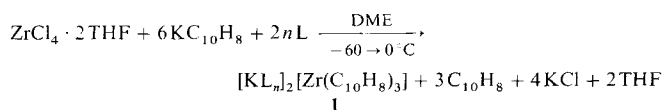# Tris(η^4-naphthalene)zirconate(2 −)

Meehae Jang and John E. Ellis*

*Dedicated to Professor Ernst Otto Fischer
on the occasion of his 75th birthday*

Naphthalene radical anion reductions of a variety of transition metal precursors including MCl_3 (M = V, Cr[11]), MCl_5 (M = Nb, Ta[12]), $TiCl_4$,[3] and $Co(C_5H_5)_2$[4] have been suggested or claimed to provide *anionic* homoleptic naphthalene complexes, but only one has been isolated, that is $[Ti(C_{10}H_8)_2]^{2-}$,[5] and none have been structurally characterized. Since naphthalene ligands can often be readily substituted by other Lewis bases,[6] compounds of the general formula $[M(C_{10}H_8)_x]^{z-}$ are potentially valuable synthetic equivalents for corresponding "naked" transition metal anions, M^{z-}, and are thereby related to Jonas's homoleptic ethylene complexes, $[Co(C_2H_4)_4]^-$ and $[Fe(C_2H_4)_4]^{2-}$.[7] For these reasons, we felt that it was important to determine the nature of an especially robust product obtained from the reaction of potassium naphthalenide and $ZrCl_4 \cdot 2THF$ (Scheme 1). To our surprise, salts 1 containing the anion $[Zr(\eta^4\text{-}C_{10}H_8)_3]^{2-}$ were obtained, instead of the expected and still unknown $[Zr(\eta^6\text{-}C_{10}H_8)_2]^{2-}$, which is isoelectronic with $[Mo(\eta^6\text{-}C_{10}H_8)_2]$.[6a, 8] The anion of 1 may be regarded as the first tris(arene)metal complex to contain only independent or unlinked arene ligands.[9, 10] It has also been identified in this study as the intermediate in the original synthesis of $[Zr(CO)_6]^{2-}$.[11]

$$ZrCl_4 \cdot 2THF + 6KC_{10}H_8 + 2n L \xrightarrow[-60 \to 0\,°C]{DME}$$

$$[KL_n]_2[Zr(C_{10}H_8)_3] + 3C_{10}H_8 + 4KCl + 2THF$$
$$1$$

Scheme 1. 1a: $n = 1$, L = [2.2.2]cryptand; 1b: $n = 2$, L = [15]crown-5; DME = 1,2-dimethoxyethane.

Microcrystalline, deep red to nearly black 1a and 1b were isolated in 46 and 55 % yields, respectively, as satisfactorily pure substances. Although highly reactive and air sensitive, they are thermally robust as dry solids and have survived for months at room temperature under an argon atmosphere without apparent deterioration. The ^1H and ^{13}C NMR spectra in solution and the CP/MAS ^{13}C NMR spectra of these salts showed that 1 was the only naphthalene complex present and established that its structure in solution and the solid state was identical. Also, the pattern of signals in the NMR spectra of 1 were independent of temperature (25 °C to −60 °C), solvent, concentration, counterion, and the presence of free naphthalene; this shows that the naphthalene ligands in 1 do not undergo facile exchange with free naphthalene at room temperature. The ^1H NMR spectra of 1 revealed that identical naphthalene groups were bound to zirconium through one ring each (i.e., four multiplets of equal

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intensity due to two AA'BB' systems of hydrogens were observed). Corresponding ^{13}C NMR spectra of solutions of 1 and the solid showed the presence of η^4-naphthalene ligands. The ^{13}C chemical shift value of the quaternary carbon in 1 ($\delta = +154$) is shifted downfield from that of free naphthalene and lies in the quaternary carbon region characteristic of previously reported η^4-naphthalene transition metal complexes.[12]

A single-crystal X-ray study on 1a provided proof for the tris(η^4-naphthalene)zirconate(2 −) formulation[13] and revealed a coordination environment about the zirconium of approximate C_{3v} local symmetry and trigonal-prismatic geometry as defined by midpoints of the long C−C vectors of the coordinated diene units (Fig. 1), similar to those previously observed for tris(η^4-butadiene)molybdenum(o)[14] and tris(cyclooctatetraene)niobate(1 −).[15] The noncoordinating, planar six-mem-
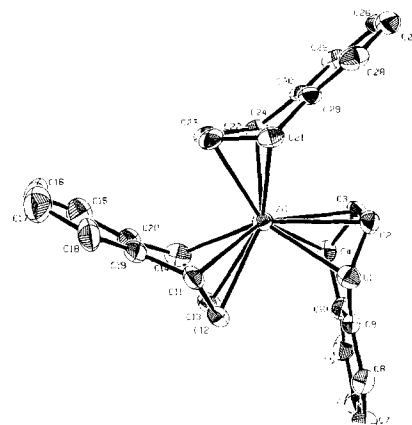

Fig. 1. Molecular structure of $[Zr(\eta^4\text{-}C_{10}H_8)_3]^{2-}$, 50% probability thermal ellipsoids. Important bond lengths [Å]: Zr-C1 2.482(6), Zr-C2 2.480(6), Zr-C3 2.474(6), Zr-C4 2.486(5), Zr-C11 2.480(6), Zr-C12 2.485(6), Zr-C13 2.471(6), Zr-C14 2.471(6), Zr-C21 2.496(5), Zr-C22 2.466(5), Zr-C23 2.470(6), Zr-C24 2.489(6), C1-C2 1.448(8), C2-C3 1.369(8), C3-C4 1.447(7), C1-C9 1.462(7), C4-C10 1.469(8), C11-C12 1.436(7), C12-C13 1.357(8), C13-C14 1.448(8), C11-C19 1.472(8), C14-C20 1.479(8), C21-C22 1.442(8), C22-C23 1.355(8), C23-C24 1.448(8), C21-C29 1.452(7), C24-C30 1.464(7). Mean C -C distance in the noncoordinating C_6 rings is 1.39(2) Å.

bered ring and coordinated diene units of the naphthalene ring have corresponding dihedral angles of 37.1, 32.4, and 38.4°, which are within the range of values previously observed for other η^4-naphthalene complexes.[16, 17] The C−C distances in the η^4-diene units in 1 are similar to analogous ones in $[Ti(\eta^4\text{-}C_{10}H_8)_2(SnMe_3)_2]^{2-}$,[5] (s-cis-$\eta^4$-2,3-dimethylbutadiene)-zirconocene (2),[18] and $[Lu(\eta^4\text{-}C_{10}H_8)(\eta^5\text{-}C_5H_5)(dme)]$ (3).[17] In particular, these compounds exhibit a very similar long, short, long pattern in the C−C distances of the coordinated diene units, a feature characteristic of many early transition metal η^4-diene complexes[18, 19] and indicative of coordinated dienes which have some degree of anionic character.

Structural and ^{13}C NMR data for the η^4-diene units bound to the metal atom in 1 and 2 are collected in Table 1 and indicate that the zirconium−diene interactions are remarkably similar in these otherwise very different compounds. For example, the ^{13}C chemical shift value for the atoms C2 and C3 in 1 is much closer to that of 2 than corresponding values previously reported for η^4-naphthalene complexes, (δ(C2,C3) = 84.0 for $[(\eta^4\text{-}C_{10}H_8)Cr(CO)_3]^{2-}$[12 a]). Notably, however, the distinctive short, long, long, short patterns of the M−C(diene) bond

lengths in **2** and **3**, which are characteristic of metallocyclic σ^2,π complexes,[18] are not obviously present in **1**. These data show that individual naphthalene ligands in **1** are undoubtedly good acceptor groups, but not as effective as the corresponding single diene units in **2** or **3** (compound **3** has been formulated as a $(C_{10}H_8)^{2-}$-Lu^{3+} complex[17]).

Table 1. ^{13}C NMR data and average C–C and Zr–C distances of η^4-diene units in **1** and **2** [a].

Compd.	C Atoms	δ(^{13}C)/J [b]	C–C [Å] [d]	Zr–C [Å] [d]
1	C1, C4	64.2/151	C1–C2 1.442(8)	Zr–C1 2.486(9)
	C2, C3	112.6/161	C3–C4 1.448(8)	Zr–C4 2.482(10)
			C2–C3 1.360(8)	Zr–C2 2.477(10)
				Zr–C3 2.472(6)
2	C1, C4	55.4/140 [c]	C1–C2 } 1.451(4)	Zr–C1 } 2.300(3)
	C2, C3	119.9/– [c]	C3–C4 }	Zr–C4 }
			C2–C3 1.398(4)	Zr–C2 } 2.597(3)
				Zr–C3 }

[a] See ref. [12 a] for the numbering system of the naphthalene rings in **1**, counterion is [K[2.2.2]cryptand]+. Data for **2** are from ref. [18]. [b] Chemical shifts are relative to Me₄Si, [1]J(C,H) in Hz. [c] δ([1]J(C,H)) values for C1,C4 and C2,C3 of (s-cis-η^4-butadiene)zirconocene are 49.6 (144) and 112.0 (165), respectively [18]. [d] The average C–C and Zr–C distances in **1** are for corresponding carbon atoms of the three η^4-$C_{10}H_8$ groups.

On this basis, an unambiguous formal oxidation state assignment for the zirconium center in **1** cannot be made at this time, but the value is most likely to lie somewhere between the extremes of -2 and $+4$. The Zr–C bond lengths in **1** are within the range of average values (2.40–2.60 Å) previously observed for unsaturated hydrocarbon–zirconium complexes.[20] Also the [K([2.2.2]cryptand)] cations are well separated from the anions in the crystalline lattice and have structures which are essentially identical to those previously observed in the iodide salt.[21]

The chemical properties of **1** will be reported on separately, but its reaction with CO is described here to establish its role as an intermediate in the naphthalenide-promoted reductive carbonylation synthesis of $[Zr(CO)_6]^{2-}$.[11] For example, when 1.50 g of pure **1 b** was treated with CO at atmospheric pressure in DME (50 mL) at $-55\,°C$, the deep red brown reactant slowly changed to an insoluble purple product. Under the same conditions as originally described,[11] except the filtration step was conducted at $-30\,°C$, 1.17 g (92%) of satisfactorily pure **4** was isolated. A ^{1}H NMR spectrum (CDCl₃, $20\,°C$) of the pentane-soluble component of this reaction showed only free naphthalene and small amounts of [15]crown-5, thus confirming that coordinated naphthalene was liberated during the carbonylation step [Eq. (a)].

$$\textbf{1 b} + 6\,CO \xrightarrow[DME]{-55\,°C} [K([15]crown-5)_2]_2[Zr(CO)_6] + 3\,C_{10}H_8 \qquad (a)$$
$$\textbf{4}$$
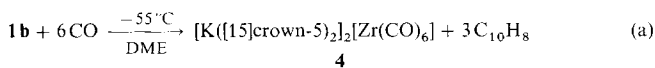
In summary, we have established that the reduction of ZrCl₄ · 2THF by naphthalene radical anion provides good yields of the first tris(naphthalene)metal complex, $[Zr(\eta^4\text{-}C_{10}H_8)_3]^{2-}$, which bears an obvious resemblance to the previously known neutral tris(butadiene) complexes of molybdenum and tungsten.[14, 22] Whether analogous or related anionic tris(arene) or tris(diene) complexes of the early transition metals are generally accessible by the methods described in this report is currently under examination in this laboratory.

Experimental Procedure

All operations were carried out under an atmosphere of argon.

1 a: A cold ($-50\,°C$) solution of ZrCl₄ · 2THF (1.00 g, 2.65 mmol) in DME (120 mL) was added to a stirred, cold ($-60\,°C$) solution of $KC_{10}H_8$ (16.1 mmol, prepared in the usual way [23] from K (0.63 g, 16.1 mmol) and $C_{10}H_8$ (2.72 g, 21.2 mmol)) in DME (55 mL). The reaction mixture became orange-red within minutes and was stirred at $-60\,°C$ for 12 h and then allowed to warm to $-10\,°C$ over a period of about 3 h with constant stirring. It was then filtered into a stirred solution of [2.2.2]cryptand (2.00 g, 5.31 mmol) in DME (10 mL) at $0\,°C$, whereupon product began to precipitate. The mixture was cooled to $-60\,°C$ with stirring and filtered at this temperature to collect a dark red microcrystalline powder, which was carefully washed with cold ($-60°C$) DME (3 × 20 mL), pentane (2 × 20 mL), and dried in vacuo. By this procedure 1.58g (46%) of **1 a** was obtained, based on ZrCl₄ · 2THF, m.p. 171–173 °C (decomp.), correct elemental analyses. IR (mineral oil mull in C=C region): 1560, 1541 cm⁻¹; UV/VIS (THF): 470 nm, $\varepsilon = 2400$; 275 nm, $\varepsilon = 9700$ Lmol⁻¹cm⁻¹; ^{1}H NMR: (500 MHz, [(CD₃)₂N]₃PO or [D_{18}]HMPA, $20\,°C$), only resonances due to anion shown: $\delta = 2.64$ (m, H1,H4), 3.92 (m, H2,H3), 5.42 (m, H6,H7 or H5,H8), 5.69 (m, H5,H8 or H6,H7); ^{13}C NMR: (125.7 MHz, [D_{18}]HMPA, $20\,°C$): $\delta = 64.2$ (d, C1,C4, [1]J(C,H) = 151 Hz), 112.0 (d, C6,C7 or C5,C8, [1]J(C,H) = 146 Hz), 112.6 (d, C2,C3, [1]J(C,H) = 161 Hz), 117.2 (d, C5,C8 or C6,C7, [1]J(C,H) = 150 Hz), 154.6 (s, C9,C10). Assignment of the C2,C3 resonance is based on its high [1]J(C,H) value and trends previously established for (s-cis-η^4-butadiene)zirconocene [18] and η^4-naphthalene complexes [12]. Based on this assigment, [1]H.^{13}C correlation NMR spectra were used to assign carbon and hydrogen resonances of the coordinated portion of the naphthalene, but no unique assignment of C5,C8, C6,C7 or corresponding hydrogen atoms was possible. CP/MAS ^{13}C{^{1}H}NMR (25.1 MHz, $20\,°C$): $\delta = 63$ (s, C1,C4), 111 (s, br, C6,C7 or C5,C8, and C2,C3), 116 (s, C5, C8 or C6,C7), 153 (s, C9, C10), also resonances at 54 (br) and 70 (s) due to [2.2.2]cryptand. Single crystals of **1 a** were prepared by dissolving 0.50 g of pure **1 a** in HMPA (15 mL), in which the anion was shown to be stable for weeks at room temperature. The intensely red solution was filtered, and diethyl ether was carefully layered on it. After two days at room temperature well-shaped crystals had deposited. A red-black prism was selected for this X-ray study. Red-black needles were also present and were shown to contain **1 a** in the same space group but different unit cell by an independent X-ray study. NMR spectra of the crystals grown for the X-ray study were identical to those of the bulk microcrystalline sample of **1 a**.

1 b: By the same procedure as described for **1 a**, ZrCl₄ · 2THF (2.00 g, 5.30 mmol) was treated with $KC_{10}H_8$ (32.0 mmol) in DME (250 mL) at $-60\,°C$. The reaction mixture was stirred over a period of 6 h while slowly warming to $0\,°C$, and then filtered into a solution of [15]crown-5 (5.5 g, 25 mmol) in DME (20 mL). After stirring the resulting deep red filtrate for 0.5 h at $0\,°C$, it was cooled to $-55\,°C$ and stirred at this temperature for 12 h. The sparingly soluble product was separated by filtration at $-50\,°C$, thoroughly washed with cold DME and methylbutane at $-50\,°C$, and then dried in vacuo at room temperature. By this procedure deep red brown microcrystalline **1 b** was obtained (4.2 g, 55% yield) based on ZrCl₄ · 2THF, darkens above 135 °C, m.p. 179–181 °C (decomp.). Correct elemental analyses. IR, UV/VIS, and NMR spectra properties of **1 b** were identical to those of **1 a** except for absorptions due to the cations. When the above procedures were carried out in DME alone or with [18]crown-6 in DME, thermally stable red microcrystalline powders having the composition (by ^{1}H NMR spectroscopy) $K_2[Zr(C_{10}H_8)_3]$ · DME or [K([18]crown-6)]₂[Zr(C₁₀H₈)₃] · 2THF (following crystallization from THF/pentane) were obtained in about the same yields. NMR spectra established that **1** was the only naphthalene complex present in these products.

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[9] Compound **1** may also be called a tris(diene)metal complex, but since free naphthalene is generally regarded to be an arene, rather than a substituted diene, we prefer the tris(arene)metal classification.

[10] The only previous examples of tris(arene)metal complexes appear to be the [2.2.2]paracyclophane derivatives, [(p-C₆H₄CH₂CH₂)₃M]⁺ (M = Ag, Ga), where the metal ions are located at the edge of or within the cyclophane cavity, respectively. See: H. Schmidbaur, R. Hager, B. Huber, G. Müller, *Angew. Chem.* **1987**, *99*, 354; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 338.

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[13] Crystal data for **1a**: C₆₆H₉₆K₂N₄O₁₂Zr, monoclinic, P2₁/n (no. 14), a = 21.78(1); b = 12.331(6), c = 26.55(1), β = 110.11(5)°, V = 6695(12) Å³, Z = 4, ρ_calcd = 1.296 g cm⁻³, μ(Mo_Kα) = 3.43 cm⁻¹, crystal dimensions = 0.60 × 0.50 × 0.35 mm³. The intensities of 9933 reflections were measured at −96 °C (0 < θ < 23°) on an Enraf-Nonius CAD 4 diffractometer using Mo_Kα radiation. The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically (full-matrix least-squares). For 5997 unique observed reflections [(I) ≥ 2.0σ(I)], R = 0.053 and R_w = 0.046, GOF = 1.285. Further details of the crystal structure determination are available on request from the Director of Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ (UK), on quoting the full journal citation.

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the fluorescence of the light-emitting unit. Changes of fluorescence intensity of two orders of magnitude and more are often observed, in other words the fluorescence can be switched on and off.[2] By virtue of its strong luminescence and chemical stability, the anthracene unit has been widely used in the design of fluorescent sensors. In the classical approach, a tertiary amino group is attached to the aromatic framework, and the thermodynamically favored amine-to-anthracene electron transfer quenches fluorescence.[3] Binding of H⁺ [4] or a metal ion (e.g., Na⁺,[5] Zn²⁺)[6] substantially increases the oxidation potential of the amine, thus preventing the photoinduced electron transfer and allowing fluorescence. Incorporation of the tertiary amino group in a crown ether type framework has paved the way to fluorescent sensors for alkali and alkaline-earth metal cations.[5]

We wished to extend this concept to the recognition of transition metal cations. To this end we attached a chelating dioxotetraaza unit to the 9-position of anthracene, according to the synthetic route outlined in Scheme 1.
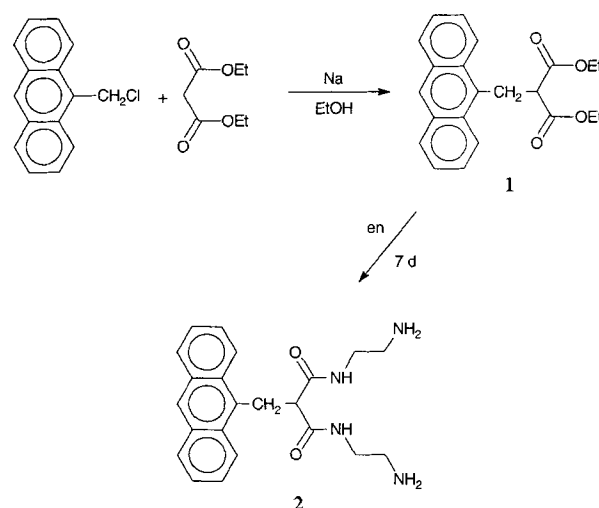
Scheme 1. Synthesis of fluorescent sensor **2**. en = ethylenediamine.

An Anthracene-Based Fluorescent Sensor for Transition Metal Ions**

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Fluorescence quenching and enhancement can be used effectively for the identification of ions in solution. Fluorescent sensors have been and are currently being designed for various cations and anions.[1] A fluorescent sensor is essentially a two-component compound, in which a light-emitting group is covalently linked to a receptor specific for a particular ion. Sensor efficiency requires that the ion–receptor interaction modifies

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Compound **2** (H₂L) displays the typical emission spectrum of anthracene in acetonitrile/water (4:1); the intensity does not change over the pH range 2–12. Its pK_a1 and pK_a2 values are 8.3 and 9.6, respectively. This indicates that the following three species are present in solution: H₄L²⁺, in which the two terminal amino groups are protonated, the predominant species at pH < 8, H₃L⁺ at pH values from 8 to 10, and H₂L at pH >10. The protonation state of the dioxotetraaza unit does not alter the fluorescence of the adjacent anthracene unit. However, if one equivalent of Cu^II is added to an acidic solution of **2**, the fluorescence intensity I_F steadily decreases on titration with NaOH. Complete fluorescence quenching is observed when the excess strong acid has been neutralized and two further equivalents of OH⁻ have been added. The plot of I_F vs. pH (Fig. 1) displays a sigmoidal curve typical of a switching effect. Insights on the quenching mechanism are provided by an analogous titration experiment performed inside a spectrophotometric cuvette. On addition of base, the solution becomes pink-violet, and an absorption band at 520 nm develops. The absorbance A reaches its limiting value after neutralization of the excess strong acid and addition of two further equivalents of base. The plot of A vs. pH (Fig. 1) shows a sigmoidal curve, which is symmetrical