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Tris(η4-naphthalene)- and Tris(1-4-η4-anthracene)tantalate(1−): First Homoleptic Arene Complexes of Anionic Tantalum[1]

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Homoleptic arene transition metal complexes have a rich history in chemistry,[2] are significant precursors to numerous inorganic, organometallic, and organic compounds,[3] and hold considerable promise as electro- and photoactive substrates.[4] The most important routes to these substances are the metal atom vapor and Fischer−Hafner syntheses.[5] However, neither method has been used to directly produce *anionic* species, which in some cases are more accessible or stable than analogous cations or neutrals.[6] A much less investigated route to these species involves arene anion reductions of transition metal halides, metallocenes, and related reactants.[7,8] This method promises to be particularly effective in the synthesis of anionic homoleptic arene transition metal complexes. In 1983, it was proposed that the reduction of $TaCl_5$ by alkali metal naphthalenes provided bis(naphthalene)tantalate(1−), as an intermediate in the synthesis of $[Ta(CO)_6]^-$.[9] Establishing the nature of this naphthalenetantalate has been of considerable interest, in part, because bis(benzene)tantalum(0)[10] is the only previously known homoleptic arene complex for the heaviest group 5 element.[11] Also, because tantalum has an atomic radius between that of zirconium and molybdenum,[12] which exclusively provide the 18 electron homoleptic naphthalene complexes $[Zr(\eta^4\text{-}C_{10}H_8)_3]^{2-}$ [13] and $[Mo(\eta^6\text{-}C_{10}H_8)_2]$,[14a,b] respectively, it was not obvious, on the basis of steric considerations, whether tantalum would prefer to form $[Ta(\eta^4\text{-}C_{10}H_8)_3]^-$, $[Ta(\eta^6\text{-}C_{10}H_8)_2]^-$, or a mixture thereof.[14c] We now report on the isolation, structural characterization, and some chemical properties of tris(η^4-naphthalene)tantalate(1−), **1**, the first homoleptic naphthalene complex of a third row (5d) transition metal and the first unsubstituted arenetantalate(1−).

Addition of $TaCl_5$ to 6 equiv of sodium naphthalene in 1,2-dimethoxyethane, dme, at −60°, as previously described in detail,[9,15] provided within minutes a deep red-brown reaction mixture. Filtration at −60 °C gave a yellow-brown solid, which was crystallized from tetrahydrofuran, THF, to give a homogeneous, bright yellow-orange pyrophoric powder of composition [Na(THF)][**1**], by ^{1}H NMR.[16] Treatment of [Na(THF)][**1**] with 18-crown-6 or cryptand 2.2.2 in THF gave much less air sensitive and satisfactorily pure yellow-orange microcrystals of [Na(18-crown-6)(THF)][**1**] or [Na(crypt 2.2.2)][**1**] (Scheme 1), respectively.[17a]

^{1}H and ^{13}C NMR spectra of **1** in solution were independent of the cation and indicated that **1** was the only naphthalene complex present in solution.[16] Specifically, proton-coupled ^{13}C NMR spectra show only one sharp singlet at δ +149.0 ppm, which is in the characteristic region for quaternary carbons in η^4-naphthalene complexes.[13] Single-crystal X-ray structural characterization of [Na(crypt 2.2.2)][**1**] confirmed the formulation of **1** on the basis of NMR data.[18] In particular, the anion (Figure 1) is well separated from an unexceptional cation and contains three essentially identical nonplanar naphthalene units bound as η^4-conjugated dienes in an approximately trigonal prismatic array about tantalum. Overall, the structure of **1** is very similar to that found for tris(η^4-naphthalene)zirconate(2−), the only other structurally characterized homoleptic naphthalenemetalate,[13] and bears a striking resemblance to that of tris(η^4-butadiene)molybdenum(0).[17b] Notably, group 5 analogues of this molybdenum complex are unknown; however, **1** may be considered to be a substituted version thereof.

Scheme 1. Synthesis and Some Reactions of **1** and **2**[a]

$$\mathrm{TaCl_5+6NaC_{10}H_8} \xrightarrow[\text{(ii)}]{\text{(i)}} \mathrm{[Na(THF)][\mathbf{1}]} \xrightarrow[\text{(iv)}]{\text{(iii) or}} \mathrm{[Na(L)(THF)_x][\mathbf{1}]}$$

$$\mathrm{[Na(THF)][\mathbf{1}]+3C_{14}H_{10}} \xrightarrow{\text{(v)}} \mathrm{[Na(THF)_2][\mathbf{2}]} \xrightarrow{\text{(vi)}} \mathrm{[Na(L)][\mathbf{2}]}$$

$$\mathrm{[Na(L)][\mathbf{2}] + 3\ COT} \xrightarrow{\text{(vii)}} \mathrm{[Na(L)][Ta(COT)_3]}$$

[a] Reagents, conditions, isolated percent yields: (i) $C_{10}H_8$ = naphthalene, dme, −60 to +20 °C, 12 h; (ii) THF, 20 °C, 55%; (iii) L = 18-crown-6, x = 1, THF, 20 °C, 62%; (iv) L = crypt 2.2.2, x = 0, THF, 20 °C, 76%; (v) $C_{14}H_{10}$ = anthracene, THF, 20 °C, 6 h, 52%; (vi) L = crypt 2.2.2, THF, 20 °C, 99%; (vii) L = crypt 2.2.2, THF, 12 equiv of COT, 20 °C, 12 h, 94%.

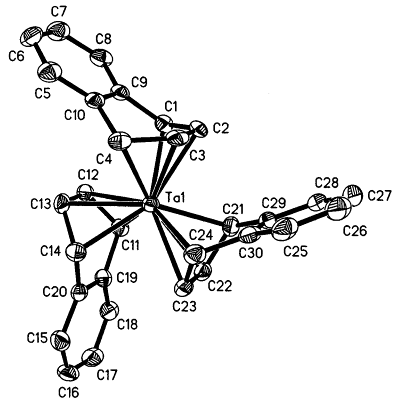

Figure 1. Molecular structure of **1**; 50% probability thermal ellipsoids; hydrogens omitted for clarity. Selected bond lengths (Å): Ta−C(1) 2.342(4), Ta−C(2) 2.375(4), Ta−C(3) 2.394(3), Ta−C(4) 2.368(4), C(1)−C(2) 1.455(5), C(2)−C(3) 1.368(5), C(3)−C(4) 1.451(5).

Chemical properties of **1** are consistent with its characterization as the first synthon for "naked" atomic Ta$^-$. For example, **1** readily reacts in THF with excess CO at ambient pressure (−60 °C, 10 min) and 3 equiv of anthracene (20 °C, 6 h) to provide salts of yellow $[Ta(CO)_6]^-$, 99% yield, and orange $[Ta(C_{14}H_{10})_3]^-$, **2** (Scheme 1). ^{1}H and ^{13}C NMR spectra unambiguously established that **2** in solution was tris(1-4-η^4-anthracene)tantalate(1−), the first homoleptic anthracene complex of a group 5 metal,[19] and only the third one known, the others being $Cr(\eta^6\text{-}C_{14}H_{10})_2$[20] and $[Co(\eta^4\text{-}C_{14}H_{10})_2]^-$.[1] The conversion of **1** to **2** involves the displacement of

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bound naphthalene by anthracene, which is an unprecedented reaction for a *homoleptic* system. Exchange of both naphthalenes in bis(naphthalene)chromium(0) by 1,4-dimethylnaphthalene under comparatively forcing conditions (120 °C, 25 h) to yield bis(1,4-dimethylnaphthalene)chromium(0) appears to be the only known related reaction involving multiple polyarene substitutions on one metal center.[21]

Treatment of [Na(THF)$_2$][**2**] in THF with 1 equiv of cryptand 2.2.2 rapidly caused quantitative precipitation of slightly soluble orange-red microcrystals of [Na(crypt 2.2.2)][**2**]. A single-crystal X-ray study on the latter salt confirmed the formulation of **2** on the basis of the NMR data. Structural properties of **2** are remarkably similar to those of **1**; for example, the average interatomic distances associated with the Ta-diene units in these anions are statistically identical.[22] Structural evidence indicates that both naphthalene and anthracene bind about as tightly to the tantalum atoms in **1** and **2**. Thus, the driving force for the conversion of **1** to **2** appears to be influenced more by the displacement of naphthalene and restoration of its full aromaticity than by any intrinsic differences in the donor/acceptor abilities of naphthalene and anthracene.[23] For these reasons, it was expected that **2**, like **1**, would also function as a labile source of "naked" Ta$^-$ in chemical reactions. Indeed, **2** undergoes facile substitution reactions with a variety of good acceptor ligands such as PF_3, $P(OMe)_3$, and conjugated polyenes.[24] For example, **2** reacted with 1,3,5,7-cyclooctatetraene, COT, in THF to provide a high yields of deep purple $[Ta(COT)_3]^-$ (Scheme 1). A single crystal X-ray structure confirmed the nature of this previously known anion, which is essentially isostructural with the niobium complex in [Ph$_4$As][Nb(COT)$_3$].[25]

The present study establishes for the first time that a homoleptic arene tantalum complex, $[Ta(\eta^4\text{-}C_{10}H_8)_3]^-$, **1**, is readily accessible in good yields by alkali metal naphthalene reductions of $TaCl_5$. **1** promises to be a very useful precursor for the general exploration of low-valent tantalum chemistry, which remains poorly investigated.[11a,26] Efforts are underway to prepare other homoleptic polyarene complexes of third row transition metals, because **1** and **2** represent the very first examples of such substances.

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Supporting Information Available: Tables of crystallographic data, thermal parameters, and bond lengths and angles for [Na(crypt 2.2.2)] salts of **1**, **2**, and $[Ta(COT)_3]^-$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) *Caution:* [Na(THF)][**1**] spontaneously ignites in perfluoroalkanes under an argon atmosphere. ^{1}H NMR (300 MHz, 298 K, [d_8]THF): δ 1.79 (m, 4H; THF), 2.81 (m, 6H; $H_{1,4}$), 3.62 (m, 4H; THF), 3.78 (m, 6H, $H_{2,3}$), 6.25 (m, 6H; $H_{5,8\text{ or }6,7}$), 6.34 (m, 6H; $H_{6,7\text{ or }5,8}$). ^{13}C{^{1}H} NMR (75 MHz, 298 K, [d_8]THF, THF resonances omitted): δ 61.5 (s; $C_{1,4}$), 109.2 (s; $C_{2,3}$), 118.3 (s; $C_{5,8\text{ or }6,7}$), 119.5 (s; $C_{6,7\text{ or }5,8}$), 149.0 (s; $C_{9,10}$) ppm. Assignments based on ^{1}H−^{13}C heteronuclear multiple quantum correlation (HMQC) and trends previously established for η^4-naphthalene and η^4-anthracene complexes,[1,13] but no unique assignment of $C_{5,8}$, $C_{6,7}$, or corresponding hydrogens was possible.
(17) (a) 18-Crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane; cryptand 2.2.2 = 4,7,13,16,21,24-hexaoxa-1.10-diazabicyclo[8.8.8]hexacosane. (b) Skell, P. S.; McGlinchey, M. J. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 195.
(18) Crystal data for [Na(crypt 2.2.2)][**1**]: $C_{48}H_{60}N_2NaO_6Ta$; triclinic; yellow plate; space group, $P1$; $a = 13.397(1)$, $b = 13.501(1)$, $c = 14.046(1)$ Å; $\alpha = 70.564(1)$; $\beta = 63.203(1)$; $\gamma = 82.918(1)°$; $V = 2137.4(3)$ Å^3; $Z = 2$; $T = 173(2)$ K; R value of 0.0361 for 9640 independent reflections; goodness of fit, 0.992.
(19) [Na(THF)$_2$][**2**] has also been prepared independently by the reduction of $TaCl_5$ with sodium anthracene in dme, details to be presented elsewhere. ^{1}H NMR (300 MHz, 298 K, [d_8] THF): δ 1.79 (m, 8H; THF), 3.25 (m, 6H; $H_{1,4}$), 3.62 (m, 8H; THF), 3.77 (m, 6H; $H_{2,3}$), 6.53 (s, 6H; $H_{9,10}$), 6.92 (m, 6H; $H_{5,8\text{ or }6,7}$), 7.26 (m, 6H; $H_{6,7\text{ or }5,8}$). ^{13}C{^{1}H} NMR (75 MHz, 298 K, [d_8]THF, THF resonances omitted): δ 61.6 (s; $C_{1,4}$), 111.5 (s; $C_{2,3}$), 114.3 (s; $C_{9,10}$), 122.4 (s; $C_{5,8\text{ or }6,7}$), 126.7 (s; $C_{6,7\text{ or }5,8}$), 132.7 (s; $C_{13,14}$), 150.4 (s; $C_{11,12,}$). Assignments based on same considerations discussed previously.[16] Also, as in the case of **1**, no unique assignment of $C_{5,8}$, $C_{6,7}$, or corresponding hydrogens was possible.
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