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Synthesis and structures of titanium complexes bearing tetradentate tripodal [O_2XC] ligands (X = C, P)†

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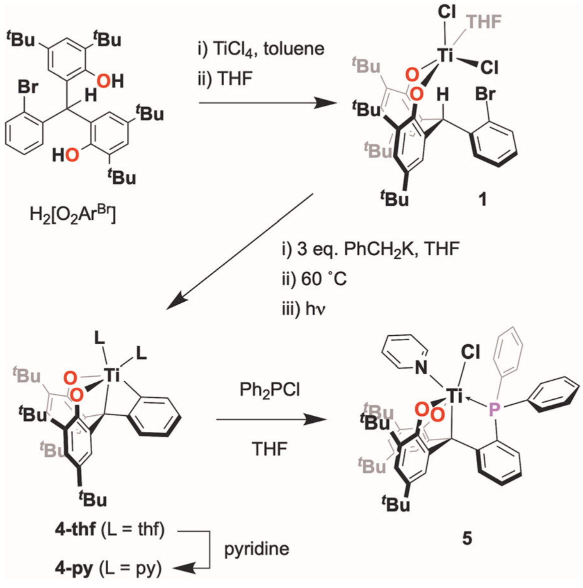
We report the synthesis and structures of titanium complexes supported by tripodal mixed-donor [O_2CC] and [O_2PC] ligands. Stepwise cyclometallation of a chelating bis(phenoxide) complex led to tetradentate binding of the [O_2CC] ligand to the titanium center. Phosphination of a Ti–C bond of the [O_2CC] complex afforded the tripodal [O_2PC] ligand.

Tridentate and tetradentate ligands with tripodal topology have received a great deal of attention.[1–6] Two main features make this class of ligands useful in coordination chemistry. First, tripodal ligands can enforce a single site of reactivity upon coordination to a metal center, thereby providing a desirable platform for small molecule activation and atom transfer chemistry. Second, the choice of substituents and donor groups incorporated into the arms of the tripodal ligands allows for the tailored synthesis of ligands for specific applications. Our group has been examining the use of tris(2-hydroxylphenyl)methane as a supporting ligand.[8,9] A triphenylmethane ligand framework has a propeller conformation with all *ortho*-substituted groups aligned with the central methine hydrogen, which appears to be well suited to accommodate a metal ion.[10] Therefore, deprotonation of three hydroxyl groups of triphenoxymethane effectively provides a facially tridentate [O_3]$^{3-}$ ligand, and subsequent activation of the bridgehead methine C–H bond results in a tetradentate [O_3C]$^{4-}$ ligand.[8,9] These highly charged tripodal [O_3] and [O_3C] ligands are suitable for exploring the chemistry of metal ions in high oxidation states.

Within the family of tripodal ligands, those containing different types of donor functions are particularly interesting to us, because mixed-donor multidentate ligands can bind various transition metals, stabilize a range of oxidation states, and induce remarkable reactivity patterns.[7,11–14] As an extension of our work on the coordination chemistry of triphenylmethane-based ligands, we were motivated to incorporate different donor groups into the arm units of the tripodal ligand backbone. Here we describe the synthesis and structures of titanium complexes bearing tripodal [O_2CC]$^{4-}$ and [O_2PC]$^{3-}$ ligands.

A triphenylmethane derivative (2-Br-C_6H_5)(2,4-^{t}Bu$_2$-$C_6H_2OH)_2CH$ ($H_2[O_2Ar^{Br}]$) is readily available and used as a ligand precursor in this study.[15] Treatment of $TiCl_4$ with 1 equivalent of $H_2[O_2Ar^{Br}]$ in toluene at room temperature for 12 h gave a red solution along with elimination of HCl. After removal of all volatiles under vacuum, $[O_2Ar^{Br}]TiCl_2(thf)$ (**1**) was obtained as brown crystals in 94% yield upon extraction of the solid residue with THF, evaporation to dryness, and washing with pentane (Scheme 1). The molecular structure of



Scheme 1 Synthesis of titanium complexes.

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† Electronic supplementary information (ESI) available: Experimental and characterization data, and crystallographic data for **1′**, **4-thf** and **5**. CCDC 1957864–1957866. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/C9DT03969D

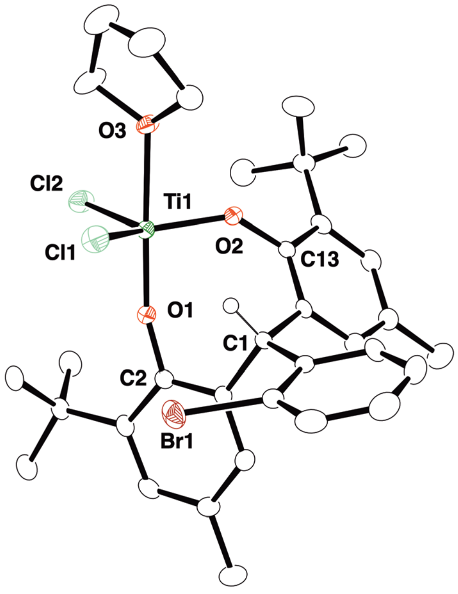

Fig. 1 The molecular structure of **1′** with thermal ellipsoids set at the 50% probability level. All hydrogen atoms are omitted for clarity except for the methine proton.

the 2-*tert*-butyl-5-methylphenoxide analogue **1′** has been determined by X-ray diffraction (Fig. 1), confirming that the complex is monomeric in the solid state.[16] The structure of **1′** closely resembles the chelating bis(phenoxide) ligand complex [mbmp]$TiCl_2$(thf) (mbmp = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenoxide)).[17] The geometry of the titanium center is trigonal bipyramidal (τ = 0.96)[18] with two equatorial chloride ligands (Ti–Cl = 2.244(1) and 2.2835(9) Å), an axial THF molecule (Ti–O = 2.181(2) Å), and a bidentate [O_2Ar^{Br}] ligand spanning axial and equatorial sites. The equatorial phenoxide ligand is more bent (138.7(2)°) than the axial phenoxide ligand (159.4(2)°). This is likely correlated to the extent of π donation from the oxygen lone pairs to the titanium metal, as the equatorial Ti–O bond distance (1.819(2) Å) is longer than the axial Ti–O bond distance (1.773(2) Å). The ^1H and $^{13}C\{^1H\}$ NMR spectra of **1** show the presence of equivalent phenoxide groups, indicating average C_s symmetry due to reversible THF dissociation in solution.

We previously reported that zirconium and niobium benzyl complexes supported by the triphenoxymethane ligand underwent C–H activation of the bridgehead methine to provide the tetradentate tripodal [O_3C] ligand.[8,9] Cyclometalation *via* σ-bond metathesis is common in early transition metal complexes with *ortho*-substituted phenoxide ligands.[19,20] For example, $M(OAr)_2(CH_2Ph)_2$ (M = Ti, Zr; OAr = 2,6-di-*tert*-butylphenoxide) has been reported to give a cyclometalated complex $M(OC_6H_3{}^tBuCMe_2CH_2)(OAr)(CH_2Ph)$ with elimination of toluene.[19] Complex **1′** adopts a flattened boat conformation for the eight-membered TiO_2C_5 chelate ring, which causes the bridgehead methine proton to be in close proximity to the titanium center. When the metal center is alkylated, this constrained geometry could promote the coordination of the bridgehead carbon atom *via* C–H bond activation.

Addition of 3 equivalents of $PhCH_2K$ to **1** in THF produced the tribenzyl complex K[(O_2Ar^{Br})Ti(CH_2Ph)$_3$] (**2**) according to ^1H NMR spectroscopy. The three sets of benzyl protons appear to be in rapid exchange on the NMR time scale at room temperature, as evidenced by the presence of one broad peak integrating to six protons at 3.03 ppm. The phenoxide groups remain equivalent. The bridgehead methine proton is observed at 5.23 ppm, shifted upfield relative to that for **1** at 6.69 ppm. All attempts to isolate **2** were unsuccessful due to its thermal instability and light-sensitivity.

To determine the identity of decomposition products, the thermal reaction of **2** was monitored by ^1H NMR spectroscopy. An NMR tube sample of **2** in THF-d_8 was heated to 60 °C for 12 h in the absence of light, leading to full conversion to a mixture of products, as seen by the disappearance of the signal for the bridgehead methine proton at 5.23 ppm. The reaction mixture included K[(O_2CAr^{Br})Ti(CH_2Ph)$_2$] (**3**) and toluene concomitant with small amounts of [O_2CC]Ti(thf)$_2$ (**4-thf**) and dibenzyl. The Ti-containing products **3** and **4-thf** were inseparable. However, **3** was light sensitive and cleanly converted to **4-thf** and dibenzyl when exposed to light from a xenon lamp at room temperature. Although single crystals of **4-thf** suitable for X-ray structure determination were grown from pentane, purification of **4-thf** on a preparative scale has met with difficulties due to its high solubility in common organic solvents. However, the [O_2CC] complex was isolated as a pyridine adduct. A preparative scale reaction carried out in THF gave a brown solution accompanied by precipitation of KBr. Addition of pyridine to the supernatant followed by workup afforded [O_2CC]Ti(py)$_2$ (**4-py**) as purple powder in 29% yield. The ^1H NMR spectrum of **4-py** in THF-d_8 shows that the molecule has average C_s symmetry with equivalent pyridine ligands, implying reversible pyridine dissociation in solution.

The molecular structure of **4-thf** is shown in Fig. 2. The bridgehead methine C–H bond of the ligand backbone is activated followed by *ortho*-metalation of the pendant phenyl ring to furnish a four-membered titanabenzocyclobutene, leading to tetradentate binding of the [O_2CC] ligand to the metal center. Two THF molecules are bound to the metal to complete its coordination sphere. The coordination environment of the titanium metal in **4-thf** is significantly distorted because of the four-membered ring. This metallacycle is puckered with the Ti–C(31)–C(30)–C(15) torsion angle of 21.9(1)°, rather than planar as observed frequently in the titanacyclobutene fragments of less preorganized systems,[21–24] suggesting that severe strains are present in this complex. The Ti–C(sp^3) and Ti–C(sp^2) bond distances of 2.143(2) and 2.071(2) Å are comparable to those found in titanacyclobutene complexes,[21–24] and the C(15)–C(31) bond distance of 1.523(2) Å is in accordance with a C(sp^3)–C(sp^2) single bond (1.51 Å).[25] The *ortho*-metalated benzene ring is completely planar, and its C–C bonds are practically non-alternating and have normal distances. The bridgehead carbon C(15) atom adopts a distorted tetrahedral geometry. The Ti–O bond distances of 1.929(1) and 1.909(1) Å are longer than those in **1**.

Titanacyclobutene complexes have been reported to react with $PhPCl_2$ and R_2PCl (R = Ph, ^iPr), yielding

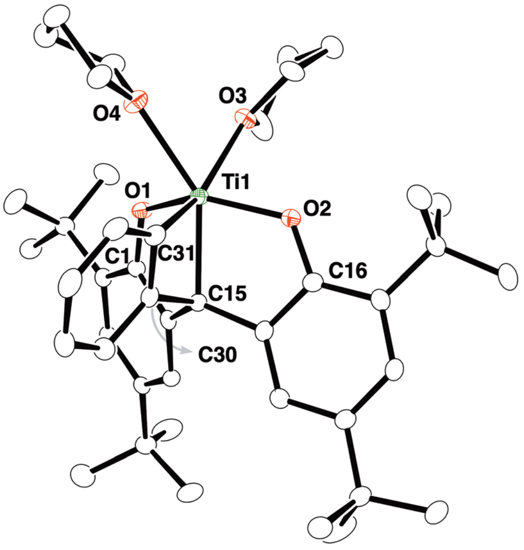

Fig. 2 The molecular structure of **4-thf** with thermal ellipsoids set at the 50% probability level. All hydrogen atoms are omitted for clarity.

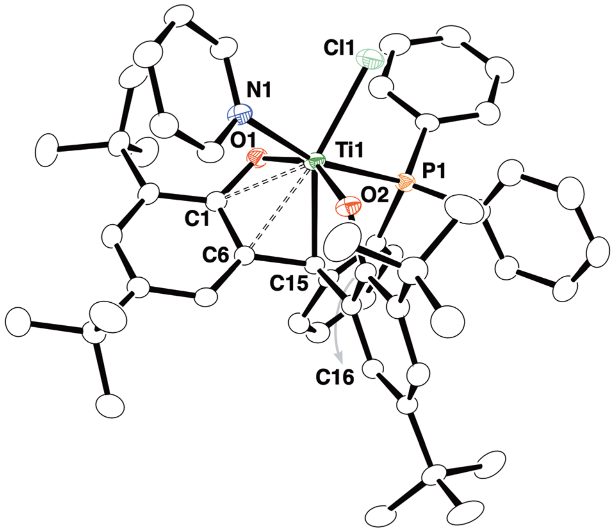

Fig. 3 The molecular structure of **5** with thermal ellipsoids set at the 50% probability level. All hydrogen atoms are omitted for clarity.

phosphacyclobutenes[26,27] or allylphosphines,[28] respectively. Based on this precedent, we were interested in the synthesis of a phosphine–phenoxide mixed-donor ligand by phosphination of a Ti–C bond of **4-py**. Treatment of **4-py** with a slight excess of Ph_2PCl in THF at room temperature gave a brown solution from which $[O_2PC]TiCl(py)$ (**5**) was obtained as brown powder in 85% yield after workup. Product **5** results from selective P–C bond formation at the $C(sp^2)$ carbon of the titanabenzocyclobutene ring. The ^1H NMR spectrum of **5** in C_6D_6 shows the presence of a single complex with C_s symmetry. A $^{13}C\{^1H\}$ NMR signal at 114.2 ppm is identified as the metal-bound bridgehead carbon resonance, which appears as a ^{31}P-coupled doublet with $^3J_{CP}$ = 13.8 Hz. Compared to the free ligand $H_2[O_2P]$ (−16.8 ppm), a $^{31}P\{^1H\}$ NMR signal is shifted downfield and found at 44.3 ppm.

The molecular structure of **5** has been determined by the X-ray diffraction study (Fig. 3), displaying the tetradentate coordination of the $[O_2PC]$ ligand with one phosphorus, one carbon, and two phenoxide oxygen donor atoms bound to the metal center. Complex **5** possesses a distorted octahedral geometry at titanium, with a chloro and a pyridine ligand *trans* to the carbon and the phosphine donor atom, respectively. The most salient structural feature is the presence of Ti–C(*ipso*) (2.423(2) Å) and Ti–C(*ortho*) (2.448(2) Å) interactions with one of the phenoxide groups. Similar η^3 bonding interactions have been structurally observed with binaphtholate ligands coordinated to Ru, Rh, and Ir[29–31] and are often observed with benzyl and anilide ligands.[32–37] The Ti–O(η^3) bond distance (1.929(1) Å) is longer than the Ti–O(η^1) bond distance (1.897(1) Å). The Ti–P bond distance of 2.5605(5) Å is within the range reported for Ti(IV) complexes.[38–41] The geometry of the bridgehead carbon C(15) atom is distorted tetrahedral. The solid-state structure is in contrast to the presence of equivalent phenoxide groups in solution. This discrepancy could be explained by the reversible η^1 to η^3 slippage of the phenoxide groups on the NMR time scale. However, we cannot rule out the possibility that both phenoxide groups are η^1-bound to the metal center in solution.

In summary, we have prepared the $[O_2CC]$ complex by stepwise metalation of the bis(phenoxide) ligand. Subsequent phosphination of the titanabenzocyclobutene unit resulted in the $[O_2PC]$ tripodal ligand. It should be noted that the reaction of $Ti(CH_2Ph)_4$ with the ligand precursor $H_2[O_2P]$ gave a mixture of uncharacterized products. Efforts towards the synthesis of $[O_2CC]$ complexes of other transition metals using this methodology are ongoing. We are also attempting the insertion of different donor groups into a metal–carbon bond of the $[O_2CC]$ complexes to prepare new mixed-donor tripodal ligands.

Conflicts of interest

There are no conflicts to declare.

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