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Synthesis and Chemistry of the First Isolable Bis(naphthalene)titanium Complexes. Structural Characterization of $[Ti(\eta^4\text{-}C_{10}H_8)_2(SnMe_3)_2]^{2-}$ [1,2]

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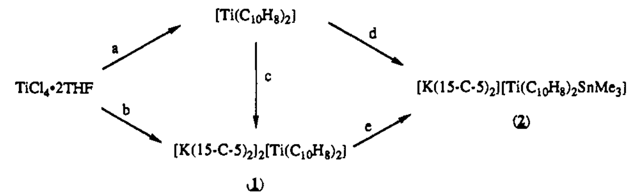
Bis(naphthalene)metal complexes are a highly reactive and potentially useful class of sandwich compounds as they readily undergo metal-centered substitution reactions with a variety of ligands.[3] In the past, homoleptic naphthalene or substituted naphthalene complexes have been isolated only from metal–atom ligand cocondensation[4] and potassium or magnesium atom reactions[5] for vanadium, chromium, and molybdenum. Bis(naphthalene)titanium(0)[6a] and bis((5–8-η)-1,4-dimethylnaphthalene)titanium(0)[6b] also have been prepared by the former method but could not be isolated in pure form due to their poor thermal stabilities. All of these syntheses required specialized equipment unavailable to most chemists. Except for bis(naphthalene)chromium(0)[3,4,7] and analogous molybdenum complexes,[5c] their properties remain poorly explored due to their relative inaccessibility.

Since alkali metal naphthalenides are readily prepared by conventional methods[8] and have been shown to be effective precursors to several mononaphthalene metal complexes,[9,10] we have been exploring their possible use in the synthesis and *isolation* of bis(naphthalene)metal species. Although conventional naphthalenide reductions of metal precursors have been *suggested* previously to provide homoleptic naphthalene complexes, products from these reactions were not isolated and were formulated only on the basis of EPR spectroscopy[11] or their reaction chemistry.[12]

Scheme I[a]



(1)

(2)

[a] (a) Four equivalents of $KC_{10}H_8$, THF, –60 °C, product was not isolated; (b) 6 equiv of $KC_{10}H_8$, THF, –60 °C, then 15-crown-5; (c) 2 equiv of $KC_{10}H_8$, THF, –60 °C, then 15-crown-5; (d) $KSnMe_3$, 15-crown-5, THF, –78 °C; (e) Me_3SnCl, THF, –60 °C.

We now report that the first examples of isolable bis(naphthalene)titanium complexes, $[Ti(C_{10}H_8)_2]^{2-}$, **1**, and $[Ti(C_{10}H_8)_2SnMe_3]^-$, **2**, have been prepared by this method. Both of these compounds are stable derivatives of the very unstable $Ti(C_{10}H_8)_2$.[6] Bright purple solutions of the latter substance, or a solvated version thereof, were readily prepared by reduction of $TiCl_4{\cdot}2THF$, THF = tetrahydrofuran, with 4 equiv of $KC_{10}H_8$ at –60 °C in THF, but these quickly decomposed below –20 °C to finely divided titanium metal and naphthalene. Rapid treatment of these purple solutions with an additional 2 equiv of $KC_{10}H_8$ or 1 equiv of $KSnMe_3$ at –60 °C caused the solutions to become dramatically more thermally stable and to change to a deep red brown or dark green color, characteristic of **1** or **2**, respectively. Following filtration, addition of 15-crown-5, solvent removal, and washing with pentane and either, satisfactorily pure microcrystals of **1** or **2** as $[K(15\text{-crown-}5)_2]^+$ salts were isolated in 75–90% yields.[13] Also, **2** was independently prepared by treatment of **1** with Me_3SnCl. These interconversions and reaction conditions are summarized in Scheme I.

Elemental analyses, ^1H NMR spectra, and reaction chemistry, vide infra, are in full accord with our formulation of **1** as containing bis(naphthalene)titanate(2–),[13] formally analogous to the known isoelectronic $Cr(C_{10}H_8)_2$.[7] The ^1H NMR spectra of freshly prepared solutions of **1** showed no evidence for free naphthalene and consisted of four multiplets of equal intensity due to two AA′BB′ systems of hydrogens on the coordinated and uncoordinated rings.[13] These δ values are shifted substantially upfield relative to those previously observed for $Cr(C_{10}H_8)_2$,[7] in accord with the trend expected for a more electron rich naphthalene complex. Poor solubility of **1** in unreactive solvents has prevented us from obtaining ^{13}C NMR spectra for this species, so we cannot state with certainty that $[Ti(C_{10}H_8)_2]^{2-}$ is isostructural with $Cr(C_{10}H_8)_2$. Also, attempts to obtain definitive ^1H or ^{13}C NMR data for **2** have been frustrated by its thermal instability in solution, so presently the formulation of **2** is based only on elemental analyses and reaction chemistry. However, on the basis of the latter, **2** unquestionably contains bound naphthalene groups, vide infra.

Compounds **1** and **2** readily absorbed CO at atmospheric pressure and low temperature, –60 to –20 °C, to provide the previously reported $[K(15\text{-crown-}5)_2]_2[Ti(CO)_6]$[14] and $[K(15\text{-crown-}5)_2][Ti(CO)_6SnMe_3]$[2] in 60–65% and 40% isolated yields, respectively. Naphthalene is the only hydrocarbon eliminated from **1** and **2** in these carbonylation reactions. On the basis of this present study, **1** was identified as the previously uncharacterized intermediate in the original naphthalenide-promoted

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[1] This paper is dedicated to the memory of Professor Paul G. Gassman, a friend and colleague who is greatly missed.

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[13] Anal. Calcd for **1**, $C_{60}H_{96}O_{20}K_2Ti$: C, 57.04; H, 7.66; K, 6.19; Ti, 3.79. Found: C, 56.75; H, 7.47; K, 5.95; Ti, 3.69. ^1H NMR for **1** (500 MHz, THF-d_8, –20 °C): δ = 5.49 (m, 2H, free ring), 5.28 (m, 2H, free ring), 4.51 (m, 2H, bound ring), 3.60 (s, 80H, 15-crown-5), 2.90 (m, 2H, bound ring) ppm. Anal. Calcd for **2**, $C_{43}H_{65}O_{10}KSnTi$: C, 54.50; H, 6.91; Sn, 12.52; K, 4.13; Ti, 5.05. Found: C, 54.44; H, 6.80; Sn, 12.35; K, 4.32; Ti, 4.92.

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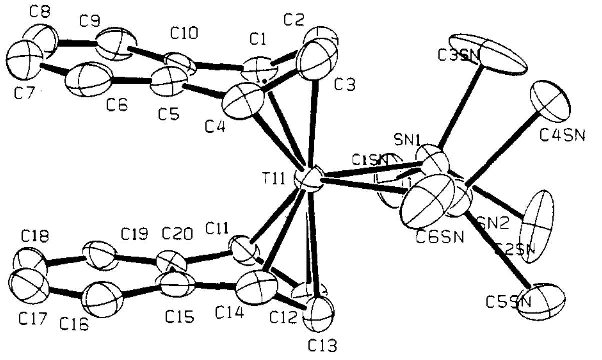

Figure 1. ORTEP drawing and labeling scheme for $[Ti(\eta^4\text{-}C_{10}H_8)_2(SnMe_3)_2]^{2-}$. Thermal ellipsoids are drawn with 50% probability boundaries, and hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ti–Sn(1) = 2.869(3), Ti–Sn(2) = 2.865(3), Ti–C(1) = 2.32(1), Ti–C(2) = 2.32(1), Ti–C(3) = 2.30(1), Ti–C(4) = 2.31(1), Ti–C(11) = 2.31(1), Ti–C(12) = 2.34(1), Ti–C(13) = 2.32(1), Ti–C(14) = 2.30(1), C(1)–C(2) = 1.43(2), C(2)–C(3) = 1.36(2) , C(3)–C(4) = 1.44(2), C(4)–C(5) = 1.45(2), C(5)–C(10) = 1.42(2), C(1)–C(10) = 1.47(2), C(11)–C(12) = 1.43(2), C(12)–C(13) = 1.38(2), C(13)–C(14) = 1.43(2), C(14)–C(15) = 1.45(2), C(15)–C(20) = 1.42(2), C(11)–C(20) = 1.46(2), mean C–Sn = 2.19(2), other mean exobenzene C–C = 1.38(2), Sn(1)–Ti–Sn(2) = 76.44(6).

synthesis of $[Ti(CO)_6]^{2-}$ from $TiCl_4{\cdot}2THF$.[14] Perhaps more significant, however, is that **1** has been established to be an early transition metal analog of Jonas's remarkable homoleptic ethylene complexes, $[Co(C_2H_4)_4]^-$ and $[Fe(C_2H_4)_4]^{2-}$, which function as synthetic equivalents of "naked" Co(1–) and Fe(2–) in their reactions with CO[15] and CNR.[16]

Nearly saturated solutions of **2** in THF were unstable and over a 2-week period at –20 °C deposited small amounts of single crystals of an unusual new substance, $[K(15\text{-crown-}5)_2]_2[Ti(C_{10}H_8)_2(SnMe_3)_2]$, **3**, which has been structurally characterized (Figure 1),[17] and independently synthesized and isolated in 55% yield by the reaction of **2** and $KSnMe_3$ in the presence of 15-crown-5.[18] This result is important as it corroborates our other evidence that bis(naphthalene)titanium complexes are accessible by this facile route. The only previous bis(naphthalene)metal complex to have been structurally characterized is $Cr(C_{10}H_8)_2$, which has two planar $\eta^6\text{-}C_{10}H_8$ groups bound to an 18-electron chromium center.[7b] In contrast, the dianionic titanium species is formally a 16-electron complex and contains two distinctly nonplanar $\eta^4\text{-}C_{10}H_8$ units. The individual planar exobenzene and coordinated diene units of the naphthalene groups have CC distances (Figure 1) and corresponding dihedral angles of 31.0° and 35.4°, which are similar to those of other η^4-naphthalene complexes.[19] For comparison, a corresponding dihedral angle of only 12.4° was observed for the 16-electron species $Ti(\eta^6\text{-}C_{10}H_8)(tBuSi(CH_2PMe_2)_3)$, the only other structurally characterized titanium naphthalene complex.[9e] The average Ti–C bond distance of 2.32(2) Å in **3** is within the range of Ti–C distances observed in the latter complex[9e] and $[Ti(biphenyl)_2]^-$,[20a] but longer than corresponding values (average = 2.24 Å) reported for $Ti(benzene)_2$.[20b] The average Ti–Sn distance of 2.866(4) Å is slightly longer than the corresponding value of 2.83(2) Å reported for $[Ti(CO)_5(SnPh_3)_2]^{2-}$,[21] perhaps due to a more crowded environment about the titanium in **3**. A long Sn–Sn separation of 3.54 Å in **3** indicates that no significant Sn–Sn bonding is present in this substance.[22] The sandwich like $[K(15\text{-crown-}5)_2]^+$ counterions are well separated from the anions in the crystalline lattice and have structures[17] very similar to that previously reported for $[Rb(15\text{-crown-}5)_2]^+$.[23]

In summary, interactions of $TiCl_4{\cdot}2THF$ with potassium naphthalenide have been shown for the first time to be useful routes to isolable but quite labile bis(naphthalene)titanium complexes, including the unusual formally 16 electron dianion, $[Ti(\eta^4\text{-}C_{10}H_8)_2(SnMe_3)_2]^{2-}$. The latter is the initial example of a structurally characterized bis(naphthalene)metal complex containing tetrahapto bound naphthalene groups. It is expected that $C_{10}H_8^-$ and substituted naphthalenides generated by conventional procedures will prove to be versatile reagents in the synthesis and isolation of a host of similar sandwich complexes of other metals, which until now have been available only by metal atom vapor techniques.

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Supplementary Material Available: Experimental details and additional characterization data for compounds **1–3** and further details of the crystal structure determination for **3** including tables of atomic coordinates, thermal parameters, bond lengths and angles, and least squares planes (44 pages); listing of observed and calculated structure factors for **3** (56 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(17) Single crystals of **3** were obtained by layering a nearly saturated solution of **2** in THF at 0 °C with diethyl ether and then storing the mixture at –20 °C for 2 weeks. Thick black crystals of **3** deposited in low (<5%) yield. One of these was selected for the X-ray study. Two independent attempts to grow crystals of **2** in this fashion provided only crystalline **3** with identical unit cell parameters. Crystal data for **3**: $C_{66}H_{114}O_{20}K_2Sn_2Ti$, monoclinic, $P2_1/n$ (No. 14), $a = 16.094(6)$ Å, $b = 18.732(9)$ Å, $c = 27.48(1)$ Å, $\beta = 103.71(3)°$, $V = 8048(11)$ Å^3, $Z = 4$, D(calcd) = 1.313 g cm^{-3}, μ(Mo Kα) = 8.76 cm^{-1}; crystal dimensions, 0.20 × 0.50 × 0.60 mm^3. The intensities of 14 361 reflections were measured at –101 °C ($0 < \theta < 25$) on an Enraf-Nonius CAD 4 diffractometer using Mo Kα radiation. The structure was solved by direct methods, and all ordered non-hydrogen atoms were refined anisotropically (full matrix least squares). For 8319 unique observed reflections [$I \geq 2.0\sigma(I)$], $R = 0.084$ and $R_w = 0.092$. There is one potassium in a general position, and there are two potassiums on centers of symmetry in the unit cell. The crown ethers associated with two of the potassium ions are sufficiently ordered to establish the 10-coordinate nature of the potassium ions, with a mean K–O distance of 2.89(6) Å, but those associated with the third potassium, K3, on one of the centers, are highly disordered. The atoms for these disordered 15-crown-5 rings have been put in with variable occupancies to try to fit the map, but the fit was poor. However, in all attempts to model the disorder in the cation rings, the structural parameters of the anion remained essentially unchanged, leading us to believe that the anionic unit in **3** is very well defined despite the poor R values.

(18) Nearly black microcrystalline **3** is so poorly soluble in THF and other unreactive solvents that no NMR spectral characterization was possible. Anal. Calcd for **3**, $C_{66}H_{114}O_{20}K_2Sn_2Ti$: C, 49.82; H, 7.22; Sn 14.92. Found: C, 49.54; H, 7.12; Sn, 14.75.

(19) For example, corresponding dihedral angles of 37.1°, 41°, 41.5°, and 43° were observed in $[Mn(\eta^4\text{-}C_{10}H_8)(CO)_3]^-$,[10] $Fe((5\text{–}8\text{-}\eta^4)\text{-}1,4\text{-}C_{10}H_6Me_2)(P(OMe)_3)_3$ [(a) Schäufele, H.; Hu, D.; Pritzkow, H.; Zenneck, U. *Organometallics* **1989**, *8*, 396], $Ru(\eta^4\text{-}C_{10}Me_8)(\eta^6\text{-}C_6Me_6)$ [(b) Hull, J. W.; Gladfelter, W. L. *Organometallics* **1984**, *3*, 605], and $Ta(\eta^4\text{-}C_{10}H_8)(Me_2PCH_2CH_2PMe_2)_2Cl$,[9b] respectively.

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