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An anionic η^2 -naphthalene complex of titanium supported by a tripodal $[O_3C]$ ligand and its reactions with dinitrogen, anthracene and THF

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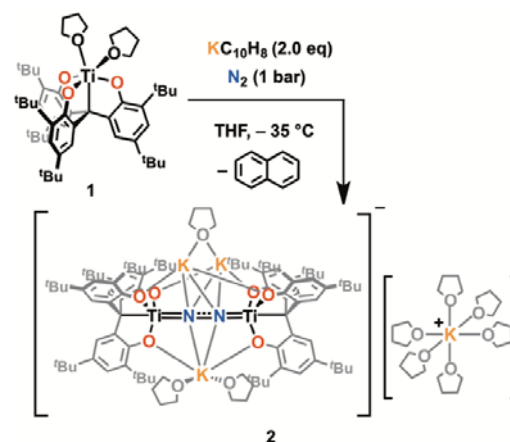
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We report the synthesis and characterization of a dianionic titanium naphthalene complex supported by a tripodal triaryloxidemethyl ligand, which is a rare example of an η^2 -coordinated arene complex of low-valent early transition metal. The η^2 -naphthalene ligand is readily displaced by N_2 and anthracene along with release of free naphthalene, resulting in formation of the end-on N_2 bridging dititanium complex and the anthracene complex, respectively. The naphthalene complex undergoes C–O bond cleavage of THF to produce a 1-oxa-2-titanacyclohexane.

Metal arene complexes constitute a vast family of compounds that have been of long-standing interest because of the fundamental nature of such species¹ and their applications in organic synthesis^{2,3} and materials.⁴ Among them, naphthalene and anthracene complexes play a crucial role in the study of low-valent metal chemistry. This is mainly due to their synthetic utility. Naphthalene and anthracene are readily available. Naphthalene and anthracene ligands are very labile, and these complexes are more reactive than the benzene analogues with respect to substitution of the arene ligand by a variety of substrates, including carbon monoxide, isocyanides, phosphines, and alkenes.^{5–10} In addition, complexes containing anionic naphthalene and anthracene ligands can act as reducing agents with concurrent release of neutral arenes.^{11,12} For example, a homoleptic naphthalene titanate $[Ti(\eta^4-C_{10}H_8)_3]^{2-}$ was found to react with P_4 to produce a decaphosphatitanocene dianion $[Ti(\eta^5-P_5)_2]^{2-}$.^{11a}

We recently reported reduction of $[(O_3C)Ti(thf)_2]$ (**1**) (where $[O_3C]^{4-} = [(3,5-tBu_2-2-O-C_6H_2)_3C]^{4-}$) with potassium naphthalenide ($KC_{10}H_8$) under an atmosphere of N_2 to afford a dinitrogen complex $[K(thf)_6][[(O_3C)Ti]_2(\mu-N_2)K_3(thf)_3]$ (**2**), in which the strongly activated N_2 unit binds end-on to two



Scheme 1 Synthesis of the dinitrogen complex **2**.

titanium metals and side-on to three potassium metals (Scheme 1).¹³ Alkali metal naphthalenides are widely utilized as reductants, and they have proven useful for the synthesis of naphthalene complexes.⁵ Therefore, we speculate that the N_2 reaction of **1** with $KC_{10}H_8$ yields a titanium naphthalene intermediate that subsequently undergoes irreversible substitution by dinitrogen. Herein we wish to describe the synthesis and characterization of titanium arene complexes supported by the tripodal $[O_3C]$ ligand and their reactions with dinitrogen.

Treatment of **1** with two equivalents of $KC_{10}H_8$ in THF under an atmosphere of Ar effected a colour change from dark brown to black. A standard workup followed by crystallization from THF/hexane provided $[K_2(thf)_6][[(O_3C)Ti(C_{10}H_8)K(thf)_2]_2]$ (**3-K**) as black crystals in 82% yield (Scheme 2). Formation of **3** has been formulated on the basis of its NMR spectra and combustion analysis. Moreover, the X-ray analysis of **3-K** revealed that the asymmetric unit consists of two crystallographically independent but chemically identical $[(O_3C)Ti(C_{10}H_8)]^{2-}$ dianions and four potassium cations, and that infinite polymeric chains are constructed through multihapto potassium–arene

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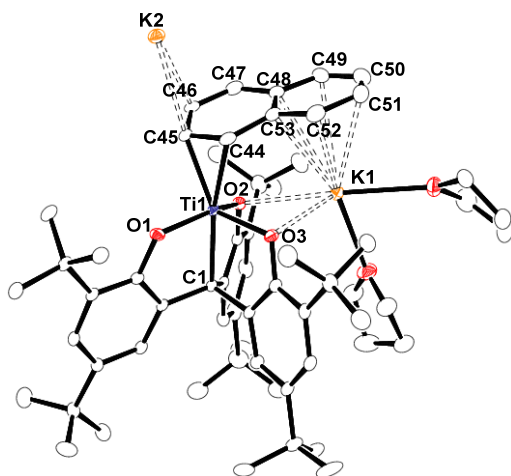


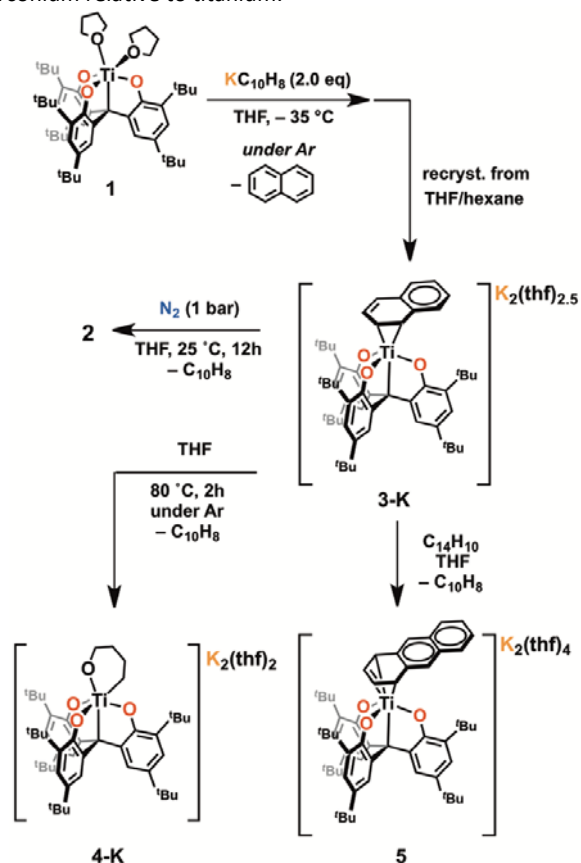
Fig. 1 Structure of one unit of the infinite polymeric chain in **3-K** with thermal ellipsoids set at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti(1)–O(1) 1.922(2), Ti(1)–O(2) 1.926(2), Ti(1)–O(3) 2.024(2), Ti(1)–C(1) 2.230(4), Ti(1)–C(44) 2.243(4), Ti(1)–C(45) 2.208(4), C(44)–C(45) 1.459(5), C(44)–C(53) 1.446(5), C(45)–C(46) 1.423(5), C(46)–C(47) 1.345(5), C(47)–C(48) 1.428(6), C(48)–C(49) 1.396(6), C(48)–C(53) 1.427(6), C(49)–C(50) 1.356(7), C(50)–C(51) 1.364(7), C(51)–C(52) 1.430(7), C(52)–C(53) 1.414(6), O(1)–Ti(1)–O(2) 142.91(10), O(1)–Ti(1)–O(3) 103.02(10), O(2)–Ti(1)–O(3) 103.29(9), C(45)–Ti(1)–C(44) 38.26(13), C(45)–C(44)–Ti(1) 69.57(19), C(44)–C(45)–Ti(1) 72.17(19).

interactions. The structure of one unit of the infinite polymeric chain in **3-K** is presented in Fig. 1.

An intriguing structural feature of **3-K** is an η^2 -coordination of the $[(O_3C)Ti]$ fragment to the 1,2-position of naphthalene. The Ti–C(naphthalene) distances of 2.208(4) and 2.243(4) Å are shorter than those reported for η^2 -arene titanium complexes $[K(cryptand-222)]_2[Ti(\eta^4-C_{10}H_8)_2(\eta^2-C_{10}H_8)]$ [2.277(8), 2.331(8) Å],⁹ $[K(cryptand-222)]_2[Ti(\eta^4-C_{14}H_{10})_2(\eta^2-C_{14}H_{10})]$ [2.290(2), 2.326(2) Å]⁹ and $[K(18-crown-6)(thf)_2][Ti(\eta^4-C_{14}H_{10})(\eta^2-C_{14}H_{10})(\eta^5-C_5Me_5)]$ [2.264(3), 2.273(3) Å],¹⁰ indicating strong π back-donation of the $[(O_3C)Ti]$ unit to the naphthalene ring. The coordinated C(44)–C(45) bond of 1.459(5) Å is long relative to the uncoordinated C–C bonds, while the C(46)–C(47) bond of 1.345(5) Å is short and suggestive of a nearly localized double bond. There is a loss of planarity in the naphthalene unit owing to back-bonding of titanium, as evidenced by the C(44)–C(53)–C(48)–C(47) torsion angle of 10.4(8)°. A similar disruption of aromaticity in the coordinated naphthalene ring is observed in η^2 -naphthalene complexes.^{9,14}

The naphthalene hapticity of the $[(O_3C)Ti(C_{10}H_8)]$ unit is independent from crystallization solvent. The solid-state structure of $[K(cryptand-222)][[(O_3C)Ti(C_{10}H_8)]\{K(thf)_2\}]$, crystallized from THF/cryptand-222, shows the η^2 -coordinated naphthalene ligand similar to that of **3-K**.¹⁵ Low-valent early transition metal complexes with η^2 -arene ligands are uncommon compared to η^4 and η^6 -arene species,^{6–10,16} and **3-K** is a rare example of structurally characterized complexes of this class.^{9,10,17} The η^2 -coordinated naphthalene in **3-K** is in marked contrast to the previously described η^4 -naphthalene zirconium complex $[(O_3C)Zr(C_{10}H_8)\{K(dme)\}_2]$.¹² The difference in

naphthalene coordination modes may reflect the larger size of zirconium relative to titanium.



Scheme 2 Synthesis and reactions of the naphthalene complex **3-K**.

Complex **3** is well soluble in THF and poorly soluble in aromatic and aliphatic hydrocarbon solvents. The 1H NMR spectrum of **3-K** in THF- d_8 is temperature invariant down to 193 K and displays four naphthalene resonances upfield shifted to 3.85, 4.67, 6.01, and 6.08 ppm, rather than eight environments expected for a C_1 symmetric complex in the solid state. The J_{CH} value of the 1,4-carbon atoms in **3-K** (150.5 Hz) is significantly larger than that found in $[(O_3C)Zr(\eta^4-C_{10}H_8)\{K(dme)\}_2]$ (136.7 Hz),¹² implying that these carbon atoms of **3-K** have more sp^2 hybrid character than the corresponding carbon atoms of the zirconium analogue. These NMR data lead us to conclude that the $[(O_3C)Ti]$ fragment undergoes facile 1,3-shift from the 1,2- η^2 -coordinated form to the 3,4- η^2 -form on the NMR time scale in solution. However, we cannot rule out the possibility of the η^4 -naphthalene ligation in solution.

Upon exposure of a solution of **3-K** to an atmosphere of N_2 at room temperature, a colour of the solution changed from black to brown. Monitoring the reaction by NMR spectroscopy revealed conversion of **3-K** to **2** with elimination of naphthalene for 12 h (Scheme 2). The dinitrogen complex **2** was isolated as a right brown solid in 73% yield on a preparative scale. The binding of N_2 is irreversible in **2**, and the isolated dinitrogen complex **2** was not observed to react with naphthalene in THF.

The synthesis of **2** from **3-K** supports the intermediacy of the naphthalene complex during the formation of **2** from **1** by reduction with KC_{10}H_8 under N_2 directly. Arene complexes are known to eliminate an arene and bind dinitrogen, where the coordinated N_2 is weakly activated.¹⁸ However, such transformations have been rarely observed with isolable arene complexes of early transition metals.¹⁹ Since dinitrogen is a weak donor ligand, the ability of the arenes to π -coordinate to low-valent metal centers often hampers formation of dinitrogen complexes.²⁰

The outcome of the reduction of **1** under N_2 can be altered by using KC_8 as a reductant in the place of KC_{10}H_8 . Analysis of the crude reaction mixture by NMR spectroscopy exhibited resonances due to the dinitrogen complex **2** and a 1-oxa-2-titanacyclohexane $[(\text{O}_3\text{C})\text{Ti}\{\text{O}(\text{CH}_2)_4\}\text{K}_2(\text{thf})_2]$ (**4-K**) in a 3:1 ratio as major products along with unidentified products. Alternatively, **4-K** was prepared in 66% by heating a THF solution of **3-K** for 2 h at 80 °C, and the product was characterized by NMR spectroscopy and combustion analysis. The formation of **4-K** is a result of the ring-opening reaction of THF, and C–O bond cleavage reactions of THF to produce oxametallacyclohexanes are well known for group 4 metal complexes.²¹ Reduced titanium species may undergo competing reactions rather than activation of N_2 . In the reaction using KC_{10}H_8 , the Ti(II) intermediate could be trapped by naphthalene and subsequently react with N_2 to generate **2**, thereby preventing formation of undesired products such as **4-K**.

The anthracene analogue was readily prepared by arene exchange. Treatment of **3-K** with anthracene in THF immediately produce a colour change from black to dark purple concurrent with formation of $[(\text{O}_3\text{C})\text{Ti}(\text{C}_{14}\text{H}_{10})\{\text{K}(\text{thf})_2\}_2]$ (**5**) and

free naphthalene. The reaction involves displacement of the coordinated naphthalene by anthracene, which is well established in early transition metal complexes.^{6,8,9,12,22} The identity of **5** has been confirmed by NMR spectroscopy and combustion analysis. The solution behavior of **5** is fluxional and temperature dependent. The variable-temperature ^1H NMR spectra in THF-d_8 indicate migration of the $[(\text{O}_3\text{C})\text{Ti}]$ fragment between the two ends of the coordinated anthracene. At 193 K, the anthracene protons are observed as five broad resonances at 3.98, 5.22, 5.50, 6.35, and 6.35 ppm. On warming the sample to 346 K, these resonances further broaden except for the 5,10-proton resonance at 5.50 ppm, but the high-temperature limiting spectrum is not observed.

The anthracene coordination mode of the $[(\text{O}_3\text{C})\text{Ti}(\text{C}_{14}\text{H}_{10})]$ unit in the solid state depends on crystallization solvent. The η^2 and η^4 -anthracene complexes crystallize from DME/pentane, while the η^4 -coordination mode is preferred in the presence of THF.¹⁵ The observation of both η^2 and η^4 -anthracene ligands in the $[(\text{O}_3\text{C})\text{Ti}(\text{C}_{14}\text{H}_{10})]$ fragment suggests that these two forms are close in energy and that packing forces and interactions with the counter cations dictate the structure.

The solid-state molecular structure of **5** with the η^4 -coordinated anthracene, crystallized from THF/hexane, is presented in Fig. 2. The complex occurs in a tight ion-pair form, two potassium cations being solvated by two aryloxy groups, two THF molecules, and one naphthalene carbon atom. The C–C bonds of the coordinated anthracene carbons display a long–short–long pattern [C(44)–C(45) 1.424(3), C(45)–C(46) 1.380(4), C(46)–C(47) 1.416(4) Å], typical for η^4 -arene complexes.^{7–10} The coordinated arene ring of the anthracene ligand is folded about the C(44)–C(47) vector with a dihedral angle of 25.9°. The Ti–C(anthracene) bonds have a long–short–short–long pattern [Ti–C(44) 2.515(2), Ti–C(45) 2.361(2), Ti–C(46) 2.393(3), Ti–C(47) 2.583(3)], which is unusual for early transition metal η^4 -arene complexes and is due to steric congestion around the metal center and the K–anthracene interactions.⁹

In contrast to the reaction of the naphthalene complex **3-K** to give **2**, the anthracene complex **5** was observed to be inert toward N_2 under comparable conditions. This difference in reactivity is presumably ascribed as a consequence of the strong Ti–anthracene interaction relative to the Ti–naphthalene interaction, because anthracene is a better acceptor ligand and back-bonding is more efficient.²³

In order to probe the influence of alkali cations, attention turned to the synthesis of Ti/Li and Ti/Na naphthalene complexes analogous to **3-K**. Complex **1** was treated with $\text{LiC}_{10}\text{H}_8$ in THF to yield an intractable material, whereas the analogous reaction with $\text{NaC}_{10}\text{H}_8$ afforded $\text{Na}_2[(\text{O}_3\text{C})\text{Ti}(\text{C}_{10}\text{H}_8)]$ (**3-Na**) as a brown powder. The NMR spectra of **3-Na** are very similar to those observed for **3-K**, indicating that **3-Na** contains an η^2 -coordinated naphthalene ligand. Complex **3-Na** was contaminated with a small amount of unidentified products, and their similar solubility complicated the preparation of pure **3-Na**.

Stirring a THF solution of **3-Na** under N_2 at room temperature for 2 h resulted in multiple unidentified products, from which a small amount of the 1-oxa-2-titanacyclohexane (**4-**

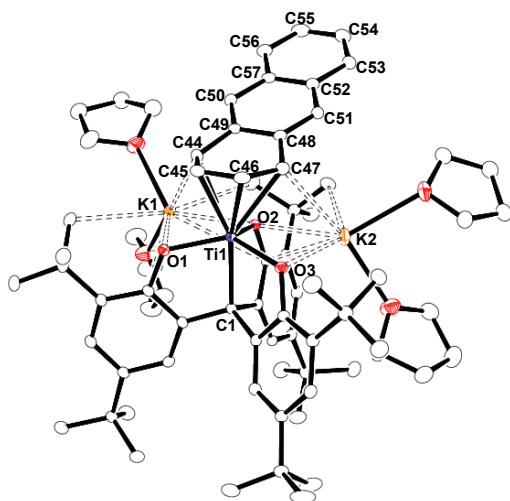


Fig. 2 Structure of **5** with thermal ellipsoids set at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti(1)–O(1) 1.9695(17), Ti(1)–O(2) 2.0172(16), Ti(1)–O(3) 1.9647(16), Ti(1)–C(1) 2.247(2), Ti(1)–C(44) 2.515(2), Ti(1)–C(45) 2.361(2), Ti(1)–C(46) 2.393(3), Ti(1)–C(47) 2.583(3), C(44)–C(45) 1.424(3), C(44)–C(49) 1.451(3), C(45)–C(46) 1.380(4), C(46)–C(47) 1.416(4), C(47)–C(48) 1.442(3), C(48)–C(49) 1.445(3), O(1)–Ti(1)–O(2) 107.05(7), O(3)–Ti(1)–O(1) 131.78(7), O(3)–Ti(1)–O(2) 108.11(7), C(45)–C(44)–C(49) 120.7(2), C(46)–C(47)–C(48) 121.5(2).

Na) was isolated. No evidence for formation of the N₂ complex was observed. The complex **4-Na** was alternatively prepared by heating a THF solution of **3-Na**, and it was characterized by NMR spectroscopy and X-ray diffraction analysis.¹⁵

In summary, we have synthesized titanium atrane complexes with an η^2 -coordinated naphthalene and anthracene ligands, which are the rare examples of complexes of this class fully characterized by X-ray crystallography. The naphthalene complex **3-K** is observed to readily eliminate arene in contact with dinitrogen which leads to formation of the end-on N₂ bridging dititanium complex **2**, while the anthracene complex **5** is not reactive toward N₂. The reactivity of the dianionic naphthalene complex $[(O_3C)Ti(C_{10}H_8)]^{2-}$ depends on the nature of counter cations. Further studies to explore the chemistry of these systems are in progress.

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Conflicts of interest

The authors declare no conflict of interest.

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For table of contents entry

A η^2 -naphthalene titanium complex supported by the tripodal ligand react with N_2 to produce a strongly activated N_2 complex.

