

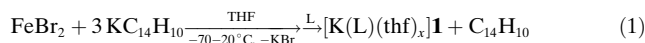
Bis(1,2,3,4- η^4 -anthracene)ferrate(1⁻): A Paramagnetic Homoleptic Polyarene Transition-Metal Anion**

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In memory of Fred Basolo

Homoleptic naphthalene and anthracene metal complexes of the d-block elements are exciting candidates for “naked” metal atom reagents^[1] owing to the unusual lability of these coordinated polycyclic aromatic hydrocarbons (or polyarenes) in ligand-substitution reactions.^[2] Although cationic and neutral homoleptic polyarene metal complexes have been established for over 25 years,^[3] the first well-defined anionic version, tris(η^4 -naphthalene)zirconate(2⁻), was only reported in 1994.^[4] Subsequent studies resulted in the synthesis and isolation of related anions, including $[\text{Co}(\eta^4\text{-L})_2]^-$,^[5] $[\text{Ta}(\eta^4\text{-L})_3]^-$,^[6] for L = naphthalene and anthracene, and $[\text{Nb}(\eta^4\text{-L})_3]^-$,^[7] 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, $[\text{Fe}(\eta^4\text{-anthracene})_2]^-$ (**1**). This paramagnetic species is also of interest as the first homoleptic polyarene iron complex^[8,9] and is a rare example of a 17-electron complex containing a metal center in a formally negative oxidation state.^[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 $[\text{K}(\text{L})(\text{thf})_x]^+$ salts in about 60% yields [Eq. (1)], where



L = [18]crown-6, $x = 2$ (**1a**) or L = [2.2.2]cryptand, $x = 1/2$ (**1b**).^[11] Magnetic susceptibilities of **1** were appropriate for a 17-electron organoiron sandwich complex^[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**)^[13] well-separated from the unexceptional cations.^[14] The coordination environment about the iron center is nearly tetrahedral,^[15] and overall, the structure of anion **1** is very similar to that reported for the corresponding 18-electron cobaltate, $[\text{Co}(\eta^4\text{-C}_{14}\text{H}_{10})_2]^-$ (**2**).^[5a,16]

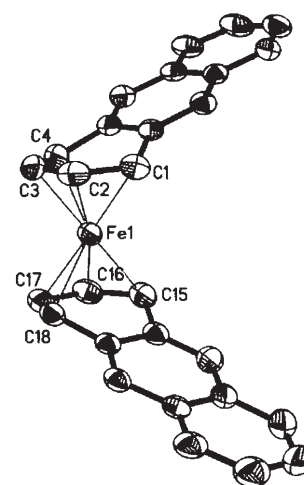


Figure 1. Molecular structure of the anion in **1b**. Thermal ellipsoids are set at the 50% probability level, with hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe–C1 2.128(2), Fe–C2 2.001(2), Fe–C3 2.024(3), Fe–C4 2.158(2), Fe–C15 2.129(2), Fe–C16 2.014(2), Fe–C17 2.035(2), Fe–C18 2.145(2), C1–C2 1.412(3), C2–C3 1.405(4), C3–C4 1.416(4), C15–C16 1.423(4), C16–C17 1.409(4), C17–C18 1.416(3), Fe–centroid(η^4) 1.66; centroid(η^4)–Fe–centroid(η^4) 161.2.

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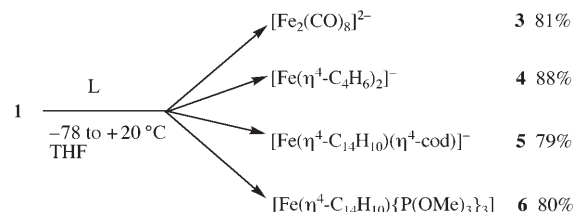
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Reactions of **1** were investigated to determine whether it would be the first available precursor to other new Fe⁻¹ complexes. Scheme 1 shows some of these reactions, including



Scheme 1. Reactions of **1** with excess L = CO, C₄H₆ (1,3-butadiene), cod (1,5-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 $[\text{Fe}_2(\text{CO})_8]^{2-}$ (**3**). Surprisingly, this classic carbonylmetallate is the only prior example of a well-characterized, isolable Fe^{-1} complex.^[17] Because of the paucity of well-defined, homoleptic, unsubstituted, 1,3-butadiene transition-metal complexes, preceded only by $[\text{Mo}(\eta^4\text{-C}_4\text{H}_6)_3]$, $[\text{W}(\eta^4\text{-C}_4\text{H}_6)_3]$,^[18] and $[\text{Co}(\eta^4\text{-C}_4\text{H}_6)_2]^-$,^[19] the reaction of **1** with 1,3-butadiene was also examined and shown to provide the first 17-electron complex of this type, $[\text{Fe}(\eta^4\text{-C}_4\text{H}_6)_2]^-$ (**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 $[\text{K}([\text{2.2.2}]\text{cryptand})]^+$ salt (Figure 2), in which the cation is well-separated from

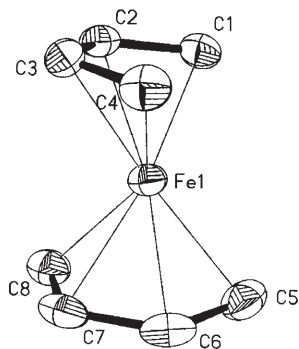


Figure 2. Molecular structure of the anion in **4**. Thermal ellipsoids are set at the 50% probability level, with hydrogen atoms omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$]: Fe–C1 2.066(2), Fe–C2 2.011(2), Fe–C3 2.031(2), Fe–C4 2.090(2), Fe–C5 2.065(2), Fe–C6 2.012(2), Fe–C7 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(η^4) 1.612; centroid(η^4)–Fe–centroid(η^4) 159.8.

the anion and has a normal structure.^[20] Anion **4** contains two structurally equivalent and discrete η^4 -1,3-butadiene groups bound to the iron center; the environment about the metal is almost tetrahedral, with a twist angle of 88° .^[15] The Fe–C and C–C bonds in **4** follow the usual patterns for iron and other late-transition-metal η^4 -1,3-diene complexes,^[21,22] in which metal-to- π^* (diene) back-bonding is not as important as for early-transition-metal 1,3-diene complexes, such as $[\text{Mo}(\eta^4\text{-C}_4\text{H}_6)_3]$.^[23,24] Structural details for **4** are also similar to those of bis(1,4-di-*tert*-butyl-1,3-butadiene)cobaltate(1 $-$), the only structurally characterized anionic complex of this type to date.^[25] Other homoleptic (1,3-butadiene)metallates, $[\text{M}(\text{C}_4\text{H}_6)_3]^{2-}$ (M = Mo, W),^[18c] 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 $[\text{Fe}(\eta^4\text{-cod})_2]^-$ or reported $[\text{Fe}(\eta^4\text{-cod})_2]^{2-}$,^[26] but instead afforded the first example of a mixed-ligand or heteroleptic Fe^{-1} complex, $[\text{Fe}(\eta^4\text{-C}_{14}\text{H}_{10})(\eta^4\text{-cod})]^-$ (**5**). This species was isolated in good yield as teal or dichroic red-violet microcrystals of the $[\text{K}([\text{18}]\text{crown-6})]^+$ (**5a**) or $[\text{K}([\text{2.2.2}]\text{cryptand})]^+$ (**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 $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-cod})]$, $\mu_{\text{eff}} =$

$2.1\mu_{\text{B}}$.^[27,28] Structural characterization showed unremarkable 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, $[\text{Co}(\eta^4\text{-C}_{10}\text{H}_8)(\eta^4\text{-cod})]^-$.^[5b,30]

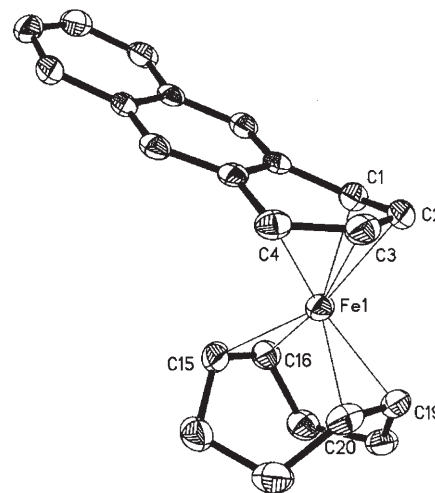


Figure 3. Molecular structure of the anion in **5**. Thermal ellipsoids are set at the 50% probability level, with hydrogen atoms omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$]: Fe–C1 2.183(3), Fe–C2 2.090(3), Fe–C3 2.067(2), Fe–C4 2.133(2), Fe–C15 2.032(3), Fe–C16 2.043(2), Fe–C19 2.055(2), Fe–C20 2.053(3), C1–C2 1.421(3), C2–C3 1.401(4), C3–C4 1.423(3), C15–C16 1.412(3), C19–C20 1.421(3), Fe–centroid(η^4) 1.71, Fe–centroid(cod) 1.34; centroid(η^4)–Fe–centroid(cod) 170.9.

Reactions of **1** with ligands that are stronger donors than cod almost invariably lead to the formation of Fe^0 rather than Fe^{-1} complexes. For example, in contrast to cobaltate **2**, which reacts with excess trimethylphosphite to afford high yields of $[\text{Co}\{\text{P}(\text{OMe})_3\}_4]^-$,^[5a] analogous reactions of **1** gave roughly equimolar amounts of the Fe^0 complex, $[\text{Fe}(\eta^4\text{-C}_{14}\text{H}_{10})\{\text{P}(\text{OMe})_3\}_3]$ (**6**), and a dark blue salt of anthracene radical anion, $[\text{K}([\text{18}]\text{c-6})(\text{thf})_2][\text{C}_{14}\text{H}_{10}]$.^[31] Because no monoiron(0) anthracene complex had been structurally characterized previously, a single-crystal X-ray study on **6** was carried out.^[32] It showed the coordination environment about the iron atom to be nearly identical to that previously reported by Zenneck and co-workers for $[\text{Fe}(5\text{-}8\text{-}\eta^4\text{-}1,4\text{-dimethylnaphthalene})\{\text{P}(\text{OMe})_3\}_3]$.^[9d,33] We believe the production of an Fe^0 complex in this and related reactions^[34] involves initial formation of a mixed-ligand Fe^{-1} 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,^[35] and because η^4 -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 $[\text{Co}(\eta^4\text{-C}_{10}\text{H}_8)(\eta^4\text{-}$

cod)]^{−[5b]} could prove to be more effective precursors than **1** to new Fe^{−1} complexes.

In conclusion, the first homoleptic polyareneiron complex, [Fe(η⁴-C₁₄H₁₀)₂][−] (**1**) has been isolated and structurally characterized. It has been shown to be an effective storable source of atomic Fe^{−1} in its reactions with carbon monoxide and 1,3-butadiene. The latter reaction is particularly interesting, because it provides the only known 17-electron and structurally authenticated homoleptic bis(1,3-butadiene)metal complex, [Fe(η⁴-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-C₁₄H₁₀)(η⁴-cod)][−] (**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-butadiene 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.^[38]

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[C₁₄H₁₀]₂ (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 THF (20 mL) was added. After addition of heptane (50 mL), solvent was slowly removed under vacuum until microcrystals of product began to form. Diethyl ether (150 mL) was then added with stirring to precipitate the product. The resulting slurry was separated by filtration, thoroughly washed with pentane (3 × 40 mL), and dried under vacuum to provide satisfactorily pure [K([18]c-6)(thf)]₂[Fe(η⁴-C₁₄H₁₀)₂] (**1a**) as brown-black microcrystals (1.216 g, 61% based on FeBr₂). Elemental analysis (%) calcd for C₄₈H₆₀FeKO₈: C 67.04, H 7.03; found: C 66.72, H 6.85. M.p. 128–129°C (dec); magnetic susceptibility (Evans method, 22°C, THF): μ_{eff} = 1.98 μ_B. X-ray quality single crystals of **1a** were grown as brown-black blocks from a pentane-layered THF solution at 0°C.^[14a] The synthesis of **1b** is identical to that of **1a**, except that [2.2.2]cryptand was used as the potassium complexant. X-ray quality single crystals of **1b** were grown as dichroic red-green plates from a pentane-layered THF solution at 0°C.^[14b]

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 had become 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([18]c-6)]₂[Fe(η⁴-C₄H₆)₂] (**4**) as a bright pink-red solid (0.238 g, 88% based on **1a**). Elemental analysis (%) calcd for C₂₀H₃₆FeKO₆: C 51.39, H 7.76; found: C 50.83, H 7.66. Magnetic susceptibility (Evans method, 22°C, hexamethylphosphoramide): μ_{eff} = 2.01 μ_B. Attempts to grow suitable single crystals of [K([18]c-6)]₂**4** for an X-ray diffraction study were unsuccessful. However, an analogous reaction of **1b** with 1,3-butadiene in THF afforded suitable red-orange blocks of [K([2.2.2]cryptand)]₂**4**, which were grown over a 24 h period from a pentane-layered THF solution at 0°C.^[20]

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.

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- [14] a) Crystal data for **1a**: $C_{48}H_{60}FeKO_8$, $M_r = 859.91$, monoclinic, space group Pn , brown-black block, $a = 10.7739(6)$, $b = 9.3435(5)$, $c = 22.262(1)$ Å, $\beta = 97.189(1)^\circ$, $V = 2223.4(2)$ Å³, $Z = 2$, $T = 173(2)$ K, $\lambda = 0.71073$ Å, 11569 reflections, 6340 independent, $R1 = 0.0407$ ($I > 2\sigma(I)$), $wR2 = 0.0850$ (all data), $\mu = 0.485$ mm⁻¹ (SADABS), full-matrix least-squares refinement on F^2 ; b) **1b**: $C_{48}H_{60}FeKN_2O_{6.5}$, $M_r = 863.93$, monoclinic, space group $C2/c$, red-green plate, $a = 22.763(3)$, $b = 11.271(1)$, $c = 36.390(4)$ Å, $\beta = 108.102(2)^\circ$, $V = 8874(2)$ Å³, $Z = 8$, $T = 173(2)$ K, $\lambda = 0.71073$ Å, 36509 reflections, 7829 independent, $R1 = 0.0399$ ($I > 2\sigma(I)$), $wR2 = 0.0988$ (all data), $\mu = 0.485$ mm⁻¹ (SADABS), full-matrix least-squares refinement on F^2 ; c) CCDC-637186 (**1a**), CCDC-637187 (**1b**), CCDC-637188 (**4**), CCDC-637189 (**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.
- [15] Coordination geometry is determined by a twist angle, θ , corresponding to the intersection of planes defined by the midpoints of the outer C–C bonds of the coordinated dienes and the iron center. For **1**, $\theta = 85^\circ$, compared to 90° for a tetrahedral geometry. In the case of the cod complex **5**, the midpoints of the olefinic C–C bonds were used in the calculation of θ .
- [16] Average outer C1–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⁻¹ may back-bond to anthracene slightly better than Co⁻¹ 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 edition, Oxford, New York, **1998**, pp. 60, 106. Also, the average fold angles for coordinated anthracenes in **1** and **2** are 24 and 28°, respectively.
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- [20] Crystal data for **4**: $C_{26}H_{48}FeKN_2O_6$, $M_r = 579.61$, monoclinic, space group $P2_1/c$, red-orange block, $a = 10.225(1)$, $b = 28.679(3)$, $c = 10.167(1)$ Å, $\beta = 91.662(2)^\circ$, $V = 2980.0(6)$ Å³, $Z = 4$, $T = 173(2)$ K, $\lambda = 0.71073$ Å, 34928 reflections, 6838 independent, $R1 = 0.0395$ ($I > 2\sigma(I)$), $wR2 = 0.0759$ (all data), $\mu = 0.685$ mm⁻¹ (SADABS), full-matrix least-squares refinement on F^2 . See reference [14] for CCDC number and related information.
- [21] 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 Fe⁰ complex $[Fe(\eta^4-C_4H_6)_2(PMe_3)]$ (2.084(4) and 2.021(4) Å).^[22a] Outer Fe–C distances in substituted $\{Fe(\eta^4-1,3\text{-diene})\}$ complexes tend to be longer, presumably because of steric effects.^[22b] Thus, the average outer Fe–C distance in **1** is 2.14(1) Å, whereas respective average inner Fe–C and coordinated diene C–C distances in **1** and **4** are nearly the same.
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- [23] Thus, the M–C distances in **4** have a distinct long-short-short-long pattern, characteristic of predominant diolefin coordination, whereas those in $[Mo(\eta^4-C_4H_6)_3]$ have a definite short-long-long-short pattern, which is indicative of a substantial metal-lacyclopentene contribution to the metal–butadiene bonding.^[18d,24]
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- [25] F. G. N. Cloke, P. B. Hitchcock, A. McCamley, *J. Chem. Soc. Chem. Commun.* **1993**, 248. However, the presence of bulky *tert*-butyl groups on the 1,4-diene carbon atoms of the cobaltate causes its average outer M–C distance, 2.15(2) Å, to be significantly longer than that of **4**.^[21]
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- [28] Several neutral 17-electron organoiron(I) complexes have been reported. See: K. Jonas, P. Klusmann, R. Goddard, *Z. Naturforsch. B* **1995**, *50*, 394.
- [29] Crystal structure determinations were carried out for both salts, **5a** and **5b**, and confirmed the presence of identical anions. However, the $[K([2.2.2]\text{cryptand})]^+$ structure solution is of higher quality and will be reported herein. Crystal data for **5b**: $C_{40}H_{58}FeKN_2O_6$, $M_r = 757.83$, triclinic, space group $P\bar{1}$, iridescent red-violet plate, $a = 12.132(5)$, $b = 13.171(6)$, $c = 14.490(7)$ Å, $\alpha = 108.412(7)$, $\beta = 107.101(7)$, $\gamma = 107.176(7)^\circ$, $V = 1897.5(15)$ Å³, $Z = 2$, $T = 173(2)$ K, $\lambda = 0.71073$ Å, 18644 reflections, 6696 independent, $R1 = 0.0377$ ($I > 2\sigma(I)$), $wR2 = 0.0779$ (all data), $\mu = 0.555$ mm⁻¹ (SADABS), full-matrix least-squares refinement on F^2 . See reference [14] for CCDC number and related information.
- [30] Average M–C1,C4 and M–C2,C3 bond lengths for the η^4 -polyarene group in **5** are 2.16(2) and 2.08(1) Å, respectively, and the corresponding values for the cobaltate are 2.15(1) and 2.010(2) Å. The average outer C1–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 groups in **5** and the cobaltate are 2.05(1) and 2.019(8) Å, respectively, whereas corresponding average olefinic C–C bond lengths are 1.416(4) and 1.406(6) Å.
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- [33] See the Supporting Information for the molecular structure of **6**, selected interatomic data, and comparisons with $[Fe(5\text{-}8\text{-}\eta^4\text{-}1,4\text{-dimethylnaphthalene})(P(OMe)_3)_3]$.^[9d]
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