Homoleptic naphthalene and anthracene metal complexes of the d-block elements are exciting candidates for “naked” metal atom reagents\textsuperscript{[1]} owing to the unusual lability of these coordinated polycyclic aromatic hydrocarbons (or polyarenes) in ligand-substitution reactions.\textsuperscript{[2]} Although cationic and neutral homoleptic polyarene metal complexes have been established for over 25 years,\textsuperscript{[3]} the first well-defined anionic and neutral homoleptic polyarene metal complexes have been made possible by the use of anionic ligands of appropriate steric bulk.\textsuperscript{[4]} Subsequent studies resulted in the synthesis and isolation of related anions, including \([\text{Co(}\eta^4\text{-L})(\text{thf})_3]^+\text{[5]}\) for \(L\) = naphthalene and anthracene, and \([\text{Nb(}\eta^4\text{-L})(\text{thf})_3]^+\text{[6]}\) for \(L\) = anthracene. All of these anionic complexes were diamagnetic 18-electron species. We now report on an unprecedented isolable 17-electron complex of this class, \([\text{Fe(}\eta^4\text{-anthracene})_2]^\text{−}\text{[7]}\). This paramagnetic species is also of interest as the first homoleptic polyarene iron complex\textsuperscript{[8, 9]} and is a rare example of a 17-electron complex containing a metal center in a formally negative oxidation state.\textsuperscript{[10]}

Treatment of iron(II) bromide with three equivalents of potassium anthracene in THF afforded a deep orange solution of highly air-sensitive but thermally stable (at 20 °C) anion \(1\), which was isolated as dark brown, nearly black microcrystalline \([K(L)(\text{thf})_3]_\text{+}\) salts in about 60% yields [Eq. (1)], where

\[
\text{FeBr}_2 + 3 K\text{C}_{14}\text{H}_{10} \xrightarrow{\text{THF}, -30 \text{ to } 20 \text{ °C, } -78 \text{ °C}} ^{-} [K(L)(\text{thf})_3]_\text{+} + C_{13}H_{10} \quad (1)
\]

\(L\) = [18]crown-6, \(x = 2\) (1a) or \(L = [2.2.2]\text{cryptand, } x = 1/2\) (1b)\textsuperscript{[11]} Magnetic susceptibilities of \(1\) were appropriate for a 17-electron organoiron sandwich complex\textsuperscript{[12]} (see the Experimental Section). Single-crystal X-ray studies established that both salts contain essentially identical anionic units (Figure 1 for the anion in 1b)\textsuperscript{[13]} well-separated from the unexceptional cations.\textsuperscript{[14]} The coordination environment about the iron center is nearly tetrahedral\textsuperscript{[15]} and overall, the structure of anion \(1\) is very similar to that reported for the corresponding 18-electron cobaltate, \([\text{Co(}\eta^4\text{-C}_{14}H_{10})_2]^\text{2−}\text{[16]}\).

Reactions of \(1\) were investigated to determine whether it would be the first available precursor to other new Fe\textsuperscript{4−} complexes. Scheme 1 shows some of these reactions, including

\[
\text{Fe}^2(\text{CO})_6 \xrightarrow{-78 \text{ to } +20 \text{ °C, THF}} [\text{Fe}^2(\text{CO})_6]^2^+ \quad 3 \quad 81\%
\]

\[
[\text{Fe}^2(\text{C}_7\text{H}_8)_2]^2^+ \xrightarrow{-78 \text{ to } +20 \text{ °C, THF}} [\text{Fe}^2(\text{C}_7\text{H}_8)_2(\text{C}_7\text{H}_8)]^+ \quad 4 \quad 88\%
\]

\[
[\text{Fe}^2(\text{C}_7\text{H}_8)_2(\text{C}_7\text{H}_8)]^+ \xrightarrow{-78 \text{ to } +20 \text{ °C, THF}} [\text{Fe}^2(\text{C}_7\text{H}_8)_2(\text{C}_7\text{H}_8)(\text{C}_7\text{H}_8)]^2^+ \quad 5 \quad 79\%
\]

\[
[\text{Fe}^2(\text{C}_7\text{H}_8)_2(\text{C}_7\text{H}_8)(\text{C}_7\text{H}_8)(\text{C}_7\text{H}_8)]^2^+ \xrightarrow{-78 \text{ to } +20 \text{ °C, THF}} [\text{Fe}^2(\text{C}_7\text{H}_8)_2(\text{C}_7\text{H}_8)(\text{C}_7\text{H}_8)(\text{C}_7\text{H}_8)(\text{C}_7\text{H}_8)]^3^+ \quad 6 \quad 80\%
\]

Scheme 1. Reactions of \(1\) with excess \(L = \text{CO}, \text{C}_7\text{H}_8 (1,3\text{-butadiene), cod (1,5}\text{-cyclooctadiene, and trimethylphosphite, with yields of isolated products. The trimethylphosphite reaction also provides anthracene radical anion.}
the carbonylation of 1, which affords high yields of diamagnetic \( \text{Fe}_2(\text{CO})_8 \) \( \text{I}^- \). Surprisingly, this classic carbonylmetalate is the only prior example of a well-characterized, isolable \( \text{Fe}^- \) complex.[17] Because of the paucity of well-defined, homoletic, unsubstituted, 1,3-butadiene transition-metal complexes, precedent only by \( [\text{Mo}(\eta^1-\text{C}_2\text{H}_4)]_2, [\text{W}(\eta^1-\text{C}_2\text{H}_4)]_2 [18] \) and \( [\text{Co}(\eta^1-\text{C}_2\text{H}_4)]_2 [19] \), the reaction of 1 with 1,3-butadiene was also examined and shown to provide the first 17-electron complex of this type, \( \text{Fe}(\eta^1-\text{C}_2\text{H}_4)_2 \) \( \text{I}^- \) (4). Like 1, pink-red and air-sensitive 4 is paramagnetic in solution and in the solid state and shows no tendency to dimerize. It was structurally characterized as the \( [\text{K}([2.2.2]\text{cryptand})]\) \( \text{+} \) salt (Figure 2), in which the cation is well-separated from the anion and has a normal structure.[20] Anion 4 contains two structurally equivalent and discrete \( \eta^1-1,3\)-butadiene groups bound to the iron center; the environment about the metal is almost tetrahedral, with a twist angle of 83°.[15] The Fe–C and C–C bonds in 4 follow the usual patterns for iron and other late-transition-metal \( \eta^1\text{-1,3-diene complexes} [21-23] \) in which metal-to-\( \pi^* \)(diene) back-bonding is not as important as for early-transition-metal 1,3-diene complexes, such as \( [\text{Mo}(\eta^1-\text{C}_2\text{H}_4)]_2 [23,24] \). Structural details for 4 are also similar to those of bis(1,4-di-tert-butyl-1,3-butadiene)cobaltate(1–) (5), the only structurally characterized anionic complex of this type to date.[25] Other homoletic (1,3-butadiene)metalates, \( [\text{M}(\eta^1-\text{C}_2\text{H}_4)]_2 (\text{M} = \text{Mo}, \text{W}) [16] \) have been claimed in the literature but are without corroborating data.

Analogous reactions of 1 with excess 1,5-cyclooctadiene (cod) gave no evidence for the formation of unknown paramagnetic \( \text{Fe}(\eta^1-\text{cod})_2 \) or reported \( \text{Fe}(\eta^1-\text{cod})_2 \) \( \text{I}^- \) (28) but instead afforded the first example of a mixed-ligand or heteroleptic \( \text{Fe}^- \) complex, \( \text{Fe}(\eta^1-\text{C}_2\text{H}_4)(\eta^1-\text{cod}) \) \( \text{I}^- \) (5). This species was isolated in good yield as teal or dichroic red-violet microcrystals of \( [\text{K}([18]\text{crown-6})] \) \( \text{5a} \) or \( [\text{K}([2.2.2] \text{cryptand})][\text{5b}] \) salts, respectively. Anion 5 was paramagnetic in solution and in the solid state, with a magnetic moment close to that previously reported for the neutral 17-electron complex \( \text{Fe}(\eta^1-\text{C}_2\text{H}_4)(\eta^1-\text{cod})_2 \). \( \mu_{\text{eff}} = 2.1 \mu_{\text{B}} [27,28] \) Structural characterization showed remarkable cations well-separated from the anionic units (Figure 3).[29] Anion 5 has a distorted tetrahedral coordination environment about the iron center, with a twist angle of 83°, which is close to that of anion 1 (85°).[15] Overall, the structure of 5 shows no unusual features and is quite similar to that of the previously reported 18-electron naphthalene cobaltate, \( \text{Co}(\eta^1-\text{C}_{10}\text{H}_{14})(\eta^1-\text{cod}) \) \( \text{I}^- \) (28,30).

Reactions of 1 with ligands that are stronger donors than cod almost invariably lead to the formation of \( \text{Fe}^0 \) rather than \( \text{Fe}^- \) complexes. For example, in contrast to cobaltate 2, which reacts with excess trimethylphosphite to afford high yields of \( [\text{Co}(\text{P}(\text{OMe})_3)_4][\text{I}^-] [3a] \) analogous reactions of 1 gave roughly equivmolar amounts of the \( \text{Fe}^- \) complex, \( [\text{Fe}(\eta^1-\text{C}_2\text{H}_4)(\text{P}(\text{OMe})_3)_2] \) \( \text{I}^- \) (6), and a dark blue salt of anthracene radical anion, \( [\text{K}([18] \text{c}-6)(\text{thf})_2]\text{C}_{14}\text{H}_{10} \) (31). Because no mononitrogen(0) anthracene complex had been structurally characterized previously, a single-crystal X-ray study on 6 was carried out.[31] It showed the coordination environment about the iron atom to be nearly identical to that previously reported by Zenneck and co-workers for \( [\text{Fe}(5\text{-S}^1-\text{C}_{14}\text{H}_{10}\text{naphthalene})(\text{P}(\text{OMe})_3)_2] [32,33] \). We believe the production of an \( \text{Fe}^- \) complex in this and related reactions \( [34] \) involves initial formation of a mixed-ligand \( \text{Fe}^- \) intermediate, which is a sufficiently strong reducing agent to convert coordinated or free anthracene to the observed anthracene anion. Because naphthalene is more difficult to reduce than anthracene,[15] and because \( \eta^1 \)-naphthalene complexes appear to be generally more labile than analogous anthracene compounds,[36,37] the unknown naphthalene analog of 1, or perhaps an iron version of the recently reported cobaltate \( \text{Co}(\eta^1-\text{C}_{10}\text{H}_{14})(\eta^1-\text{cod}) \) \( \text{I}^- \),

---

**Figure 2.** Molecular structure of the anion in 4. Thermal ellipsoids are set at the 50% probability level, with hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe–C1 2.066(2), Fe–C2 2.011(2), Fe–C3 2.031(2), Fe–C4 2.090(2), Fe–C5 2.065(2), Fe–C6 2.012(2), Fe–C7 2.028(2), Fe–C8 2.101(2), C1–C2 1.427(3), C2–C3 1.415(3), C3–C4 1.416(3), C5–C6 1.422(3), C6–C7 1.410(3), C7–C8 1.423(3), Fe–centroid(\( \eta^1 \)) 1.612; centroid(\( \eta^1 \))-Fe-centroid(\( \eta^1 \)) 159.8.

**Figure 3.** Molecular structure of the anion 5. Thermal ellipsoids are set at the 50% probability level, with hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe–C1 2.183(3), Fe–C2 2.090(3), Fe–C3 2.067(2), Fe–C4 2.133(2), Fe–C5 2.032(3), Fe–C6 2.043(2), Fe–C7 2.055(2), Fe–C8 2.053(3), C1–C2 1.421(3), C2–C3 1.401(4), C3–C4 1.423(3), C5–C6 1.412(3), C7–C8 1.417(3), Fe–centroid(\( \eta^1 \)) 1.71, Fe-centroid(cod) 1.34; centroid(\( \eta^1 \))-Fe-centroid(cod) 170.9.
Communications

oxidation states of these unusual species.[38] sheds more light on the metal–ligand interactions and metal electron dianions. However, because anthracene and 1,3-dented mixed-ligand Fe/C0 complex, [Fe(18c-6)(C4H6)2] (4). Anion 1 also readily reacts with excess 1,5-cyclooctadiene (cod) to afford an unprecedented mixed-ligand Fe–1 complex, [Fe{η4-C9H6}(μ-C5H4)2] (5). Studies on the redox behavior of 1, 4, and 5 are planned, including their possible conversions to corresponding 18-electron dianions. However, because anthracene and 1,3-buta diene are redox-active and potentially noninnocent ligands,[10] spectroscopic and theoretical characterization of the electronic structures of 1, 4, and 5 will also be important to shed more light on the metal–ligand interactions and metal oxidation states of these unusual species.[39]

Experimental Section

1a: Addition of an orange slurry of FeBr2 (0.500 g, 2.32 mmol) in THF (60 mL, −60°C) to a deep blue solution of K[18c-6](6.96 mmol) in THF (60 mL, −78°C) gave a dark orange solution, which was slowly warmed to room temperature over a period of about 12 h. The solution was filtered to remove KBr, and then [18]crown-6 (0.613 g, 2.32 mmol) in Et2O (260 mL, 20 mL), and dried under vacuum to provide satisfactorily pure K[18c-6][Fe{η4-C9H6}(μ-C5H4)2] (1a) as brown-black microcrystals (1.216 g, 61% based on FeBr2). Elemental analysis (%) calc'd for C20H36FeKO6: C 50.83, H 7.66. Magnetic susceptibility (Evans method, 22°C, THF): μeff = 1.98μB. X-ray single-crystal structures of 1a were grown as brown-black blocks from a pentane-layered THF solution at 0°C.[33] The synthesis of 1b is identical to that of 1a, except that [2.2.2]cryptand was used as the potassium complexant. X-ray single-crystal structures of 1b were grown as dichroic red-green plates from a pentane-layered THF solution at 0°C.[10]

4: A dark brown slurry of 1a (0.500 g, 0.581 mmol) in Et2O (35 mL) was prepared under an argon atmosphere. Argon was removed under vacuum until the solvent began to boil, and then excess gaseous 1,3-butadiene was introduced until a normal pressure was achieved. The reaction mixture was then stirred for 6 h at 20°C in a closed system, during which time the slurry assumed a red-brown color. The reaction vessel was then repressurized with more butadiene to about 1 atm and stirred for an additional 2 h, during which time the slurry became distinctly pink-red. The product was separated by filtration under an argon atmosphere, washed with Et2O (2×20 mL), and dried under vacuum to provide satisfactorily pure K[18c-6][Fe{η4-C9H6}(μ-C5H4)2] (4) as a bright pink-red solid (0.238 g, 88% based on 1a). Elemental analysis (%) calc'd for C30H28FeKO6: C 51.39, H 7.70; found: C 50.83, H 7.66. Magnetic susceptibility (Evans method, 22°C, hexamethylphosphoramide): μeff = 2.01μB. Attempts to grow suitable single crystals of [K[18c-6]-]4 for an X-ray diffraction study were unsuccessful. However, an analogous reaction of 1b with 1,3-buta diene in THF afforded suitable red-orange blocks of [K{[2.2.2]cryptand}4], which were grown over a 24 h period from a pentane-layered THF solution at 0°C.[33] See the Supporting Information for details on the syntheses and characterization of 3, 5, and 6, including Figure S1, showing the molecular structure of 6 and selected interatomic data.

Received: March 28, 2007
Published online: July 5, 2007

Keywords: arene ligands · diene ligands · iron · negative-valent complexes · sandwich complexes


[3] a) [Ru(C10H8)2]2+; b) [Fe(C10H8)(dcpe)]2+; c) [Cr(C14H10)2(dmpe)2]2+[Fe(C14H10)(dcpe)], dcpe = 1,2-bis(dicyclohexylphosphino)ethane, and due to its high reactivity is often called “naked nickel.” See: C. A. Tolman, S. D. Ittel, A. D. English, J. P. Jesson, J. Am. Chem. Soc. 1987, 109, 283.


For example, the average outer and inner Fe–C0/C1 bond lengths in 1 are 2.14(1) and 2.02(1) Å, respectively. These values for the cobaltate are 2.084(4) and 2.022(4) Å. Outer Fe–C distances in substituted [Fe(rη²-1,3-diene)] complexes tend to be longer, presumably because of steric effects. Thus, the average outer Fe–C distance in 1 is 2.14(1) Å, whereas the corresponding average inner Fe–C and coordinated diene C–C distances in 4 and 5 are nearly the same.

Thus, the M–C distances in 4 have a distinct long-short-long pattern, characteristic of predominant diolquin coordination, whereas those in [Mo(rη²-C₆H₅)₅] have a definite long-short-long-short pattern, which is indicative of a substantial metal-lactyclopentene contribution to the metal-buta-diene bonding.


Crystal structure determinations were carried out for both salts, 5a and 5b, and confirmed the presence of identical anions. However, the [K([2,2,2]-cryptand)⁺] structure solution is of higher quality and will be reported herein. Crystal data for 5b: C₈H₈FeK(NO₃), Mᵦ = 757.83, triclinic, space group PI, irdised red-violaceot plate, V = 12.132(5), b = 13.171(6), c = 14.490(7) Å, α = 108.142(7), β = 107.101(7), γ = 107.167(7), V = 1879.3(15) Å³, Z = 2, T = 173(2) K, λ = 0.71073 Å, 6838 reflections, 8396 independent, R₁ = 0.038 (I > 2σ(I), wR₂ = 0.080 (all data), μ = 0.485 mm⁻¹ (SADABS), full-matrix least-squares refinement on F²; c) CCDC-637186 (1a), CCDC-637187 (1b), CCDC-637188 (5), and CCDC-637190 (6) contains 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.

Average outer Cl–C2 and inner C2–C3 bond lengths in 1 are 1.417(5) and 1.407(4), whereas corresponding values in 2 are 1.416(8) and 1.420(6). A definite, though weak, long-short-long pattern in the coordinated diene C–C bond lengths of 1, but not 2, suggests that Fe⁺ may back-bond to anthracene slightly better than Co⁺ does in these compounds. However, the metal–carbon bond lengths in 1 and 2 do not support this view and are statistically identical. Thus, the average M–C1,C4 and M–C2,C3 bond lengths in 1 (M = Fe) are 2.14(1) and 2.02(1) Å, respectively, and corresponding values in 2 (M = Co) are 2.13(1) and 1.99(2) Å, where the difference in atomic radii of iron and cobalt is only about 0.01 Å. See: J. Emsley, The Elements, 3rd ed., Oxford, New York, 1998, pp. 60, 106. Also, the average fold angles for coordinated anthracenes in 1 and 2 are 24 and 28°, respectively.

Average M–C1,C4 and M–C2,C3 bond lengths for the ψ¹-polyarylene in 5 are 1.26(2) and 2.08(1) Å, respectively, and the corresponding values for the cobaltate are 2.15(1) and 2.01(2) Å. The average outer Cl–C2 and inner C2–C3 bond lengths in 5 are 1.422(3) and 1.401(4), whereas corresponding values for the cobaltate are 1.419(5) and 1.400(2) Å, respectively. Average M–C bond lengths for the cod complexes in 5 and the cobaltate are 2.08(5) and 2.019(8) Å, respectively, whereas corresponding average olefinic C–C bond lengths are 1.416(4) and 1.406(6) Å.


Crystal data for 4: C₈H₈FeK(NO₃), Mᵦ = 579.61, monoclinic, space group P2₁/c, red-orange block, a = 10.225(1), b = 28.679(3), c = 10.167(1) Å, b = 91.663(2), V = 2980.0(6) Å³, Z = 4, T = 173(2) K, λ = 0.71073 Å, 34928 reflections, 6838 independent, R₁ = 0.0395 (I > 2σ(I), wR₂ = 0.0759 (all data), μ = 0.685 mm⁻¹ (SADABS), full-matrix least-squares refinement on F². See reference [14] for CCDC number and related information.

For example, the average outer and inner Fe–C distances in 4, 2.08(2) and 2.02(2), respectively, are essentially identical to corresponding values observed for the 18-electron Fe⁺ complex [Fe(nη²-C₆H₅)(PMe₃)₂] (2.084(4) and 2.022(4) Å). Outer Fe–C distances in substituted [Fe(rη²-1,3-diene)] complexes tend to be longer, presumably because of steric effects. Thus, the average outer Fe–C distance in 1 is 2.14(1) Å, whereas the corresponding average inner Fe–C and coordinated diene C–C distances in 4 and 5 are nearly the same.

[36] This observation is consistent with an analysis of loss of resonance energies (ARE) that occur when arenes bind to a given metal, oxidation state, and ligand set. On this basis, the [M(π*-arene)] bond energy will increase in the order naphthalene < anthracene. However, the corresponding [M(π*-arene)] bond energy will increase in the opposite order, that is, anthracene < naphthalene. This simple analysis does not include steric effects or intrinsic differences in the donor and acceptor abilities of the bound arenes. A recent study by Parkin and co-workers also considers these issues.
