Negative-Valent Transition Metals

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Towards Homoleptic Naphthalenemetalates of the Later Transition Metals: Isolation and Characterization of Naphthalenecobaltates(1−)**

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Dedicated to Professor Christoph Elschenbroich

Storable sources of transition-metal atoms, or “naked-metal-atom” reagents, were first discovered in the pioneering research of Wilke and co-workers, which involved spectacular homoleptic alkene nickel(0) complexes, including [Ni(cod)$_2$],[1] (cod = 1,5-cyclooctadiene) and [Ni(C$_2$H$_4$)$_3$].[2] Subsequently, Jonas et al. isolated related anionic alkene complexes, [Co(cod)$_2$]$^-$[3] and [Co(C$_2$H$_4$)$_4$]$^-$,[4] which proved to be extremely useful synthons for the atomic cobalt anion. Kündig and Timms[5] and Elschenbroich and Möckel[6] then independently discovered that early-transition-metal “naked-atom” reagents could be isolated in the form of quite labile neutral homoleptic naphthalene complexes, [M(C$_{10}$H$_8$)$_2$] (M = V, Cr, Mo). Anionic early-transition-metal homoleptic naphthalene complexes were later established for zirconium ([Zr(η^4-C$_{10}$H$_8$)$_3$]$^{2-}$)[7] and tantalum ([Ta(η^4-C$_{10}$H$_8$)$_3$]$^-$)[8] and have been shown to function as sources of atomic Zr^{2-} and Ta$^-$ ions in their reactions with carbon monoxide and similar ligands. However, no compounds of this class are presently known for the later transition metals. Indeed, even *heteroleptic* naphthalene complexes containing formally negative-valent metals are unknown for d-block elements to the right of manganese,[9] and also unknown for the corresponding heavier metals within each triad. For these reasons, we report herein on the isolation, structural characterization, and some chemical properties of the first compound of this type, [Co(η^4-C$_{10}$H$_8$)(η^4-cod)]$^-$ (**1**). Also, two other naphthalenecobaltate(1−) complexes were unexpectedly obtained in the course of developing a “noncobaltocene” route to alkenecobaltates(1−).

Recently, we disclosed that the reaction of cobalt(II) bromide with three equivalents of potassium naphthalene gave a thermally unstable deep-red species, which functioned as a convenient source of atomic Co^{1-} ions, but defied all attempts at isolation or characterization.[10] However, when identical reactions were carried out in the presence of one equivalent of cod, bright-red and quite air-sensitive microcrystals of thermally stable (at 20 °C) anion **1** were isolable as [K(L)(thf)$_x$] salts (L = [18]crown-6) in 60–65 % yields [Eq. (1)], where x is 0.5 or 0, depending on the method of purification (see the Experimental Section). Interestingly, analogous reactions that were conducted with cobaltocene as the Co$^{\text{II}}$ precursor also provided **1** in yields of about 85 %. Thus, both reactions may involve a common intermediate, perhaps a homoleptic naphthalenecobaltate(1−)[11] that is analogous to the known bis(1,2,3,4-η^4-anthracene)cobaltate(1−) (**2**).[10]

$$\mathrm{CoBr_2 + 3\,KC_{10}H_8 + 1,5\text{-cod}} \xrightarrow[\substack{-78 \,\to\, +20\,^\circ\mathrm{C} \\ -2\,\mathrm{KBr}}]{\mathrm{THF}} \xrightarrow[\mathrm{L}]{\mathrm{Et_2O}} [\mathrm{K(L)(thf)}_x][\mathbf{1}] + 2\,\mathrm{C_{10}H_8} \qquad (1)$$

^{1}H and ^{13}C NMR spectra of **1** in solution are unexceptional and entirely consistent with its formulation, and showed resonances characteristic of η^4-naphthalene[7,8] and η^4-1,5-cyclooctadiene[3,12] groups bound in a 1:1 ratio to an electron-rich metal center. A single-crystal X-ray study on **1**, as the [K([18]crown-6)] salt, revealed an undistorted cation that was well-separated from the cobalt center of the anion and had no significant effect on its structure.[13] The latter showed a nearly tetrahedral environment about the cobalt center,[14] which is appropriate for a d^{10} cobalt(−I) complex (Figure 1). Indeed, the Co−C and C−C bond lengths of the η^4-diene units in **1** and **2**[10] are nearly identical, thus indicating that there are no great differences in the η^4-polyarene–cobalt interactions in the two anions.[15] However, the average Co−C

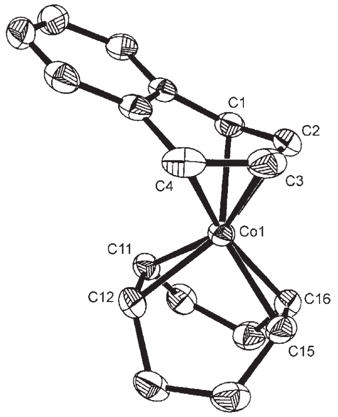

Figure 1. Molecular structure of **1**; cation is not shown. Thermal ellipsoids are set at the 50 % probability level, with hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Co-C1 2.142(1), Co-C2 2.008(1), Co-C3 2.012 (2), Co-C4 2.158(2), Co-C11 2.017(1), Co-C12 2.028(1), Co-C15 2.009(1), Co-C16 2.021(2), C1-C2 1.424(2), C2-C3 1.400(2), C3-C4 1.414(2), C11-C12 1.400(2), C15-C16 1.412(2), Co-centroid(η^4) 1.67, Co-centroid(cod) 1.30; centroid(η^4)-Co-centroid(cod) 175.2.

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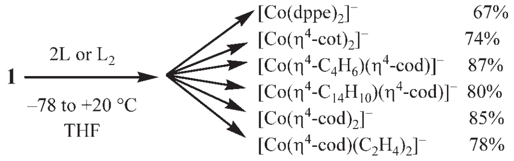
bond length of the η^4-cod group in **1** (2.019(8) Å) is slightly shorter than the corresponding value found in $[(thf)_2Li][Co(cod)_2]$ (2.05(2) Å),[3] thus suggesting that the cod ligand is a somewhat better donor in **1** than it is in $[Co(cod)_2]^-$. Thus, the relative stability of **1** compared to a homoleptic naphthalenecobaltate is likely a result, in part, of the synergy of its mixed cod/naphthalene ligand set, where cod is expected to be a better donor and weaker acceptor than naphthalene.[15,16]

Several reactions of **1** are shown in Scheme 1 to illustrate its utility as a precursor to other Co^{1-} complexes. Very good acceptor ligands, such as 1,2-bis(diphenylphosphano)ethane (dppe) or 1,3,5,7-cyclooctatetraene (cot), react with **1** to provide the identical homoleptic cobaltates in about the same yields as those obtained from analogous reactions with **2**.[10] New cobaltates that are derived from **1** include $[Co(\eta^4\text{-}C_4H_6)(\eta^4\text{-cod})]^-$ (**3**) and $[Co(\eta^4\text{-}C_{14}H_{10})(\eta^4\text{-cod})]^-$ (**4**), which were structurally characterized[17] and provide unprecedented examples of mixed 1,3-butadiene–alkene and anthracene–alkene metalates. In contrast to **4**, compound **1** readily reacts with excess cod or ethylene to afford $[Co(cod)_2]^-$ (**5**)[3] or $[Co(cod)(C_2H_4)_2]^-$ (**6**)[4] in good yields, thus indicating that the naphthalene ligand in **1** is more labile than the anthracene ligand in **4**. These reactions are noteworthy because **5** and **6** were previously available only from reductions involving cyclopentadienylcobalt precursors, such as cobaltocene.[4,18] It is clear that the naphthalene ligand in **1** fulfills the same important role of a supporting ligand, as Jonas previously established for the cyclopentadienyl group in his prior routes to these alkenecobaltates.[4,19–22]



Scheme 1. Reactions of **1** with L_2 = dppe, cot, C_4H_6 (1,3-butadiene), $C_{14}H_{10}$ (anthracene), cod (1,5-cyclooctadiene), and $L = C_2H_4$ (ethene), with yields of isolated products, obtained as [K([18]crown-6)] salts.

The ability of ethylene to readily displace naphthalene from **1** to produce **6** was an exciting result because it suggested that the long-known $[Co(C_2H_4)_4]^-$ complex[4,23] should also be accessible from reductions of $CoBr_2$ mediated by alkali metal–naphthalene reagents in the presence of excess ethylene. Indeed, a pale gray solid, identical to the previously reported $[K(thf)_x][Co(C_2H_4)_4]$ (**7**),[4] was obtained in about 80% yield by this facile procedure, which is identical to the synthesis of **1**, except excess ethylene was first added rather than cod. Treatment of **7** with [18]crown-6 or [2.2.2]cryptand in THF/pentane at 0 °C afforded $[K([18]crown\text{-}6)][Co(C_2H_4)_4]$ (**8**) as a beige solid or $[K([2.2.2]cryptand)][Co(C_2H_4)_4]$ (**9**) as light yellow needles. The formulation of **9** was confirmed by a single-crystal X-ray study, which revealed the presence of discrete $[Co(C_2H_4)_4]^-$ units in the solid state for the first time.[24]

When a light-yellow solution of **8** and three equivalents of naphthalene in THF were evaporated in vacuo at 20 °C, the concentrated solution/slurry acquired a distinct reddish appearance. Addition of diethyl ether caused precipitation of a red solid.[25] Crystallization of this product from THF/pentane at 0 °C *reproducibly* gave both yellow and red-black single crystals, in variable amounts. The crystals were manually separated under an inert atmosphere and identified by X-ray crystallography as **8** and **10**, respectively. The latter was found to be the remarkable "triple salt" $[K([18]crown\text{-}6)]_3[Co(\eta^4\text{-}C_{10}H_8)(C_2H_4)_2]_2[Co(\eta^4\text{-}C_{10}H_8)_2]$, which contained the new naphthalenecobaltates $[Co(\eta^4\text{-}C_{10}H_8)(C_2H_4)_2]^-$ (**11**) and $[Co(\eta^4\text{-}C_{10}H_8)_2]^-$ (**12**) in a 2:1 ratio.[25] Anion **12** is of particular significance because it represents the first homoleptic naphthalenemetalate of a later transition metal. Attempts to isolate pure salts of **11** and **12** have so far failed.

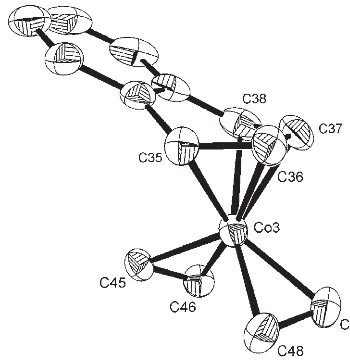


Figure 2. Molecular structure of **11**; cation is not shown. Thermal ellipsoids are set at the 50% probability level, with hydrogen atoms omitted for clarity. Selected bond lengths [Å]: Co3-C35 2.166(2), Co3-C36 2.011(3), Co3-C37 2.016(3), Co3-C38 2.158(3), Co3-C45 2.017(2), Co3-C46 2.007(2), Co3-C47 2.039(3), Co3-C48 2.012(3), C35-C36 1.416(4), C36-C37 1.402(4), C37-C38 1.405(4), C45-C46 1.399(4), C47-C48 1.405(4), Co-centroid(η^4) 1.68.

The asymmetric unit of **10**[26] contains two independent anions of **11** and one of **12**, which interact weakly with and appear to be largely unperturbed by essentially undistorted [K([18]crown-6)] cations. The independent anions of **11** are almost superimposable, and one of these is shown in Figure 2. Anion **12** is depicted in Figure 3. The structural properties of **11** are nearly identical to those of closely related **1**[27] and only differ significantly in the twist angle,[14] which has an average value of 68(1)° for **11**. The corresponding twist angles for **2** and **12** are 62°[10] and 70°, respectively. Thus, the geometry about the cobalt center in these anions is distorted tetrahedral, which is indicative of d^{10} cobalt(−I). In view of the relatively robust character of **2**[10] and the prior difficulties in accessing bona fide **12**,[28] it is noteworthy that the η^4-diene–cobalt units in both compounds are nearly identical.[29] Although the structural data suggest that the anthracene and naphthalene units bind about as strongly to cobalt in **2** and **12**, respectively, interatomic distances may prove to be rather insensitive measures of metal–arene binding in these complexes. For example, a recent computational study on low-valent molybdenum–arene complexes showed that the Mo–(η^4-arene) bond energy increased in the order naphthalene < anthracene, owing, in part, to the greater acceptor

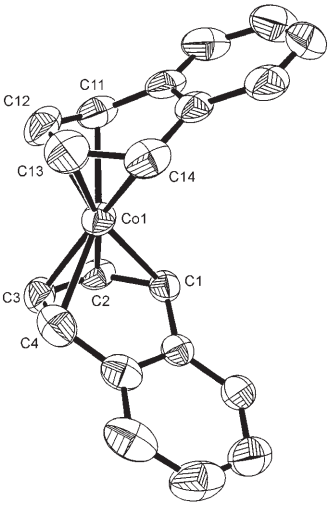


Figure 3. Molecular structure of **12**; cation is not shown. Thermal ellipsoids are set at the 50% probability level, with hydrogen atoms omitted with clarity. Selected bond lengths [Å] and angles [°]: Co1-C1 2.116(3), Co1-C2 1.960(3), Co1-C3 1.989(3), Co1-C4 2.131(3), Co1-C11 2.139(3), Co1-C12 1.992(3), Co1-C13 1.961(3), Co1-C14 2.106(3), C1-C2 1.433(4), C2-C3 1.418(4), C3-C4 1.421(5), C11-C12 1.407(5), C12-C13 1.406(5), C13-C14 1.413(5), Co-centroid(η^4) 1.63; centroid(η^4)-Co-centroid(η^4) 167.5.

ability of anthracene. However, corresponding average Mo–C and C–C bond lengths for the η^4-diene–molybdenum units in these two compounds were only marginally different.[30]

In summary, we have prepared, isolated, and fully characterized the first naphthalenecobaltate(1−) complex, $[Co(\eta^4\text{-}C_{10}H_8)(cod)]^-$ (**1**), and have shown that it functions as an effective storable source of the atomic cobalt anion in several reactions. Two related species, $[Co(\eta^4\text{-}C_{10}H_8)(C_2H_4)_2]^-$ (**11**) and $[Co(\eta^4\text{-}C_{10}H_8)_2]^-$ (**12**), were also identified in the unusual triple salt **10**. Compound **12** is of special interest because it is the first structurally characterized homoleptic bis(naphthalene)metal anion for any d-block element, and it promises to be a particularly reactive source of atomic cobalt anions in chemical reactions. Extension of this investigation to other polyarenes and transition metals is in progress.

Experimental Section

1: A bright-blue solution of anhydrous $CoBr_2$ (0.500 g, 2.29 mmol) and 1,5-cod (0.247 g, 2.29 mmol) in THF (40 mL, −78 °C) was added to a forest-green solution of $KC_{10}H_8$ (6.86 mmol) in THF (40 mL, −78 °C). The resulting red-brown solution was warmed to room temperature over a 12-hour period and then filtered to remove KBr. After the solvent was removed in vacuo, diethyl ether (50 mL) was added to extract the product. The reaction mixture was filtered into a flask containing [18]crown-6 (0.604 g, 2.29 mmol) in diethyl ether, whereupon a bright red microcrystalline product formed within seconds. The product was separated by filtration, washed thoroughly with diethyl ether, and dried in vacuo. Pure magenta microcrystals of $[K([18]crown\text{-}6)(thf)_{0.5}][Co(C_{10}H_8)(cod)]$ were thereby obtained (0.936 g, 64%). Elemental analysis (%) calcd for $C_{32}H_{48}CoKO_{6.5}$: C 60.55, H 7.62; found: C 61.15, H 7.61; m.p. 124–126 °C (decomp); ^{1}H NMR (300 MHz, [D$_8$]THF, 20 °C, cation resonances omitted; Np = naphthalene) $\delta = 0.94$ (br, 2H, CH, cod), 1.25, 1.75, 1.94, 2.44 (br m, 2H; CH_2, cod), 2.83 (m, 2H, H1,H4 of Np), 4.13 (br m, 2H, CH, cod), 4.91 (m, 2H, H2,H3 of Np), 5.49 ppm (m, 4H, H5–H8 of Np); ^{13}C NMR (75.5 MHz [D$_8$]THF, 20 °C) $\delta = 33.4$ (t, CH_2, cod), 54.3 (d, CH, cod), 60.2 (d, C1,C4 of Np), 69.9 (d, CH, cod), 84.8 (d, C2,C3 of Np), 114.7, 118.4 (d, C5,C8 and C6,C7 of Np), 149.2 ppm (s, C9,C10 of Np). Identification of C,H resonances was established by ^{1}H–^{13}C HMQC, COSY 2D NMR and trends previously established for η^4-naphthalene complexes,[7,8] but no unique assignment of C5,C8 or C6,C7 on the naphthalene ligand was possible. X-ray quality single-crystals of **1**, as a [(K[18]crown-6)] salt, were grown as red-brown plates from a pentane-layered THF solution at 0 °C.[13]

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[9] a) $[Mn(\eta^4\text{-}C_{10}H_8)(PMe_3)_3]^-$: K. Jonas, G. Burkart, C. Häselhoff, P. Betz, C. Krüger, *Angew. Chem.* **1990**, *102*, 291; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 323; b) $[Mn(\eta^4\text{-}C_{10}H_8)(CO)_3]^-$: R. L. Thompson, S. Lee, A. L. Rheingold, N. J. Cooper, *Organometallics* **1991**, *10*, 1657; c) $[Mn(\eta^4\text{-}C_{10}H_8)(\eta^6\text{-biphenyl})]^-$: K. Jonas, C.-C. Häselhoff, R. Goddard, C. Krüger, *Inorg. Chim. Acta* **1992**, *198–200*, 533.

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[13] Crystal structure analysis of **1**: $C_{30}H_{44}CoKO_6$, $M_r = 598.68$, monoclinic, space group $P2_1/c$, red-brown plates, $a = 12.954(1)$, $b = 14.038(1)$, $c = 16.213(2)$ Å, $\beta = 96.399(2)°$, $V = 2930.0(5)$ Å^3, $Z = 4$, $T = 173(2)$ K, $\lambda = 0.71073$ Å, 22987 reflections, 6702 independent, $R1 = 0.0275$ ($I > 2\sigma(I)$), $wR2 = 0.0654$ (for all data), $\mu = 0.768$ mm^{-1} (SADABS), full-matrix least-squares refinement on F^2. CCDC-614823 (**1**) and CCDC-614824 (**10**) 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.

[14] Coordination geometry is determined by a twist angle, θ, corresponding to the intersection of planes that are defined by the midpoints of the bound C–C groups of the coordinated diene units and cobalt center. For **1** the θ angle is 84°, compared to 90° for tetrahedral geometry.

[15] Average Co–C1,C4 and Co–C2,C3 bond lengths for the η^4-1,3-diene groups in **1** are 2.15(1) and 2.010(3) Å, respectively, and the corresponding values for **2** are 2.13(1) and 1.99(2) Å.[10] The

average outer C1–C2 and inner C2–C3 bond lengths in **1** are 1.419(7) and 1.400(2), whereas corresponding values in **2** are 1.416(8) and 1.420(6) Å. A definite, albeit weak, long-short-long pattern in the diene C–C bond lengths in **1**, but not **2**, suggests that slightly more back-bonding is present in the cobalt–arene interaction in **1** compared to **2**, likely because of the presence of cod in the naphthalene complex. Interestingly, Zenneck and coworkers have observed nearly identical diene C–C bond lengths for naphthalene in the X-ray structure of [Fe(η^6-C_6Me_6)(η^4-$C_{10}H_8$)], where the presence of the good donor hexamethylbenzene is critical in the stabilization of this complex, relative to a possible homoleptic naphthaleneiron(0) complex, which decomposes at about −60 °C.[16]

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[17] See the Supporting Information for syntheses and characterization of **3** and **4**. Details on the X-ray studies on **3** and **4** will be described elsewhere: W. W. Brennessel, J. E. Ellis, unpublished results. Crystal data for [K([18]crown-6)][Co(C_4H_6)(cod)] (**3**): $C_{24}H_{42}CoKO_6$, $M_r = 524.61$, triclinic, space group $P\bar{1}$, orange blocks, $a = 8.6632(7)$, $b = 10.9612(9)$, $c = 14.924(1)$ Å, $\alpha = 90.952(1)$, $\beta = 93.574(1)$, $\gamma = 112.826(1)°$, $Z = 2$, $wR2$ (all data) = 0.0988 with GOF on F^2 of 1.037. Crystal data for [K([2.2.2]cryptand)][Co($C_{14}H_{10}$)(cod)] (**4**): $C_{40}H_{58}CoKN_2O_6$, $M_r = 760.91$, triclinic, space group $P\bar{1}$, red-violet plates, $a = 12.104(1)$, $b = 13.158(1)$, $c = 14.411(1)$ Å, $\alpha = 108.664(2)$, $\beta = 107.142(2)$, $\gamma = 106.915(2)°$, $Z = 2$, $wR2$ (all data) = 0.0955 with GOF on F^2 of 1.022.

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[19] Jonas et al. were the first to prepare and examine the reactivity of non-carbonyl-containing heteroleptic naphthalenemetalates, including Mn^{-I} species[9a,c] and the M^0 complexes [C_5H_5M-($C_{10}H_8$)]$^-$ (M = V,[20,21] Cr,[22] Fe[22]).

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[24] Details on the syntheses of **7**, **8**, and **9** and the X-ray study on **9** will be described elsewhere: W. W. Brennessel, J. E. Ellis, unpublished results. Crystal data for [K([2.2.2]cryptand)][Co(C_2H_4)$_4$]: $C_{26}H_{52}CoKN_2O_6$, $M_r = 586.73$, orthorhombic, space group *Pbcn*, light-yellow needles, $a = 25.836(3)$, $b = 10.4820(12)$, $c = 22.544(3)$ Å, $Z = 8$, $wR2$ (all data) = 0.0734 with GOF on F^2 of 1.017.

[25] Interestingly, exposure of a suspension of the red product to excess ethylene in diethyl ether at 20 °C caused it to rapidly revert to pale yellow, slightly soluble **8**.

[26] Crystal structure analysis of **10**: $C_{84}H_{120}Co_3K_3O_{18}$, $M_r = 1711.89$, triclinic, space group $P\bar{1}$, red-black blocks, $a = 15.228(1)$, $b = 15.938(1)$, $c = 19.098(1)$ Å, $\alpha = 84.505(1)$, $\beta = 67.115(1)$, $\gamma = 88.147(1)°$, $V = 4250.5(5)$ Å^3, $Z = 2$, $T = 173(2)$ K, $\lambda = 0.71073$ Å, 41 889 reflections, 17 834 independent, $R1 = 0.0382$ ($I > 2\sigma(I)$), $wR2 = 0.0977$ (for all data), $\mu = 0.791$ mm^{-1} (SADABS), full-matrix least-squares refinement on F^2. See reference [13] for CCDC number and related information.

[27] Average C–C bond lengths for the η^4-diene and η^2-alkene groups in **1** are 1.413(12) and 1.406(8) Å, respectively. Corresponding values for **11** are 1.408(7) and 1.402(4) Å. Average Co–C1,C4, Co–C2,C3, and Co–C(alkene) bond lengths in **1** are 2.15(1), 2.010(3), and 2.019(8) Å, respectively. Corresponding values for **11** are 2.162(6), 2.014(3), and 2.019(14) Å. Finally, the fold angles for coordinated naphthalenes in **1** and **11** are 27 and 30°.

[28] In this regard, it is important to stress that there is no proof presently for the formation of **12** in the alkali metal naphthalene reductions of cobalt(II) bromide[10] or cobaltocene[11] in THF.

[29] Average C–C bond lengths for the η^4-diene groups in **2** and **12** are 1.417(7) and 1.416(10) Å. Average Co–C1,C4 and Co–C2,C3 bond lengths for both η^4-diene groups in **2** are 2.13(1) and 1.99(2) Å, and corresponding values for **12** are 2.12(1) and 1.98(1) Å. Average fold angles for the anthracene ligands in **2** are 28°, and those for the naphthalene ligands in **12** are 32°. The twist angles[14] in **2** and **12** are 62° and 70°, respectively.

[30] G. Zhu, K. E. Janak, J. S. Figueroa, G. Parkin, *J. Am. Chem. Soc.* **2006**, *128*, 5452.