

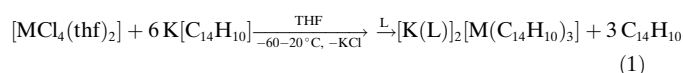
Structurally Distinct Homoleptic Anthracene Complexes, $[M(C_{14}H_{10})_3]^{2-}$, M = Titanium, Zirconium, Hafnium: Tris(arene) Complexes for a Triad of Transition Metals**

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Dedicated to Professor E. Peter Kündig

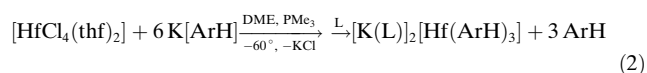
Polycyclic aromatic hydrocarbon- or polyarene-transition metal complexes continue to be exciting reagents for the exploration of low-valent chemistry of their constituent metals because of the substantial lability of the coordinated polyarenes in numerous reactions.^[1,2] For example, bis(anthracene)ferrate(1-) 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).

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 $[K([2.2.2]cryptand)]_2[6]$.^[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 $[K([18]crown-6)]_2[4]$, 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]

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^1H 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 anthracenometalates **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 $[\text{Ti}(\eta^4\text{-polyarene})_2(\eta^2\text{-polyarene})]^{2-}$, 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, $[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\eta^4\text{-C}_6\text{Me}_6)]$.^[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 approx-

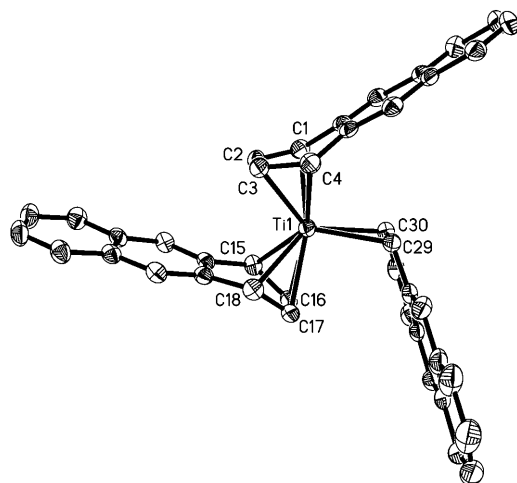


Figure 1. Molecular structure of anion **2**. Thermal ellipsoids are set at the 50% probability level, with hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles[°]: Ti–C1 2.341(3), Ti–C2 2.272(3), Ti–C3 2.286(3), Ti–C4 2.376(3), Ti–C15 2.366(3), Ti–C16 2.302(2), Ti–C17 2.300(2), Ti–C18 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.

imately 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 $[\text{Nb}(\eta^4\text{-C}_{10}\text{H}_8)_2(\text{PMe}_3)_2]^-$.^[26] Interestingly, comparison of the average M–C distances in $[\text{Ti}(\text{CO})_6]^{2-}$, 2.038(3),^[9] $[\text{Nb}(\text{CO})_6]^-$, 2.089(5), and $[\text{Ta}(\text{CO})_6]^-$ 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 $[\text{K}([2.2.2]\text{cryptand})]_2[\text{2}]$ and $[\text{K}([18]\text{crown-6})]_2[\text{5}]$, 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 $[\text{K}([18]\text{crown-6})]$ and $[\text{K}([2.2.2]\text{cryptand})]$ salts of **5** showed the presence of statistically identical anionic units.^[11,30]

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 $[\text{M}(\eta\text{-cot})_3]^-$ ($\text{M} = \text{Nb}, \text{Ta}$)^[31] and $[\text{Co}(\eta\text{-cot})_2]^-$ 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, $[\text{Hf}(\eta\text{-cot})_3]^{2-}$ (**7**).^[32] Complex **7** was isolated as an air-sensitive orange microcrystalline $[\text{K}([18]\text{crown-6})]$ salt in 85% yield.^[11] ^1H and ^{13}C NMR spectra of **7** were independent of cation, solvent, and temperature (to -95°C in THF) and showed sharp singlets at $\delta_{\text{H}} = 4.99$ and $\delta_{\text{C}} = 97.3$ ppm, respectively, with $J_{\text{CH}} = 150.3$ 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 $[\text{M}(\eta^8\text{-cot})(\eta^4\text{-cot})]$ ($\text{M} = \text{Zr}, \text{Hf}$).^[33] A single-crystal X-ray study of **7** revealed the presence of an unusual 16-electron species, $[\text{Hf}(\eta^4\text{-cot})(\eta^3\text{-cot})_2]^{2-}$, 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 $[\text{Hf}(\eta^4\text{-cot})_3]^{2-}$.^[24] Previously, only Group 5 complexes, e.g., $[\text{Nb}(\eta^4\text{-cot})(\eta^3\text{-cot})_2]^-$ ^[31] and $[\text{Cp}^*\text{M}(\eta^4\text{-butadiene})(\eta^3\text{-cot})]$ ($\text{Cp}^* =$

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 $[Zr(\eta^8\text{-cot})-(\eta^n\text{-cot})]$ 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, $[Ti(\eta^6\text{-An})(\eta^4\text{-An})(dmpe)]$ and $[Ti(\eta^5\text{-Cp}^*)(\eta^4\text{-An})(\eta^2\text{-An})]^-$, An = anthracene.^[38]

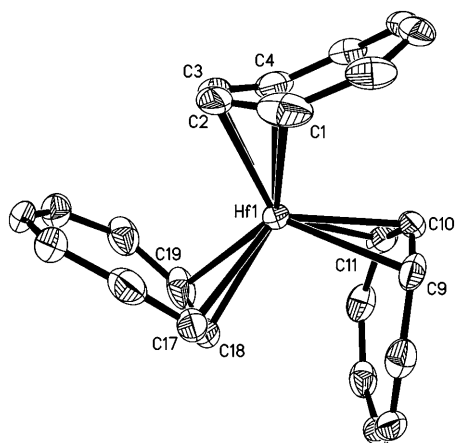


Figure 2. Molecular structure of anion **7**. Thermal ellipsoids are set at 50% probability level, with hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles[°]: Hf–C1 2.528(4), Hf–C2 2.354(4), Hf–C3 2.386(4), Hf–C4 2.624(4), Hf–C9 2.529(4), Hf–C10 2.309(4), Hf–C11 2.512(4), Hf–C17 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–C19)) 126.4.

Experimental Section

5: A yellow solution of $[TiCl_4(thf)_2]$ (1.000 g, 3.00 mmol) in THF (80 mL, $-60^\circ C$) 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, $-60^\circ C$). 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 $[K([18]crown-6)]_2[5]$ (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, $[D_8]THF$, $-35^\circ C$, cation resonances omitted): δ = 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, $[D_8]THF$, $-35^\circ C$): δ = 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 $[K([18]crown-6)]_2[5]$ were grown as green-black blocks from a THF/HMPA (10:1) solution layered at $0^\circ C$ with diethyl ether (see Figure S3 in the Supporting Information).^[19a] Synthesis and characterization of $[K([2.2.2]cryptand)]_2[5]$ 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 -C₁₄H₁₀ groups are 24.5(1), 26.8(1)°; η^2 -C₁₄H₁₀ is essentially planar (deviation from planarity, 0.034(1) Å).
- [19] a) Crystal data for [K([2.2.2]cryptand)]₂[2](thf)₂: C₈₆H₁₁₈K₂N₄O₁₄Ti, *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, α = 92.968(2), β = 104.092(2), γ = 93.171(2)°, *V* = 4020.8(8) Å³, *Z* = 2, *T* = 173(2) K, λ = 0.71073 Å, 36751 reflections, 16306 independent, *R*1 = 0.0549 (*I* > 2σ(*I*)), *wR*2 = 0.1213 (all data), μ = 0.276 mm⁻¹ (SADABS); b) [K([18]crown-6)]₂[3](dme)(Et₂O)_{0.5}: C₇₂H₉₃K₂O_{14.5}Zr, *M_r* = 1359.90, monoclinic, space group *P*2₁/*n*, red-gold plates, *a* = 17.136(2), *b* = 21.869(2), *c* = 19.841(2) Å, β = 115.169(2)°, *V* = 6730(1) Å³, *Z* = 4, *T* = 173(2) K, λ = 0.71073 Å, 36350 reflections, 11807 independent, *R*1 = 0.0433 (*I* > 2σ(*I*)), *wR*2 = 0.1059 (all data), μ = 0.352 mm⁻¹ (SADABS); c) [K([18]crown-6)]₂[4](dme)(Et₂O)_{0.5}: C₇₂H₉₃HfK₂O_{14.5}, *M_r* = 1447.15, monoclinic, space group *P*2₁/*n*, metallic red-green needles, *a* = 17.148(2), *b* = 21.877(3), *c* = 19.839(3) Å, β = 115.147(2)°, *V* = 6737(2) Å³, *Z* = 4, *T* = 173(2) K, λ = 0.71073 Å, 77117 reflections, 15415 independent, *R*1 = 0.0373 (*I* > 2σ(*I*)), *wR*2 = 0.0945 (all data), μ = 1.736 mm⁻¹ (SADABS); d) [K([18]crown-6)]₂[5]: C₅₄H₇₂K₂O₁₂Ti; *M_r* = 1039.22, monoclinic, space group *P*2₁/*c*, green-black blocks, *a* = 18.544(4), *b* = 16.039(3), *c* = 19.215(4) Å, β = 113.510(3)°, *V* = 5241(2) Å³, *Z* = 4, *T* = 173(2) K, λ = 0.71073 Å, 41416 reflections, 9296 independent, *R*1 = 0.0545 (*I* > 2σ(*I*)), *wR*2 = 0.1450 (all data), μ = 0.383 mm⁻¹ (SADABS); e) [K([2.2.2]cryptand)]₂[6](thf): C₆₆H₉₆HfK₂N₄O₁₂, *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, α = 92.419(1), β = 90.944(1), γ = 105.634(1)°, *V* = 7156.8(7) Å³, *Z*, *Z'* = 2, *T* = 173(2) K, γ = 0.71073 Å, 57213 reflections, 25108 independent, *R*1 = 0.0493 (*I* > 2σ(*I*)), *wR*2 = 0.1130 (all data), μ = 1.631 mm⁻¹ (SADABS); f) [K₂(diglyme)]₃[7]: C₄₂H₆₆HfK₂O₉, *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, α = 90.924(2), β = 92.723(2), γ = 90.612(2)°, *V* = 2213.0(7) Å³, *Z* = 2, *T* = 173(2) K, λ = 0.71073 Å, 26128 reflections, 10021 independent, *R*1 = 0.0393 (*I* > 2σ(*I*)), *wR*2 = 0.0692 (all data), μ = 2.595 mm⁻¹ (SADABS). Intensities of reflections were measured on a Bruker or Siemens SMART Platform CCD diffractometer using MoK α 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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