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Structurally Distinct Homoleptic Anthracene Complexes, $[M(C_{14}H_{10})_3]^{2-}$, M = Titanium, Zirconium, Hafnium: Tris(arene) Complexes for a Triad of Transition Metals**

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Dedicated to Professor E. Peter Kündig

Polycyclic aromatic hydrocarbon– or polyarene–transition metal complexes continue to be exciting reagents for the exploration of low-valent chemistry of their constituent metals because of the substantial lability of the coordinated polyarenes in numerous reactions.[1,2] For example, bis(anthracene)ferrate(1−) was recently shown to be a unique storable source of the atomic Fe^- ion in its reactions with CO and 1,3-butadiene to afford $[Fe_2(CO)_8]^{2-}$ and the first isolable homoleptic butadiene iron complex, $[Fe(C_4H_6)_2]^-$.[3] The first well-characterized homoleptic polyarenemetalate, tris(naphthalene)zirconate(2−) (**1**),[4] was reported nearly 15 years ago, and related complexes are now documented for Nb,[5] Ta,[6] Fe,[3] and Co.[7] However, little or nothing is known about the analogous metalates of other d-block elements.[2,8] We report herein the synthesis, isolation, and structural characterization of the first set of homoleptic polyarenemetalates for a triad of transition metals: the tris(anthracene)metalates(2−), $[M(C_{14}H_{10})_3]^{2-}$, M = Ti (**2**), Zr (**3**), and Hf (**4**). In addition, the triad of Group 4 elements has been "completed" for homoleptic naphthalene complexes with access to the tris(naphthalene)metalates(2−), $[M(C_{10}H_8)_3]^{2-}$, for M = Ti (**5**), Hf (**6**). Hafnates **4** and **6** are of particular interest as they are the first polyarene complexes of Hf and are unprecedented examples of hydrocarbon-stabilized negative-valent hafnium, Hf^{2-}, previously established for only one other compound, $[Hf(CO)_6]^{2-}$.[9,10]

Reactions of $[MCl_4(thf)_2]$ (M = Ti, Zr) with monopotassium anthracene ($K[C_{14}H_{10}]$) in THF were carried out under nearly the same conditions as recently described for the synthesis of bis(anthracene)cobaltate(1−),[7] and resulted in the formation of anions **2** or **3**, isolated in 30–40 % yields as dark purple [K([18]crown-6)] salts [Eq. (1)], where L = [18]crown-6, M = Ti, **2**, or Zr, **3**.[11] An analogous reaction of $[TiCl_4(thf)_2]$ with monopotassium naphthalene ($K[C_{10}H_8]$) in THF provided titanate **5** in 70–80 % isolated yields as brown-black to black microcrystalline [K([18]crown-6)] or [K([2.2.2]cryptand)] salts (see the Experimental Section).

$$[MCl_4(thf)_2] + 6\,K[C_{14}H_{10}] \xrightarrow[-60-20\,^\circ C,\ -KCl]{THF} \xrightarrow{L} [K(L)]_2[M(C_{14}H_{10})_3] + 3\,C_{14}H_{10} \tag{1}$$

Numerous attempts to obtain hafnates **4** and **6** by analogous procedures have been entirely unsuccessful in the past. However, we recently discovered that reduction of a 1:4 mole ratio of $[HfCl_4(thf)_2]/PMe_3$ by six equivalents of $K[C_{14}H_{10}]$ or $K[C_{10}H_8]$ in dimethoxyethane (DME) afforded the first examples of anthracene or naphthalene complexes of hafnium. The long-sought anions **4** or **6** were isolated from these reactions in approximately 20 % yield as dark purple or deep red-brown [K([18]crown-6)] salts [Eq. (2)], where ArH = $C_{10}H_8$ or $C_{14}H_{10}$, or in 36 % yield as $[K([2.2.2]cryptand)]_2[\mathbf{6}]$.[11] Efforts are underway to identify intermediates in these intriguing formal six-electron phosphane-mediated reductions, in order to help understand why $HfCl_4$ behaves differently from $ZrCl_4$ and $TiCl_4$, which do not require the presence of PMe_3 to directly access negative-valent complexes. Other significant differences in the chemistry of the Group 4 elements have been highlighted recently.[12–14] Treatment of **6** with three equivalents of anthracene between −60 and 20 °C resulted in full displacement of naphthalene after 16 h and provided a more facile route to $[K([18]crown\text{-}6)]_2[\mathbf{4}]$, isolated in 70 % yield (based on **6**).[11] Anion **6** also readily undergoes carbonylation at atmospheric pressure to afford the previously poorly accessible $[Hf(CO)_6]^{2-}$,[9] details of which will be reported separately.[15]

$$[HfCl_4(thf)_2] + 6\,K[ArH] \xrightarrow[-60^\circ,\ -KCl]{DME,\ PMe_3} \xrightarrow{L} [K(L)]_2[Hf(ArH)_3] + 3\,ArH \tag{2}$$

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^{1}H and ^{13}C NMR spectra of **2**–**6** were cation independent and in good agreement with corresponding spectra previously reported for **1**.[4] For example, proton-coupled ^{13}C NMR spectra of these species show only one singlet between 150–155 ppm, which is in the characteristic region for quaternary carbons in 1,2,3,4-η^4-anthracene (bound ring only) and η^4-naphthalene complexes.[16,17]

Single-crystal X-ray structural characterizations of the zirconate **3** and hafnates **4** and **6** confirmed the deductions from solution NMR data about the nature of these anions. In particular, the anthracenemetalates **3** and **4** contain three essentially identical η^4-anthracene groups coordinated through an outer ring to Zr and Hf in a trigonal prismatic array.[11] Also, the naphthalenehafnate **6** has a nearly identical structure to that previously reported for **1**. Because the solution NMR spectra of **2** and **5** are consistent with the presence of three equivalent η^4-polyarene ligands,[11] it was a surprise to discover that their solid-state structures are much less symmetrical, and best formulated as $[Ti(\eta^4\text{-polyarene})_2(\eta^2\text{-polyarene})]^{2-}$, the first tris(arene) complexes of 3d metals (the structure of **2** is shown in Figure 1).[18,19] These compounds are also of interest as they are the only homoleptic polyarene complexes to contain arenes of different hapticities within the same molecule, a feature previously observed for only one homoleptic arene sandwich complex, $[Ru(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)]$.[20] Anions **2** and **5** are unprecedented examples of well-defined 16-electron homoleptic polyarene complexes. Only 17- and 18-electron complexes of this type were previously known. An interesting interplay of electronic and steric effects is likely to contribute to the structural character of **2** and **5** in the solid state. These structures are unusual compared to other known tris(polyarene)metal complexes. Thus, although titanium has approximately the same atomic and covalent radii as Nb and Ta,[21] which provide unexceptional 18-electron tris(1,2,3,4-η^4-anthracene)metalates[5,6] and tris(η^4-naphthalene)tantalate,[6] the Ti−C bonds in **2** and **5** are all significantly shorter (on average about 0.05 Å) than the corresponding M−C bonds in the Group 5 complexes.[22] Undoubtedly this difference arises from a greater degree of δ- or back-bonding from Ti to the polyarene, which draws the polyarene groups closer to the Ti centers and results in sufficiently strong intramolecular polyarene repulsions to cause reduced hapticity (η^2) in one ring in both **2** and **5**.[23,24] Steric crowding around the titanium centers in **2** and **5** is also indicated by the presence of a well-developed long-short-short-long pattern in the Ti−C bond lengths of the η^4-diene units.[25] This is an unusual feature for early transition metal η^4-polyarene complexes and is diagnostic of a crowded metal center, as recently observed and discussed for $[Nb(\eta^4\text{-}C_{10}H_8)_2(PMe_3)_2]^-$.[26] Interestingly, comparison of the average M–C distances in $[Ti(CO)_6]^{2-}$, 2.038(3),[9] $[Nb(CO)_6]^-$, 2.089(5), and $[Ta(CO)_6]^-$ 2.083(6) Å,[27] shows a very similar influence of enhanced metal-to-ligand back-bonding for the more electron-rich Ti^{2-} relative to the Group 5 M^- complexes. Finally, crystalline-lattice or cation–anion interactions appear unlikely to contribute significantly to the structures of the anthracene and naphthalene titanates in $[K([2.2.2]cryptand)]_2[\mathbf{2}]$ and $[K([18]crown\text{-}6)]_2[\mathbf{5}]$, respectively, because the coordination environments of titanium are nearly identical, despite the different crystal systems (triclinic versus monoclinic, respectively) of the salts and packing arrangements of cations and anions.[28] Based on a prior study,[29] there has been concern that the structure of anion **5** could be cation-dependent. However, crystal structures of the [K([18]crown-6)] and [K([2.2.2]cryptand)] salts of **5** showed the presence of statistically identical anionic units.[11,30]

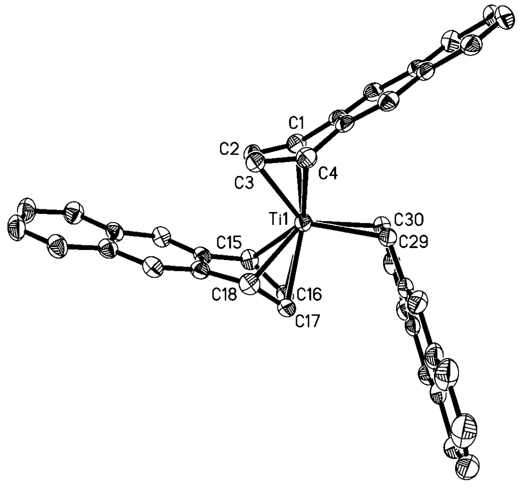

Figure 1. Molecular structure of anion **2**. Thermal ellipsoids are set at the 50% probability level, with hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles[°]: Ti–C1 2.341(3), Ti–C2 2.272(3), Ti–C3 2.286(3), Ti–C4 2.376(3), Ti–C15 2.366(3), Ti–C16 2.302(2), Ti–C17 2.300(2), Ti–C18 2.370(3), Ti–C29 2.290(2), Ti–C30 2.326(2), C1–C2 1.426(4), C2–C3 1.380(4), C3–C4 1.428(4), C15–C16 1.426(4), C16–C17 1.376(4), C17–C18 1.434(4), C29–C30 1.447(4), Ti–(η^4(C1-C4)) 1.953, Ti–(η^4(C15-C18)) 1.975, Ti–(η^2) 2.191, (η^4-Ti-η^4) 131.1, (η^2-Ti-η^4(C1-C4)) 117.5, (η^2-Ti-η^4(C15-C18)) 111.3.

Facile chemical reactions of naphthalenehafnate **6** with CO and anthracene, mentioned above, are consistent with its characterization as a source of the to date unknown atomic Hf^{2-}. Because of the paucity of well-defined anionic homoleptic 1,3,5,7-cyclooctatetraene (cot) transition metal complexes, of which only $[M(\eta\text{-cot})_3]^-$ (M = Nb, Ta)[31] and $[Co(\eta\text{-cot})_2]^-$ have been reported to date,[7] the reaction of **6** with cot was also examined; this was shown to provide the first well-defined Group 4 complex of this type, $[Hf(\eta\text{-cot})_3]^{2-}$ (**7**).[32] Complex **7** was isolated as an air-sensitive orange microcrystalline [K([18]crown-6)] salt in 85% yield.[11] ^{1}H and ^{13}C NMR spectra of **7** were independent of cation, solvent, and temperature (to −95 °C in THF) and showed sharp singlets at $\delta_H = 4.99$ and $\delta_C = 97.3$ ppm, respectively, with $J_{CH} = 150.3$ Hz, indicative of significant carbanion character for the cot groups in **7**.[7] The solution NMR data therefore indicate that **7** is highly fluxional and is analogous to many other cot complexes, including $[M(\eta^8\text{-cot})(\eta^4\text{-cot})]$ (M = Zr, Hf).[33] A single-crystal X-ray study of **7** revealed the presence of an unusual 16-electron species, $[Hf(\eta^4\text{-cot})(\eta^3\text{-cot})_2]^{2-}$, which is of interest as the first Group 4 complex to contain an unsubstituted η^3-cot group.[34] Steric effects do not appear to favor this structure over that of the unknown $[Hf(1\text{-}4\text{-}\eta^4\text{-cot})_3]^{2-}$.[24] Previously, only Group 5 complexes, e.g., $[Nb(\eta^4\text{-cot})(\eta^3\text{-cot})_2]^-$[31] and $[Cp^*M(\eta^4\text{-butadiene})(\eta^3\text{-cot})]$ ($Cp^* =$

C_5Me_5, M = Nb,[35] and Ta (**8**))[36] were established to possess this unusual cot binding mode. The η^4-cot group in **7** is normal and quite similar to that present in [Cp*Zr(allyl)(cot)].[37] However, the η^3-cot groups in **7** are best formulated as coordinated allylic units, with Hf−C bond distances in the range 2.298–2.529 Å, where all other ring carbons are more than 3.10 Å from the metal (Figure 2). Essentially planar *exo*-pentadienyl units (deviation from planarity, 0.016(1) Å) are also present in the η^3-cot ligands, with nearly identical C–C distances (on average 1.392(8) Å). Erker et al. previously proposed that the almost structurally identical η^3-cot group in **8** was effectively a dianionic ligand, comprising coordinated allylic and uncoordinated *exo*-pentadienyl anion units.[36] Interestingly, a computational study on neutral [Zr(η^8-cot)(η^n-cot)] indicated that the known ($n = 4$)[33] and unknown ($n = 3$) isomers have essentially equal stabilities and should be regarded as Zr^{IV} complexes.[34] On this basis, **7**, is provisionally formulated to contain Hf^{IV}. However, a theoretical study may help to shed more light on the nature of the metal–cot interactions in this unusual species.

In conclusion, the first examples of homoleptic anthracene complexes $[M(\eta\text{-}C_{14}H_{10})_3]^{2-}$ for a triad of transition metals have been obtained, M = Ti (**2**), Zr (**3**), and Hf (**4**), as well as naphthalene analogs, $[M(\eta\text{-}C_{10}H_8)_3]^{2-}$, for M = Ti (**5**) and Hf (**6**). Hafnates **4** and **6** are of interest as unprecedented formally negative-valent hydrocarbon complexes of Hf, and potentially important precursors for studies on low-valent Hf chemistry, which remains very poorly explored. Titanates **2** and **5** are the first examples of isolable 16-electron homoleptic polyarene complexes and contain polyarenes of different hapticities within the same molecule, a feature previously observed only in the heteroleptic Ti^0 species, [Ti(η^6-An)(η^4-An)(dmpe)] and [Ti(η^5-Cp*)(η^4-An)(η^2-An)]$^-$, An = anthracene.[38]

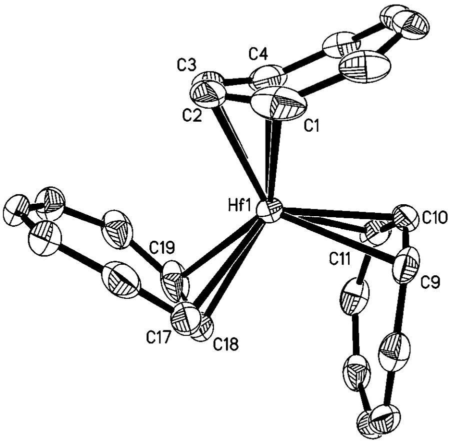

Figure 2. Molecular structure of anion **7**. Thermal ellipsoids are set at 50% probability level, with hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles[°]: Hf–C1 2.528(4), Hf–C2 2.354(4), Hf–C3 2.386(4), Hf–C4 2.624(4), Hf–C9 2.529(4), Hf–C10 2.309(4), Hf–C11 2.512(4), Hf–C17 2.494(4), Hf–C18 2.298(4), Hf–C19 2.466(4), C1–C2 1.428(8), C2–C3 1.386(8), C3–C4 1.399(7), C9–C10 1.416(5), C10–C11 1.415(6), C17–C18 1.421(7), C18–C19 1.411(7), Hf–(η^4) 2.072, Hf–(η^3(C9-C11)) 2.196, Hf–(η^3(C17-C19)) 2.163, (η^3-Hf-η^3) 116.5, (η^4-Hf-η^3(C9-C11)) 117.1, (η^4-Hf-η^3(C17-19)) 126.4.

Experimental Section

5: A yellow solution of $[TiCl_4(thf)_2]$ (1.000 g, 3.00 mmol) in THF (80 mL, −60 °C) was added to a dark green slurry of $K[C_{10}H_8]$ (18.0 mmol) and [18]crown-6 (1.583 g, 5.99 mmol) in THF (80 mL, −60 °C). The resulting red-brown reaction mixture was warmed to room temperature with stirring over a 16 h period and filtered. After thoroughly washing the filter cake with THF (10 mL), solvent was removed in vacuo until about 5 mL remained. Diethyl ether (100 mL) was then added to precipitate a nearly black solid, which was isolated by filtration, thoroughly washed with ether, and dried in vacuo to provide pure black-brown microcrystalline $[K([18]crown\text{-}6)]_2[\mathbf{5}]$ (2.256 g, 73 % based on $[TiCl_4(thf)_2]$). Elemental anal. (%) calcd for $C_{54}H_{72}K_2O_{12}Ti$: C 62.41, H 6.98; found: C 61.99, H 7.15; m.p. 101–104 °C (dec); ^1H NMR (300 MHz, $[D_8]$THF, −35 °C, cation resonances omitted): $\delta = 2.85$ (br, 6H, H1,H4), 4.45 (br, 6H, H2,H3), 5.27, 5.48 ppm (br, 6H each, H5,H8 or H6,H7); $^{13}C\{^1H\}$ NMR (75 MHz, $[D_8]$THF, −35 °C): $\delta = 78.5$ (C1,C4), 109.0 (C2,C3), 114.1, 117.9 (C5,C8 or C6,C7), 150.7 ppm (C9, C10). Identification of C,H resonances was based on previous trends[4,6] and ^1H–^{13}C HMQC and COSY 2D NMR spectroscopy, but no unique assignments for the *exo*-benzene hydrogen atoms or corresponding carbon atoms were possible. Solution NMR spectra of **5** (and **2**) are quite temperature dependent, details of which will be reported separately. X-ray quality single-crystals of $[K([18]crown\text{-}6)]_2[\mathbf{5}]$ were grown as green-black blocks from a THF/HMPA (10:1) solution layered at 0 °C with diethyl ether (see Figure S3 in the Supporting Information).[19d] Synthesis and characterization of $[K([2.2.2]cryptand)]_2[\mathbf{5}]$ and preparation of **2**–**7** and the structures of anions **3**, **4**, **5**, and **6** are described in the Supporting Information.

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[18] Additional data for **2**: fold angles for η^4-$C_{14}H_{10}$ groups are 24.5(1), 26.8(1)°; η^2-$C_{14}H_{10}$ is essentially planar (deviation from planarity, 0.034(1) Å).

[19] a) Crystal data for [K([2.2.2]cryptand)]$_2$[**2**](thf)$_2$: $C_{86}H_{118}K_2N_4O_{14}Ti$, $M_r = 1557.94$, triclinic, space group $P\bar{1}$, dichroic red-green needles, $a = 14.122(2)$, $b = 15.862(2)$, $c = 18.577(2)$ Å, $\alpha = 92.968(2)$, $\beta = 104.092(2)$, $\gamma = 93.171(2)$°, $V = 4020.8(8)$ Å^3, $Z = 2$, $T = 173(2)$ K, $\lambda = 0.71073$ Å, 36751 reflections, 16306 independent, $R1 = 0.0549$ ($I > 2\sigma(I)$), $wR2 = 0.1213$ (all data), $\mu = 0.276$ mm^{-1} (SADABS); b) [K([18]crown-6)]$_2$[**3**]-(dme)(Et$_2$O)$_{0.5}$: $C_{72}H_{93}K_2O_{14.5}Zr$, $M_r = 1359.90$, monoclinic, space group $P2_1/n$; red-gold plates, $a = 17.136(2)$, $b = 21.869(2)$, $c = 19.841(2)$ Å, $\beta = 115.169(2)$°, $V = 6730(1)$ Å^3, $Z = 4$, $T = 173(2)$ K, $\lambda = 0.71073$ Å, 36350 reflections, 11807 independent, $R1 = 0.0433$ ($I > 2\sigma(I)$), $wR2 = 0.1059$ (all data), $\mu = 0.352$ mm^{-1} (SADABS); c) [K([18]crown-6)]$_2$[**4**](dme)(Et$_2$O)$_{0.5}$: $C_{72}H_{93}HfK_2O_{14.5}$, $M_r = 1447.15$, monoclinic, space group $P2_1/n$, metallic red-green needles, $a = 17.148(2)$, $b = 21.877(3)$, $c = 19.839(3)$ Å, $\beta = 115.147(2)$°, $V = 6737(2)$ Å^3, $Z = 4$, $T = 173(2)$ K, $\lambda = 0.71073$ Å, 77117 reflections, 15415 independent, $R1 = 0.0373$ ($I > 2\sigma(I)$), $wR2 = 0.0945$ (all data), $\mu = 1.736$ mm^{-1} (SADABS); d) [K([18]crown-6)]$_2$[**5**]: $C_{54}H_{72}K_2O_{12}Ti$; $M_r = 1039.22$, monoclinic, space group $P2_1/c$, green-black blocks, $a = 18.544(4)$, $b = 16.039(3)$, $c = 19.215(4)$ Å, $\beta = 113.510(3)$°, $V = 5241(2)$ Å^3, $Z = 4$, $T = 173(2)$ K, $\lambda = 0.71073$ Å, 41416 reflections, 9296 independent, $R1 = 0.0545$ ($I > 2\sigma(I)$), $wR2 = 0.1450$ (all data), $\mu = 0.383$ mm^{-1} (SADABS); e) [K-([2.2.2]cryptand)]$_2$[**6**](thf): $C_{66}H_{96}HfK_2N_4O_{12}$, $M_r = 1394.16$, triclinic, space group $P\bar{1}$, red feathers, $a = 13.5808(7)$, $b = 22.271(1)$, $c = 24.603(1)$ Å, $\alpha = 92.419(1)$, $\beta = 90.944(1)$, $\gamma = 105.634(1)$°, $V = 7156.8(7)$ Å^3, Z,Z' = 2,2, $T = 173(2)$ K, $\gamma = 0.71073$ Å, 57213 reflections, 25108 independent, $R1 = 0.0493$ ($I > 2\sigma(I)$), $wR2 = 0.1130$ (all data), $\mu = 1.631$ mm^{-1} (SADABS); f) [K$_2$(diglyme)$_3$][**7**]: $C_{42}H_{66}HfK_2O_9$, $M_r = 971.64$, triclinic, space group $P\bar{1}$, red-orange plates, $a = 9.649(2)$, $b = 15.021(3)$, $c = 15.290(3)$ Å, $\alpha = 90.924(2)$, $\beta = 92.723(2)$, $\gamma = 90.612(2)$°, $V = 2213.0(7)$ Å^3, $Z = 2$, $T = 173(2)$ K, $\lambda = 0.71073$ Å, 26128 reflections, 10021 independent, $R1 = 0.0393$ ($I > 2\sigma(I)$), $wR2 = 0.0692$ (all data), $\mu = 2.595$ mm^{-1} (SADABS). Intensities of reflections were measured on a Bruker or Siemens SMART Platform CCDC diffractometer using MoKα radiation. All structures had full-matrix least-squares refinement on F^2. CCDC 690328 (**2**), 690327 (**3**), 677980 (**4**), 690329 (**5**), 677979 (**6**), 677981 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[22] For example, the average metal–η^4-diene centroid distances in **2** and [Nb(η^4-$C_{14}H_{10}$)$_3$]$^{-}$[5] are 1.96 and 2.04 Å, respectively. See also Ref. [26].

[23] Application of a recently developed algorithm for the quantitative assessment of steric effects around a metal center[24] to [Ti(η^4-$C_{10}H_8$)$_2$(η^x-$C_{10}H_8$)]$^{2-}$ also suggests that steric hindrance plays a role in the stabilization of $x = 2$, relative to $x = 4$, at least in the solid state; W. W. Brennessel, unpublished results.

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[25] For example, the average (outer)M–C1, C4 and (inner)M–C2, C3 distances for the η^4-anthracene units in **2** are 2.363(15) and 2.290(14) Å, respectively, whereas corresponding values in [Nb(η^4-$C_{14}H_{10}$)$_3$]$^{-}$ are statistically identical, 2.388(7) and 2.388(6) Å.[5]

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[28] For example, the average Ti-centroid(η^4) and Ti-centroid(η^2) values in **2** are 1.964 and 2.191 Å, respectively, whereas the corresponding values in **5** are 1.956 and 2.160 Å. Also the centroid(η^4)-Ti-centroid(η^4) and centroid(η^4)-Ti-centroid(η^2) angles of **2** and **5** vary by only 1.0 to 2.5°. For additional comparisons see Figure 1 and Figure S3 in the Supporting Information.

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[30] Efforts to determine the nature of a previously reported [K([15]crown-5)$_2$] salt of **5**[29] by X-ray crystallography have been unsuccessful. However, the present study has established that the ^{1}H and ^{13}C NMR solution spectra of anion **5** in this salt are identical to those of the analogous [K(L)]$_2$[**5**], L = [18]crown-6 and [2.2.2]cryptand reported herein. On this basis, there is no compelling evidence to support the prior claim that [K([15]crown-5)$_2$]$_2$[**5**] contains a homoleptic "bis(naphthalene)-titanate(2-)",[29] which should now be regarded as an unknown substance.

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