the reaction mixture. This reaction afforded bimetallic sodium titanium catecholate derivatives. Thus, a portion of red-orange crystals was obtained after the replacement of THF by diethyl ether, the filtration from a sodium chloride precipitate, and prolonged crystallization. The resulting compound is the bimetallic complex 3,6-$Cat_4Ti_2(OH)_2Na_2(THF)_2$ (**2**), which is apparently produced by the hydrolysis of one of the reaction products

Scheme 2



3,6-$Cat_4Ti_2(OH)_2Na_2(THF)_2$ (**2**)

3,6-$Cat_3TiNa_2(TMEDA)_2$ (**3**)

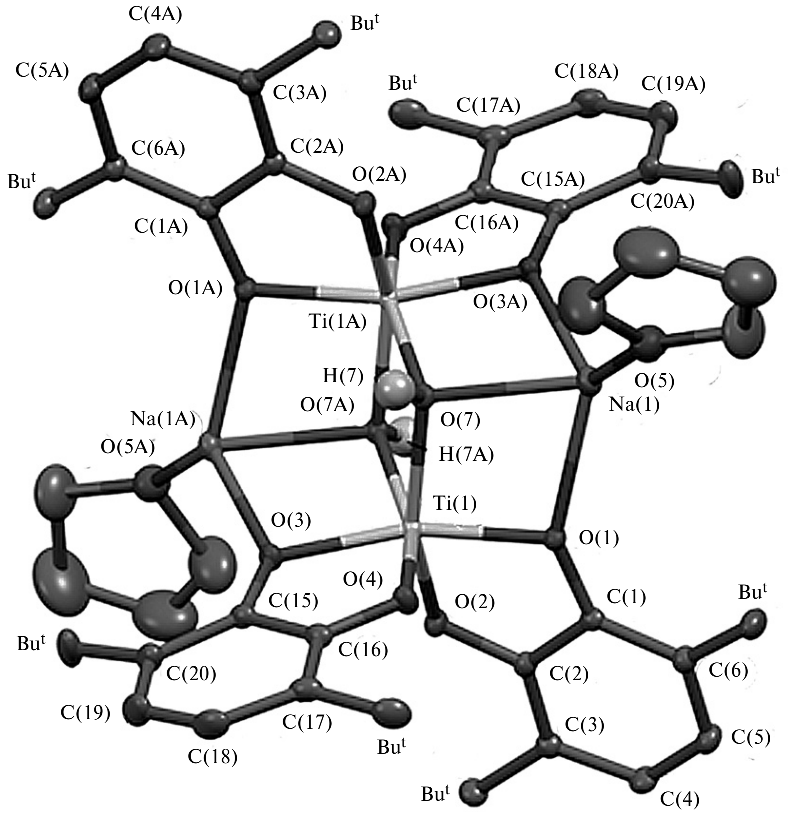


Fig. 2. Molecular structure of complex **2** • 2THF with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms (except for hydrogens of hydroxy groups) and methyl groups of *tert*-butyl substituents are omitted for clarity.

due to the uncontrolled presence of trace moisture in the reaction system. Minor compound **2** was characterized by X-ray diffraction (Fig. 2). The major product of this reaction, the bimetallic complex 3,6-Cat$_3$TiNa$_2$(TMEDA)$_2$ (**3**), was isolated in 54% yield by the treatment of the mother liquor in diethyl ether with the bidentate chelating base tetramethylethylenediamine (TMEDA) (see Scheme 2). Complex **3** was characterized by elemental analysis, IR and ^{1}H NMR spectroscopy, and X-ray diffraction.

The molecular structures of complexes **2** and **3** are shown in Figs 2 and 3, respectively. Selected bond lengths and bond angles of these complexes are given in Tables 2 and 3, respectively. Compound **2** crystallizes in space group *C*2/*c*. The molecule of complex **2** lies in a special position. There is one THF solvent molecule per asymmetric unit. Therefore, complex **2** crystallizes as solvate **2** • 2THF. The coordination polyhedra of Ti^{IV} in complexes **2** and **3** can be described as distorted octahedra with the O(1), O(3) (**2**) and O(1), O(1A) (**3**) atoms in apical positions and the oxygen atoms of the catecholate ligands in the equatorial planes. The O(1)—Ti(1)—O(3) (**2**) and O(1)—Ti(1)—O(1A) (**3**) angles are 163.92(4)° and 168.70(6)°, respectively. Like in complex **1**, the bond length distribution in the catecholate moieties of complexes **2** and **3** (C—O,

Table 2. Selected bond lengths (*d*) and bond angles (ω) in complex **2** • 2THF

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Ti(1)—O(1)	1.9673(8)	O(2)—C(2)	1.351(2)	O(2)—Ti(1)—O(4)	105.26(4)	O(1)—Ti(1)—O(7)	87.18(3)
Ti(1)—O(2)	1.8820(9)	O(3)—C(15)	1.366(2)	O(2)—Ti(1)—O(1)	80.12(4)	O(3)—Ti(1)—O(7)	103.31(4)
Ti(1)—O(3)	1.9745(8)	O(4)—C(16)	1.349(2)	O(4)—Ti(1)—O(1)	87.44(4)	O(2)—Ti(1)—O(7A)	89.21(4)
Ti(1)—O(4)	1.8852(9)	Na(1)—O(1)	2.338(2)	O(2)—Ti(1)—O(3)	94.13(4)	O(4)—Ti(1)—O(7A)	160.11(4)
Ti(1)—O(7)	2.0250(9)	Na(1)—O(3A)	2.343(2)	O(4)—Ti(1)—O(3)	79.56(4)	O(1)—Ti(1)—O(7A)	108.80(3)
Ti(1)—O(7A)	2.0515(9)	Na(1)—O(7)	2.2865(9)	O(1)—Ti(1)—O(3)	163.93(4)	O(3)—Ti(1)—O(7A)	85.95(3)
O(1)—C(1)	1.366(2)	O(7)—H(7)	0.873(9)	O(2)—Ti(1)—O(7)	155.09(4)	O(7)—Ti(1)—O(7A)	74.66(4)
				O(4)—Ti(1)—O(7)	95.40(4)		

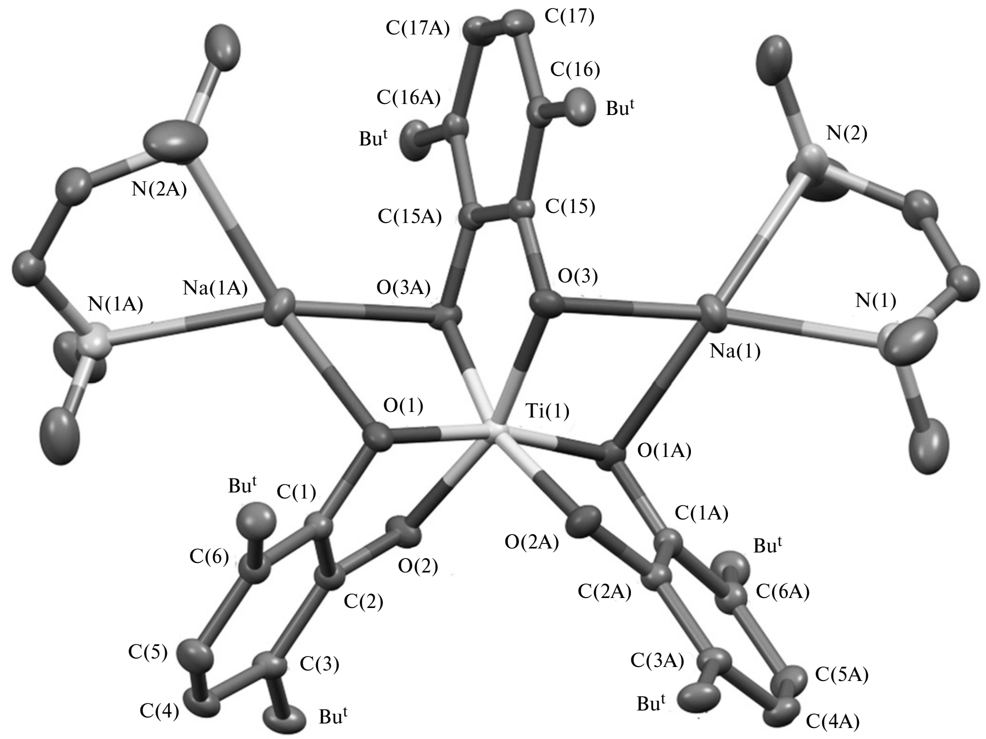


Fig. 3. Molecular structure of complex **3** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms and methyl groups of *tert*-butyl substituents are omitted for clarity.

1.347(2)—1.366(2) Å; C—C in the six-membered carbon ring, 1.385(2)—1.411(3) Å) suggests that the redox-active ligand exists as the dianion.[33,35] The Ti—O$_{cat}$ distances in **2** and **3** vary in a broad range (1.8820(9)—1.976(2) Å) and are smaller than the sum of the covalent radii of the corresponding elements (2.03 Å[34]). The Ti—O(2) and Ti—O(4) bond lengths are in the range of 1.8820(9)—1.9251(9) Å and are comparable with the corresponding distances in complex **1** (1.901(2)—1.905(2) Å). The Ti—O(1) and Ti—O(3) bonds (1.9652(9)—1.976(2) Å) are longer than the Ti—O(2) and Ti—O(4) bonds, which is apparently due to additional coordination of the oxygen atoms O(1) and O(3) to the Na atom. The Na—O$_{cat}$ distances are 2.338(2)—2.419(2) Å. Besides, each Na$^+$ cation in complexes **2** and **3** is coordinated by one THF (in **2**; Na—O, 2.253(3) Å) or TMEDA (in **3**; Na—N, 2.448(2)—2.500(4) Å) molecule. The hydroxyl oxygen atoms in complex **2** are coordinated in a μ^3 mode and are linked to two Ti^{4+} cations (Ti—O(7), 2.0250(9), 2.0515(9) Å) and one Na$^+$ cation (Na—O(7), 2.2865(9) Å). The Ti(1) and Ti(1A) atoms in complex **2** are at a distance of 3.2415(5) Å from each other.

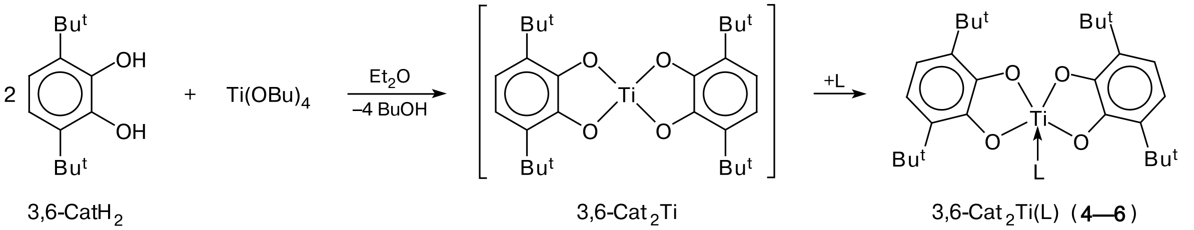
Therefore, the use of a solution of $TiCl_4$ in toluene or a solution of $TiCl_4(THF)_2$ in THF in the exchange reaction with sodium catecholate resulted in the formation of different products. The presence of toluene in the reaction mixture apparently leads to a decrease in the reaction rate of nucleophilic substitution of chloride anions[32] in 3,6-$CatTiCl_2(THF)_2$ that formed in the first step. In pure THF, the exchange reaction proceeds much faster and to a greater extent but affords heterometallic sodium titanium catecholate derivatives.

Hence, in order to prepare the mononuclear titanium(IV) bis-catecholate complex, we studied the reaction of 3,6-di-*tert*-butylpyrocatechol (3,6-$CatH_2$) with titanium(IV) tetrabutoxide (Scheme 3). The appropriate pyrocatechol was prepared by the reduction of 3,6-di-*tert*-

Table 3. Selected bond lengths (*d*) and bond angles (ω) in complex **3**

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Ti(1)—O(1)	1.9652(9)	O(2)—C(2)	1.347(2)	O(2A)—Ti(1)—O(2)	101.40(6)	O(2)—Ti(1)—O(3A)	91.62(4)
Ti(1)—O(2)	1.9251(9)	O(3)—C(15)	1.351(2)	O(2A)—Ti(1)—O(1A)	79.65(4)	O(2)—Ti(1)—O(3)	162.61(4)
Ti(1)—O(3)	1.976(2)	Na(1)—O(1A)	2.419(2)	O(2)—Ti(1)—O(1A)	93.16(4)	O(1)—Ti(1)—O(3)	88.25(4)
O(1)—C(1)	1.362(2)	Na(1)—O(3)	2.419(2)	O(1A)—Ti(1)—O(1)	168.71(6)	O(3)—Ti(1)—O(3A)	78.28(5)
				O(1)—Ti(1)—O(3A)	100.55(4)		

Scheme 3



L = TMEDA (**4**), DME (**5**), bipy (**6**)

butyl-*o*-benzoquinone (3,6-Q) with hydrazine hydrate in methanol and was characterized by IR and ^{1}H NMR spectroscopy. The spectroscopic characteristics of this compound were not reported in the previous study.[36] The reaction of titanium tetraalkoxides with diols is widely used for the synthesis of titanium oxo clusters, the reaction generally being performed under solvothermal conditions.[4—9,18] The reaction at ambient temperature favors the formation of low-molecular-weight products.[1—3,11,13] Upon the mixing of colorless solutions of $Ti(OBu)_4$ and 3,6-CatH_2 in Et_2O at room temperature, the reaction mixture immediately turned deep brown. The addition of TMEDA to the reaction mixture is accompanied by a change in the color of the solution to orange and the formation of the crystalline complex 3,6-Cat$_2$Ti(TMEDA) (**4**) (see Scheme 3). By analogy with complex **4**, we also synthesized titanium bis-catecholate derivatives containing coordinated 1,2-dimethoxyethane (3,6-Cat$_2$Ti(DME) (**5**)) and 2,2´-bipyridyl (3,6-Cat$_2$Ti(bipy) (**6**)) molecules (see Scheme 3). Compounds **5** and **6** were isolated in high yields as brown and maroon-red finely crystalline powders, respectively. The compositions and structures of compounds **4**—**6** were confirmed by IR and ^{1}H NMR spectroscopy and elemental analysis. The molecular structure of complex **4** is shown in Fig. 4. Selected bond lengths and bond angles of complex **4** are given in Table 4.

Like in complexes **1**—**3**, the coordination environment of the titanium atom in compound **4** can be described as a distorted octahedron. The equatorial base of the octahedron is formed by the oxygen atoms O(1) and O(1A) of two catecholate ligands and nitrogen atoms of the TMEDA molecule. The oxygen atoms O(2) and O(2A) are in apical positions. The titanium atom lies in the O(1)O(1A)N(1) N(1A) plane; the O(2)—Ti(1)—O(2A) angle is 161.84(5)°. The Ti—O bond lengths (1.9054(8)—1.9216(8) Å) are comparable with the Ti—O_{cat} distances in complexes **1**—**3** (1.8820(9)—1.9251(9) Å). The bond length distribution in the catecholate moieties (C—O, 1.355(2)—1.357(2) Å; C—C, 1.389(2)—1.410(2) Å) is also similar to that in complexes **1**—**3** (C—O, 1.347(2)—1.366(2) Å; C—C,

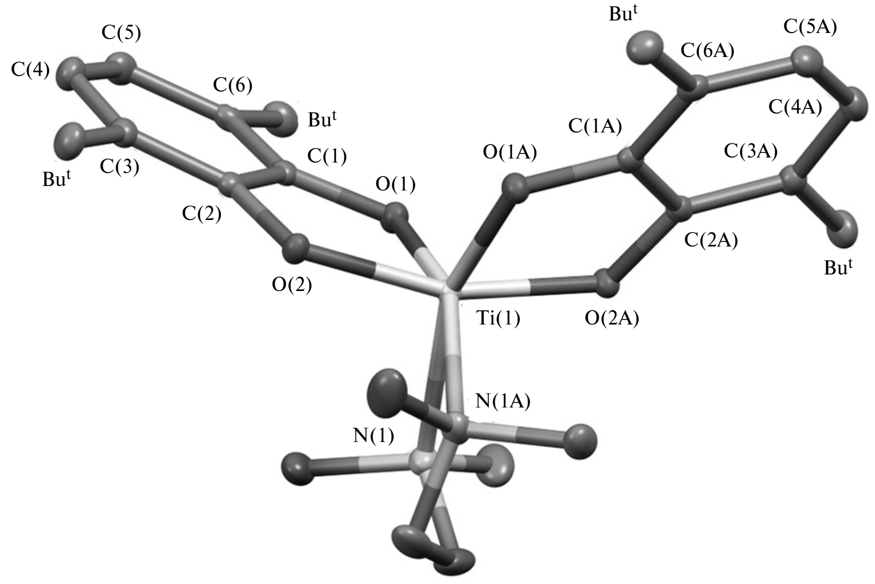


Fig. 4. Molecular structure of complex **4** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms and methyl groups of *tert*-butyl substituents are omitted for clarity.

Table 4. Selected bond lengths (*d*) and bond angles (ω) in complex **4**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Ti(1)—O(1)	1.9216(8)	O(2A)—Ti(1)—O(2)	161.84(5)	O(2)—Ti(1)—N(1)	104.30(4)
Ti(1)—O(2)	1.9054(8)	O(2A)—Ti(1)—O(1)	90.31(3)	O(1)—Ti(1)—N(1)	85.42(4)
Ti(1)—N(1)	2.255(2)	O(2)—Ti(1)—O(1)	79.93(3)	O(1A)—Ti(1)—N(1)	156.94(4)
O(1)—C(1)	1.355(2)	O(1)—Ti(1)—O(1A)	115.08(5)	N(1)—Ti(1)—N(1A)	76.97(6)
O(2)—C(2)	1.357(2)	O(2A)—Ti(1)—N(1)	90.00(3)		

1.385(2)—1.411(3) Å) and corresponds to the dianionic form of coordination of the redox-active ligand. The Ti—N bond lengths (2.255(2) Å) in complex **4** are larger than the sum of the covalent radii of the corresponding elements (2.04 Å[34]) but are significantly smaller than the sum of their van der Waals radii (3.7 Å[34]).

The ^{1}H NMR spectrum of a dilute solution of compound **4** in $CDCl_3$ shows proton signals of *tert*-butyl groups at δ 1.24, catecholate moieties at δ 6.77, and the TMEDA molecule. The chemical shifts of diamine protons (3.40, 3.55 ppm) substantially differ from those of the free ligand (2.24, 2.38 ppm), which is indicative of the retention of Ti—TMEDA coordination in solution. Noteworthy is that the ^{1}H NMR spectra of complex **4** are also characterized by the dependence of the chemical shifts and the line width of the signals on the concentration. An increase in the concentration of compound **4** in a solution in $CDCl_3$ or $C_6D_5CD_3$ leads to a broadening of the proton signals of *tert*-butyl groups, the catecholate moiety, and TMEDA. As in the case of compound **1**, this is most probably attributed to the existence of the monomer—oligomer equilibrium. This equilibrium is evidenced by the temperature dependence of the line width of the signals in the ^{1}H NMR spectrum. A decrease in the temperature of the sample leads to a narrowing of the signals corresponding to protons of the catecholate ligand and to an increase in the number of these signals. This attests to dynamic processes, resulting in the magnetic nonequivalence of these hydrogen atoms. Currently, we failed to identify compounds existing in equilibrium. The investigation of this process is underway.

To summarize, we synthesized and characterized for the first time titanium(IV) complexes based on the 3,6-di-*tert*-butylpyrocatecholate dianion. The exchange reactions between titanium tetrachloride and sodium catecholate or between titanium(IV) tetrabutoxide and 3,6-di-*tert*-butylpyrocatechol allows the targeted synthesis of mono- and bis-diolate derivatives of titanium, respectively. The structures of four new compounds were established by X-ray diffraction. The geometric parameters of the synthesized complexes are generally similar to those of the known titanium(IV) catecholate derivatives. The presence of bulky *tert*-butyl substituents, which shield the oxygen atoms of the catecholate ligand, was shown to facilitate the formation of monomeric structures. The synthesized titanium diolate compounds are rare examples of complexes with the ratio Cat : Ti ≥ 1.

Experimental

All operations associated with the synthesis of titanium(IV) catecholate complexes were performed under conditions excluding exposure to atmospheric oxygen and moisture using a Schlenk vacuum line. All solvents were purified and dried according to standard procedures.[37] The following commercial reagents were used: $TiCl_4$, $Ti(OBu)_4$, TMEDA, and 2,2′-bipyridyl (all from Aldrich). The reagents 3,6-Q and $TiCl_4(THF)_2$ were synthesized by the procedures described in the literature (see Refs 38 and 39, respectively).

The ^{1}H NMR spectra were recorded on Bruker DPX-200 (200 MHz) and Bruker Avance III (400 MHz) spectrometers with trimethylsilane as the internal standard. The IR spectra were measured on a FSM 1201 Fourier-transform infrared spectrometer as Nujol mulls in KBr cells.

Synthesis of (3,6-di-*tert*-butylcatecholato)dichlorobis(tetrahydrofuran)titanium(IV), 3,6-CatTiCl$_2$(THF)$_2$ (1). *A*. Reaction of 3,6-CatNa$_2$ with TiCl$_4$ (2 : 1). A solution of 3,6-Q (0.2 g, 0.9 mmol) in THF (15 mL) was added to sodium metal (2.3 g, 0.1 mol). The mixture was stirred until the initial color of quinone completely disappeared and a pale yellow solution of 3,6-CatNa$_2$ was obtained. The solution was separated from excess metal, and then a solution of $TiCl_4$ (0.05 mL, 0.45 mmol) in toluene (3 mL) was slowly added with continuous stirring to the resulting solution at room temperature. The reaction mixture immediately turned deep wine-red. The mixture was stirred for 30 min, THF was removed, and the dry residue was dissolved in Et_2O. The ethereal solution was filtered off from the NaCl precipitate on a Schott glass filter no. 4. The filtrate was concentrated and kept overnight at room temperature resulting in the formation of a maroon-brown finely crystalline product. The preparative yield of analytically pure complex **1** was 0.13 g (30% with respect to the starting 3,6-Q). Found (%): C, 54.93; H, 7.84. $C_{22}H_{36}Cl_2O_4Ti$. Calculated (%): C, 54.68; H, 7.51. IR, ν/cm^{-1}: 1588 m, 1488 m, 1389 m, 1383 s, 1358 s, 1344 w, 1299 w, 1285 m, 1269 w, 1248 w, 1238 w, 1203 m, 1174 m, 1045 m, 1032 m, 1011 s, 990 s, 945 m, 922 m, 856 v.s, 827 m, 815 m, 692 s, 652 m, 605 s, 560 w, 475 v.s, 467 v.s. ^{1}H NMR (200 MHz, C_6D_6, 20 °C), δ: 1.22 (m, 8 H, H_2C_{THF}); 1.41 (s, 18 H, Bu^t); 4.35 (m, 8 H, CH_2O_{THF}); 6.64 (s, 2 H, $CH_{catechol}$).

***B*. Reaction of 3,6-CatNa$_2$ with TiCl$_4$ (1 : 1).** The reaction was performed as described in *A*. The starting reagents were used in the following amounts: 0.2 g (0.9 mmol) of 3,6-Q and 0.1 mL

(0.9 mmol) of $TiCl_4$. The yield of the analytically pure product was 0.354 g (81.3%).

Synthesis of (μ^3-3,6-di-*tert*-butylcatecholato)-bis(μ^2-3,6-di-*tert*-butylcatecholato)-bis(*N*,*N*,*N*,*N*-tetramethylethylenediamine)-disodium titanium(IV), 3,6-$Cat_3TiNa_2(TMEDA)_2$ (3). A solution of $TiCl_4(THF)_2$ (0.15 g, 0.45 mmol) in THF (3 mL) was slowly added with continuous stirring to a solution of 3,6-$CatNa_2$, which was synthesized by the above-described procedure from 3,6-Q (0.2 g, 0.9 mmol), in the same solvent (15 mL) at room temperature. The color of the solution immediately changed from pale yellow to orange-brown. The reaction mixture was stirred for 30 min, THF was removed, and the dry residue was dissolved in Et_2O. The solution was separated from the white NaCl precipitate on a Schott glass filter no. 4. The filtrate was concentrated to 30% of the initial volume and kept overnight at room temperature. A small amount of red-orange crystals of complex **2**•2THF that precipitated were separated and studied by X-ray diffraction. Tetramethylethylenediamine (0.5 mL) was added to the residual solution. An orange crystalline product precipitated within 1—2 h. The yield of complex **3** was 0.16 g (54%). Found (%): C, 66.17; H, 9.18. $C_{54}H_{88}N_4Na_2O_6Ti$. Calculated (%): C, 65.97; H, 9.02. IR, ν/cm^{-1}: 1590 w, 1573 w, 1534 w, 1481 s, 1400 v.s, 1357 s, 1309 m, 1291 s, 1283 s, 1261 s, 1239 v.s, 1202 m, 1181 m, 1158 m, 1141 s, 1129 m, 1101 m, 1074 m, 1034 m, 1025 s, 980 s, 945 s, 939 s, 927 m, 922 s, 828 w, 810 s, 789 s, 776 m, 691 v.s, 650 s, 608 w, 598 w, 572 v.s, 501 s, 468 s, 423 w. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C), δ: 1.36 (s, 54 H, Bu^t); 2.23 (s, 24 H, Me_{TMEDA}); 2.39 (s, 8 H, H_2C_{TMEDA}); 6.47 (s, 6 H, $CH_{catechol}$).

Synthesis of 3,6-di-*tert*-butylpyrocatechol, 3,6-$CatH_2$. Hydrazine hydrate was added dropwise with continuous stirring to a solution of 3,6-Q (2 g, 9.08 mmol) in methanol (30 mL) until the solution was completely colorless. Then water was added dropwise to the methanolic solution resulting in the formation of a white finely crystalline precipitate of 3,6-$CatH_2$. The precipitate was separated by filtration, dried in air, and recrystallized from hexane. The yield of the product was 1.88 g (93%). Found (%): C, 75.79; H, 10.05. $C_{14}H_{22}O_2$. Calculated (%): C, 75.63; H, 9.97. IR, ν/cm^{-1}: 3532 m, 3502 m, 3469 s, 1611 m, 1501 m, 1483 s, 1429 s, 1418 s, 1387 s, 1361 s, 1277 s, 1217 s, 1202 s, 1165 s, 1143 s, 1027 m, 964 s, 933 m, 904 m, 812 s, 770 m, 668 w, 652 s, 580 w, 533 w, 520 w. ^{1}H NMR (200 MHz, C_6D_6, 20 °C), δ: 1.36 (s, 18 H, Bu^t); 4.78 (s, 2 H, OH); 6.82 (s, 2 H, $CH_{catechol}$).

Reaction of 3,6-$CatH_2$ with $Ti(OBu)_4$. *A*. Synthesis of bis(3,6-di-*tert*-butylcatecholato)(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)-titanium(IV), 3,6-$Cat_2Ti(TMEDA)$ (4). A solution of 3,6-$CatH_2$ (0.2 g, 0.9 mmol) in Et_2O (10 mL) was gradually added with continuous stirring to a solution of $Ti(OBu)_4$ (0.15 mL, 0.45 mmol) in the same solvent (5 mL). The solution immediately turned brown. The reaction mixture was stirred for 30 min at room temperature. Then Et_2O was removed, the dry residue was dissolved in hexane (15 mL), and TMEDA (0.5 mL) was added. The color of the solution changed to orange-brown followed by

Table 5. Crystallographic data and the X-ray diffraction data collection and structure refinement statistics for complexes **1—4**

Parameter	**1**	**2**•2THF	**3**	**4**
Formula	$C_{22}H_{36}Cl_2O_4Ti$	$C_{72}H_{114}Na_2O_{14}Ti_2$	$C_{54}H_{92}N_4Na_2O_6Ti$	$C_{34}H_{56}N_2O_4Ti$
Molecular weight	483.31	1345.41	987.19	604.70
Crystal system	Monoclinic	Monoclinic	Monoclinic	Tetragonal
Space group	$P2_1/n$	$C2/c$	$C2/c$	$P4_2/n$
a/Å	10.940(2)	22.7672(17)	13.5016(4)	15.1310(3)
b/Å	15.9464(13)	13.8148(10)	22.0513(6)	15.1310(3)
c/Å	14.226(4)	24.0782(18)	20.1625(6)	14.8527(4)
α/deg	90	90	90	90
β/deg	94.11(3)	102.8690(10)	107.8390(10)	90
γ/deg	90	90	90	90
V/Å^3	2475.4(8)	7383.0(9)	5714.3(3)	3400.48(16)
Z	4	4	4	4
F_{000}	1024	2896	2144	1312
d_{calc}/Mg m^{-3}	1.297	1.210	1.147	1.181
μ/mm^{-1}	0.585	0.287	0.213	0.289
Crystal size/mm	0.20×0.20×0.05	0.38×0.36×0.16	0.40×0.27×0.11	0.37×0.11×0.10
Scan range, θ/deg	2.93—26.02	2.31—28.68	2.13—28.79	2.35—28.71
hkl ranges	$-13 \le h \le 13$ $-19 \le k \le 19$ $-17 \le l \le 17$	$-30 \le h \le 30$, $-18 \le k \le 18$, $-32 \le l \le 32$	$-18 \le h \le 18$, $-29 \le k \le 29$, $-27 \le l \le 27$	$-20 \le h \le 16$, $-20 \le k \le 20$, $-20 \le l \le 20$
Number of reflections				
observed	35676	40941	36174	30122
unique	4871	9465	7426	4400
R_{int}	0.0509	0.0264	0.0461	0.0389
$S(F^2)$	1.013	1.021	1.036	1.002
R_1, wR_2 ($I > 2\sigma(I)$)	0.0367, 0.0735	0.0354, 0.0896	0.0428, 0.1023	0.0330, 0.0856
R_1, wR_2 (based on all reflections)	0.0538, 0.0788	0.0439, 0.0947	0.0592, 0.1097	0.0430, 0.0917
Residual electron density, (ρ_{max}/ρ_{min})/e Å^{-3})	0.37/−0.29	0.36/−0.37	0.30/−0.49	0.33/−0.42

the gradual formation of crystalline complex **4**. The reaction mixture was kept at room temperature for 2 h to achieve more complete precipitation of the product. The product was separated from the mother liquor by decantation and dried under reduced pressure. The yield of analytically pure complex **4** was 0.196 g (72%). Found (%): C, 67.62; H, 9.38. $C_{34}H_{56}N_2O_4Ti$. Calculated (%): C, 67.53; H, 9.33. IR, ν/cm^{-1}: 1477 s, 1440 s, 1397 s, 1351 s, 1313 m, 1281 s, 1258 s, 1248 s, 1232 m, 1203 m, 1169 w, 1155 w, 1144 m, 1121 m, 1103 w, 1065 m, 1049 w, 1019 m, 1013 w, 1001 w, 986 m, 953 m, 938 m, 925 m, 827 s, 811 s, 794 m, 778 v.s, 729 v.s, 691 v.s, 674 v.s, 648 s, 604 w, 586 w, 567 s, 551 m, 531 m, 501 m. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C), δ: 1.24 (s, 36 H, Bu^t); 3.40 (s, H, H_2C_{TMEDA}); 3.55 (s, H, Me_{TMEDA}); 6.77 (s, 4 H, $CH_{catechol}$).

***B*. Synthesis of bis(3,6-di-*tert*-butylcatecholato)(1,2-dimethoxyethane)titanium(IV), 3,6-Cat$_2$Ti(DME) (5).** Compound **5** was synthesized by the procedure described above for complex **4**. The starting reagents were used in the following amounts: 0.2 g (0.9 mmol) of 3,6-CatH$_2$ and 0.15 mL (0.45 mmol) of Ti(OBu)$_4$. Then DME (0.5 mL) was added to the resulting solution in hexane (15 mL). The brown crystalline precipitate that formed was isolated as described above. The yield of the analytically pure product was 0.164 g (63%). Found (%): C, 66.64; H, 8.77. $C_{32}H_{50}O_6Ti$. Calculated (%): C, 66.43; H, 8.71. IR, ν/cm^{-1}: 1552 m, 1482 m, 1422 m, 1365 s, 1310 w, 1283 m, 1262 w, 1242 m, 1202 m, 1181 w, 1141 w, 1101 m, 1036 m, 1029 m, 981 s, 954 m, 939 m, 924 w, 869 m, 831 m, 812 m, 800 m, 715 s, 704 s, 682 m, 651 s, 619 w, 589 m, 552 s, 526 w, 501 s, 493 s, 474 w. ^{1}H NMR (200 MHz, $(CD_3)_2CO$, 20 °C), δ: 1.25 (s, 36 H, Bu^t); 3.27 (s, 6 H, CH_3O (DME)); 3.45 (s, 4 H, CH_2 (DME)); 6.39 (s, 4 H, $CH_{catechol}$).

***C*. Synthesis of bis(3,6-di-*tert*-butylcatecholato)(2,2′-bipyridyl)titanium(IV), 3,6-Cat$_2$Ti(bipy) (6).** Compound **6** was synthesized by the procedure described above for complex **4**. The starting reagents were used in the following amounts: 0.2 g (0.9 mmol) of 3,6-CatH$_2$ and 0.15 mL (0.45 mmol) of Ti(OBu)$_4$. Then bipy (0.07 g, 0.45 mmol) was added to the resulting solution in hexane (15 mL). The maroon finely crystalline precipitate that formed was isolated as described above. The yield of the analytically pure product was 0.258 g (89%). Found (%): C, 70.98; H, 7.65. $C_{38}H_{48}N_2O_4Ti$. Calculated (%): C, 70.80; H, 7.51. IR, ν/cm^{-1}: 1601 m, 1574 w, 1567 w, 1485 m, 1447 s, 1394 s, 1357 m, 1315 m, 1283 m, 1259 m, 1245 s, 1232 w, 1204 w, 1174 w, 1143 w, 1062 w, 1045 w, 1028 m, 982 s, 958 w, 940 m, 923 w, 853 w, 812 m, 798 s, 766 s, 733 s, 714 s, 695 s, 650 m, 638 w, 613 w, 586 m, 567 s, 550 m, 504 s, 475 m, 465 m. ^{1}H NMR (200 MHz, $(CD_3)_2CO$, 20 °C), δ: 1.21 (s, 36 H, Bu^t); 6.40 (s, 4 H, $CH_{catechol}$); 7.97 (m, 2 H, C(5)H (bipy)); 8.42 (m, 2 H, C(4)H (bipy)); 8.68 (m, 2 H, C(3)H (bipy)); 9.37 (m, 2 H, C(6)H (bipy)).

X-ray diffraction studies of 1—4. Single crystals suitable for X-ray diffraction were grown from Et_2O (**1**—**3**) or a hexane—Et_2O—THF mixture (1 : 1 : 0.1) (**4**). The X-ray diffraction data sets for complexes **1**—**4** were collected on Agilent Xcalibur E (**1**) and Bruker D8 Quest (**2**—**4**) diffractometers (ω-scanning technique, Mo-Kα radiation, λ = 0.71073 Å, T = 100 K). The intensity data were measured and integrated, absorption corrections were applied, and the structures were refined using the CrysAlis Pro,[40] APEX3,[41] SADABS,[42] and SHELX program packages.[43] The structures were solved by direct methods and refined by the full-matrix least squares based on F^2_{hkl} with anisotropic displacement parameters for nonhydrogen atoms. The hydroxyl hydrogen atom in complex **2** was found in a difference Fourier map and refined isotropically. The other hydrogen atoms of complexes **1**—**4** were positioned geometrically and refined isotropically with fixed thermal parameters $U(H)_{iso} = 1.2U(C)_{eq}$ ($U(H)_{iso} = 1.5U(C)_{eq}$ for the methyl groups).

Selected geometric parameters of complexes **1**—**4** are given in Tables 1—4, respectively. The crystallographic data and the X-ray diffraction data collection and structure refinement statistics are given in Table 5. The structures were deposited with the Cambridge Crystallographic Data Centre (CCDC 1879922 (**1**), 1879923 (**2**), 1879924 (**3**), 1879925 (**4**)) and are available at ccdc.cam.ac.uk/structures.

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