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Naphthalene and Anthracene Cobaltates(1−): Useful Storable Sources of an Atomic Cobalt Anion

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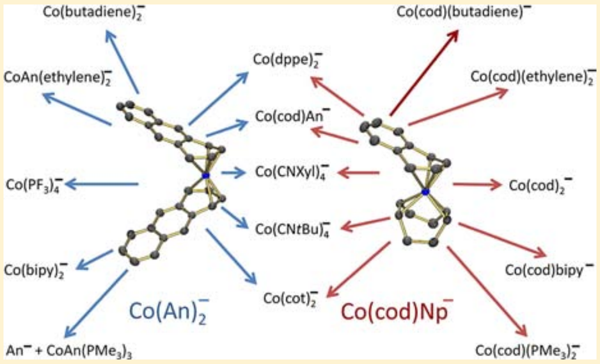
Ⓢ *Supporting Information*

ABSTRACT: Reductions of $CoBr_2$ or cobaltocene by 3 equiv of potassium anthracene radical anion in tetrahydrofuran (THF) afford 60−80% yields of bis(anthracene)cobaltate(1−) (**1**), of interest as a readily accessible and quite labile source of spin-paired atomic Co^-. Although the unsolvated potassium salt of **1** is thermally unstable at 20 °C, the $[K(18\text{-crown-6})(THF)_2]^+$ salt of **1** functions as a useful storable crystalline reagent for Co^- in several reactions. Previously known classic cobaltates, $[CoL_4]^-$, for L = 1/2 (1,3-butadiene) (**2**), PF_3 (**3**), and $P(O\mathit{i}Pr)_3$ (**5**), were obtained directly from **1** and structurally characterized for the first time. Anion **3** is noteworthy because it appears to possess the shortest known Co−P distance, av = 2.012(4) Å. Although the naphthalene analogue of **1** is not yet available as a pure substance, low-temperature reductions of $CoBr_2$ or cobaltocene by naphthalene radical anion in the presence of 1,5-cyclooctadiene (COD) afford variable yields (80−90% from $CoCp_2$) of (naphthalene)(COD)cobaltate(1−) (**10**). Ready displacement of naphthalene in **10** by L = 1,3-butadiene, 2,2′-bipyridine, and COD occurs to give good yields of the respective $[Co(L)(COD)]^-$, all of which have been structurally characterized. Both ligands in **10** are displaced by *tert*-butylisocyanide to afford $[Co(CN\mathit{t}Bu)_4]^-$ (**16**), the first isolable and structurally characterized homoleptic alkylisocyanometalate. The molecular structure of **16** shows unprecedented bending of the isocyanides, av C−N−C = 137(2)°, for homoleptic isocyanide complexes.



■ INTRODUCTION

Wilke introduced metal-atom reagents, i.e., storable sources of atomic metals, with his remarkable "naked-nickel" compounds, including *trans,trans,trans*-1,5,9-cyclododecatriene- and bis(1,5-cyclooctadiene)nickel.[1] For over 40 years, these and related highly labile hydrocarbon−nickel complexes have been key precursors to countless new species including numerous homoleptic nickel(0) complexes.[2] Notably, Wilke's initial studies significantly predated syntheses of nickel(0) complexes via nickel vapor in metal-atom reactors.[3] Jonas extended Wilke's conventional syntheses of metal-atom reagents to anionic complexes with the isolation of bis(1,5-cyclooctadiene)-cobaltate(1−),[4] tetrakis(ethylene)ferrate(2−),[5] and related metalates, prepared by the reductive cleavage of metallocenes in the presence of appropriate olefins.[6]

Originally, Jonas employed alkali metals in reductions of metallocenes but, in 1986 and later, often used alkali-metal naphthalenes, which resulted in the formation of new heteroleptic naphthalene sandwich complexes $[(\eta^5\text{-Cp})M(C_{10}H_8)]^-$, for M = V,[7] Cr,[8] and Fe,[8] and related manganese species.[9] Cooper et al. also examined the reduction of cobaltocene by potassium naphthalene and obtained a highly labile and thermally unstable species, speculated to be a naphthalene-stabilized cobaltate(1−).[10] Success in isolating the first well-characterized homoleptic polyarenemetalate complex, tris(naphthalene)zirconate(2−),[11] encouraged efforts to determine whether polyarenecobaltates were accessible. Although heteroleptic polyarenecobalt complexes had been described, including $Co(1,2\text{-}\eta^2\text{-An})(PMe_3)_3$, where An = anthracene $Co(1,2\text{-}\eta^2\text{-An})(PMe_3)_3X$, with X = H, $SnPh_3$,[12] and $CpCo(1\text{–}4\text{-}\eta^4\text{-An})$,[13] homoleptic polyarenecobalt species were previously unknown. Indeed, prior to starting our research in this area,[14] the only well-known middle−late, i.e., groups 7−12, transition-metal complex of this type was $[Ru(C_{10}H_8)_2]^{2+}$, $C_{10}H_8$ = naphthalene,[15a] which until recently was the only reported cationic homoleptic polyarene complex.[15b]

A key development in the isolation of the first anionic homoleptic polyarene complex of a later transition metal was a prior study, involving polyarenetitanium complexes, in which anthracene species were shown to be much more stable in solution and the solid state than formally analogous naphthalene compounds.[16] Although all initial attempts to isolate naphthalenecobaltates(1−) were fruitless, switching to anthracene quickly resulted in the isolation and characterization of bis(anthracene)cobaltate(1−).[17] Preliminary results have also been reported for (naphthalene)(1,5-cyclooctadiene)-cobaltate(1−).[18] Herein the first full account of this work is presented. Significant new results include a facile route to and X-ray structural characterization of the long known [Co-

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$(PF_3)_4]^-$,[19] structural authentications of the previously reported bis(butadiene)cobaltate(1−),[6a] $[Co(P(OiPr)_3)_4]^-$,[20] and the first structurally characterized homoleptic alkylisocyanidemetalate, $[Co(CNtBu)_4]^-$.

■ EXPERIMENTAL SECTION

General Procedures and Reagents. All operations were performed under an atmosphere of 99.5% argon further purified by passage through columns of activated BASF catalyst and molecular sieves. Standard Schlenk techniques were employed for all reactions with a double-manifold vacuum line attached to a two-stage mechanical pump. Solutions were transferred via stainless steel double-ended needles (cannulas).[21] All reactions involving anionic species were stirred with glass-covered magnetic stir bars because Teflon is often attacked by these strongly reducing species.

Carbon monoxide (CO, 99.9%) was purified in the same manner as the argon and also passed through a column of Ascarite, which is a trademark for self-indicating sodium hydroxide nonfibrous silicate formulation, for the quantitative absorption of carbon dioxide (CO_2). Ethylene (99.5+%) and butadiene (99+%) were purchased from Aldrich and used as received. Commercial-grade PF_3 was purchased from Pennwalt Ozark Mahoning and purified by passage through −78 °C traps and 4 Å molecular sieves. Except where noted, the solvent and reagents were obtained from commercial sources, used without further purification, and stored under argon. Solvents tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), diethyl ether (Et_2O), toluene, heptane, hexanes, and pentane were purged with nitrogen, followed by distillation from sodium benzophenone ketyl. Cobalt dibromide hydrate ($CoBr_2 \cdot xH_2O$) was dried under a static vacuum at 130 °C in a drying pistol loaded with phosphorus pentoxide. THF-d_8 was distilled from a NaK alloy, while other deuterated solvents were distilled from CaH_2 under an argon atmosphere.

Caution! *CO, 1,3-butadiene, and phosphorus trifluoride are very toxic gases that must be handled in a well-ventilated hood.*

[K(18-crown-6)(THF)$_2$][Co(η^4-$C_{14}H_{10}$)$_2$] (1). A bright-blue solution of $CoBr_2$ (0.500 g, 2.29 mmol) in THF (60 mL, −78 °C) was added to a deep-blue solution of $K[C_{14}H_{10}]$ (6.86 mmol in THF (60 mL, −78 °C). The resulting deep-pinkish-red solution was warmed slowly to room temperature, at which time it was filtered to remove KBr. To the filtrate was added 18-crown-6 (0.604 g, 2.29 mmol) in THF (20 mL). Heptane (50 mL) was added, and the volume was reduced to ~50 mL in vacuo, at which point a microcrystalline solid was observed. Et_2O (100 mL) was then added to extract the majority of $C_{14}H_{10}$ and any unreacted $[K(18\text{-crown-}6)(THF)_x][C_{14}H_{10}]$. After the slurry was filtered, the product was washed with pentane (3 × 20 mL) and dried in vacuo, yielding a brown-black microcrystalline solid (1.627 g, 83%). Elem anal. Calcd for $C_{48}H_{60}CoKO_8$: C, 66.80; H, 7.01. Found: C, 66.41; H, 6.65. Mp: 139−140 °C (dec). ^1H NMR (300 MHz, THF-d_8, 20 °C, δ, ppm): 6.86 (m, 4H, $H_{5,8}$ or $H_{6,7}$), 6.64 (m, 4H, $H_{5,8}$ or $H_{6,7}$), 6.21 (s, 4H, $H_{9,10}$), 5.05 (br, 4H, $H_{2,3}$), 3.62 (8H, THF), 3.47 (24H, 18-crown-6), 3.08 (vbr, 4H, $H_{1,4}$), 1.73 (8H, THF). ^{13}C NMR (75.5 MHz, THF-d_8, 20 °C, δ, ppm): 146.0 (s, $C_{13,14}$), 134.1 (s, $C_{11,12}$), 124.7 (d, J = 154.4 Hz, $C_{5,8}$ or $C_{6,7}$), 121.3 (d, J = 157.2 Hz, $C_{5,8}$ or $C_{6,7}$), 108.8 (d, J = 153.8 Hz, $C_{9,10}$), 75.1 (vbr, $C_{2,3}$), 71.2 (t, J = 141.4 Hz, 18-crown-6), 67.5 (quintet, THF), 55.9 (vbr, $C_{1,4}$), 25.4 (quintet, THF). Assignments were confirmed by HMQC and COSY 2D NMR experiments. The X-ray structural characterization of **1** was previously reported.[17]

[K(18-crown-6)][Co(η^4-C_4H_6)$_2$] (2). Argon was removed in vacuo from a room temperature slurry of **1** (0.500 g, 0.579 mmol) in Et_2O (35 mL) and replaced with butadiene (~1 atm, tank attached to line), with the system open to a mercury bubbler. During 5 h of stirring, the slurry became dark brown and finally pale reddish-brown. The butadiene atmosphere was replaced with argon, and the slurry was filtered. The product was washed with Et_2O (20 mL) and dried in vacuo, yielding a pale-red solid (0.248 g, 91%). Elem anal. Calcd for $C_{20}H_{36}CoKO_6$: C, 51.05; H, 7.71. Found: C, 50.81; H, 6.78. ^1H NMR (500 MHz, THF-d_8, 20 °C, δ, ppm): 3.92 (br, 4H, $H_{2,3}$), 3.64 (br, THF and 18-crown-6), 1.73 (THF), 1.02 (br, 4H, *exo*-$H_{1,4}$), −1.13 (br, 4H, *endo*-$H_{1,4}$). ^{13}C NMR (125.7 MHz, THF-d_8, 20 °C, δ, ppm): 76.2 ($C_{2,3}$), 71.2 (18-crown-6), 67.5 (quintet, THF), 25.4 (quintet, THF), 24.6 ($C_{1,4}$). Assignments were confirmed by HMQC and COSY 2D NMR experiments. X-ray-quality red blocks were grown from a pentane-layered THF solution at 0 °C (Table 1).

K[Co(PF$_3$)$_4$] (3). A clear-blue solution of $CoBr_2$ (0.750 g, 3.43 mmol) in THF (40 mL, −78 °C) was added to a deep-blue solution of $K[C_{14}H_{10}]$ (10.3 mmol) in THF (40 mL, −78 °C). The argon atmosphere was removed in vacuo and replaced with excess PF_3 (500 mL, ~1.8 g, ~21 mmol), which caused a rapid color change from dark red to yellow-brown. After warming to room temperature, the unreacted PF_3 was removed in vacuo and replaced with argon. The reaction mixture was filtered to remove KBr, and the solvent was removed in vacuo. At this point, all further operations were carried out in air. The product was extracted into water (100 mL), filtered to remove $C_{14}H_{10}$, washed with water (2 × 50 mL), and dried in vacuo. Following dissolution of the residue in acetone (50 mL), the solution was again filtered and dried in vacuo. The final product was a pale-pink solid (0.313 g, 20%). IR (ν_{PF}, Nujol mull, cm^{-1}): 801 vs br. ^{19}F NMR (282 MHz, THF, 20 °C, reference benzotrifluoride, −63.8 ppm, δ, ppm): −2.71 (d, $^1J(^{31}P^{19}F)$ = 1292 Hz, with additional hyperfine splitting present at the top of the peaks due to $^{19}F-^{59}Co$ coupling). ^{31}P NMR (25.2 MHz, THF, 20 °C, external reference 85% H_3PO_4 at 0.0 ppm, δ, ppm): 157.5 ("undectet"). ^{59}Co NMR (7.11 MHz, THF, 20 °C, external reference 0.1 M $K_3[Co(CN)_6]$ in D_2O at 0.00 ppm, δ ppm): −4081.3 (quintet, $^1J(^{31}P^{59}Co)$ = 1199 Hz, $^2J(^{19}F^{59}Co)$ = 56 Hz). The "undectet" in the ^{31}P NMR spectrum is a result of the similar $^{31}P-^{19}F$ and $^{31}P-^{59}Co$ coupling constants; peaks on either side of the "undectet" were not resolved. The product was spectroscopically identical with bona fide complex **3**.[19] No attempts to optimize this synthesis were made. X-ray-quality colorless blocks were grown by the slow evaporation of an acetone/hexane (1:1) solution at room temperature in air (Table 1).

[K(cryptand-222)][Co(P(OMe)$_3$)$_4$] (4). Excess $P(OMe)_3$ (0.5 mL, 4 mmol) in cold THF (30 mL, −78 °C) was added via cannula to a deep-red solution of $[K(\text{cryptand-}222)][Co(\eta^4\text{-}C_{14}H_{10})_2]$[17] (0.250 g, 0.288 mmol) in cold THF (50 mL, −78 °C). The reaction mixture slowly warmed to room temperature over a period of about 12 h. At about −40 °C, the color changed to a deep green. Following filtration at room temperature and the addition of heptane (30 mL), all but 30 mL of the solvent was removed in vacuo. The addition of pentane (150 mL) and subsequent washing with pentane (2 × 20 mL) provided cream-colored homogeneous **4** (0.231 g, 92% based on **1**). ^1H and ^{13}C NMR chemical shifts matched those previously reported for the identical salt.[22] $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN, 20 °C, reference 85% H_3PO_4, δ, ppm): 187.7 (octet). $^{59}Co\{H\}$ NMR (71.1 MHz, CD_3CN, 20 °C, reference 0.1 M $K_3[Co(CN)_6]$, δ, ppm): −3756 (quintet). X-ray-quality single crystals of **4** were grown as colorless blocks from THF/pentane at 0 °C for 24 h. Crystal data: monoclinic, $P2_1/c$; cell constants a = 10.6444(9) Å, b = 20.543(2) Å, c = 21.227(2) Å, and β = 98.218(2)°; V = 4593.8(7) Å^3; Z = 4; T = 173(2) K; 10513 reflections (8184 for $[I > 2\sigma(I)]$); R1 = 0.0368 $[I > 2\sigma(I)]$; wR2 = 0.0991 (all data). This crystal was a polymorph of one used in a prior structural characterization of **4**.[22]

[K(18-crown-6)(THF)$_2$][Co(P(OiPr)$_3$)$_4$] (5). Excess $P(OiPr)_3$ (0.844 g, 4.05 mmol) was added dropwise to a deep-pinkish-red solution of **1** (0.400 g, 0.463 mmol) in THF (40 mL, −78 °C). The solution was warmed slowly to room temperature, at which point it was pale yellow-brown. After removal of the solvent in vacuo, Et_2O (10 mL) was added to the gummy residue, followed by heptane (50 mL) with vigorous stirring. The product was filtered, washed with pentane (2 × 15 mL), and dried in vacuo, leaving a yellowish-white solid (0.352 g, 57%). The composition of **5** was only established by single-crystal X-ray diffraction. Colorless blocks were grown from a pentane-layered THF solution at 0 °C (Table 1). A sodium salt of the identical anion was previously described.[20]

Co(η^2-$C_{14}H_{10}$)(PMe$_3$)$_3$ (6). Excess PMe_3 was added dropwise to a deep-pinkish-red solution of **1** (0.400 g, 0.463 mmol) in THF (50 mL, −78 °C). The solution was warmed slowly to room temperature, at which point it was pale yellow-green. After removal of the solvent in vacuo, heptane (50 mL) was added with vigorous stirring and the resulting slurry was filtered. The blue filter cake was washed with pentane (30 mL) and dried in vacuo, yielding [K(18-crown-6)(THF)$_2$][C$_{14}$H$_{10}$] (0.152 g, 52%). Single crystals grown from a pentane-layered THF solution at 0° confirmed the nature of the salt via a unit cell comparison.[23] Solvent was removed from the reddish filtrate in vacuo, and the brown-violet solid was isolated (0.131 g, 61%). Single crystals of **6** were grown from an Et$_2$O solution that had been cooled to −78 °C. A unit cell comparison confirmed the nature of product **6**, which was originally prepared by a different route.[12]

[K(18-crown-6)(THF)$_2$][Co(η^4-C$_{14}$H$_{10}$)(η^4-COD)] (7). Excess 1,5-COD (0.882 g, 8.15 mmol) was added dropwise to a solution of **1** (0.500 g, 0.579 mmol) in THF (50 mL, −78 °C), and the solution was slowly warmed to room temperature, at which point it was blue-green. The solvent was removed in vacuo, and Et$_2$O (10 mL) was added to precipitate the product. Heptane (50 mL) was added with vigorous stirring, and the slurry was filtered. The product was washed with pentane (20 mL) and dried in vacuo, yielding a blue-violet solid (0.318 g, 69%). Elem anal. Calcd for C$_{42}$H$_{62}$CoKO$_8$: C, 63.62; H, 7.88. Found: C, 64.35; H, 7.82. NMR spectra are reported for the closely related compound [K(18-crown-6)][Co(η^4-C$_{14}$H$_{10}$)(η^4-COD)] (**12**), obtained from the reaction of anthracene with [K(18-crown-6)][Co(η^4-C$_{10}$H$_8$)(η^4-COD)] (**10**; see below). Metallic red-violet (to reflected light) plates were grown from a pentane-layered THF solution at 0 °C. Crystal data: triclinic, $P\bar{1}$; cell constants a = 10.2506(12) Å, b = 10.5311(12) Å, c = 21.773(3) Å, α = 79.567(2)°, β = 76.509(2)°, and γ = 64.693(2)°; V = 2057.4(4) Å^3; Z = 2; T = 173(2) K; 7244 reflections (5220 for $[I > 2\sigma(I)]$); R1 = 0.1041 $[I > 2\sigma(I)]$; wR2 = 0.2092 (all data). Severe disorder (the cobalt atom was over two positions) was present, so the corresponding cryptand-222 salt was analyzed (see below).

[K(cryptand-222)][Co(η^4C$_{14}$H$_{10}$)(η^4-COD)] (8) and [K(cryptand-222)][Co(η^4-COD)$_2$] (9). A clear-blue solution of CoBr$_2$ (0.250 g, 1.14 mmol) in THF (40 mL, −78 °C) was added to a deep-blue solution of K[C$_{14}$H$_{10}$] (3.43 mmol) and excess 1,5-COD in THF (40 mL, −78 °C). The resulting blue-green solution was warmed slowly to room temperature, at which time it was filtered to remove KBr. The solvent was removed in vacuo, and heptane (50 mL) was added. The resulting slurry was filtered, and the product was washed with pentane (2 × 25 mL) and dried in vacuo, yielding a grayish-blue-green solid (0.652 g), presumed to be [K(THF)$_x$][Co(η^4-C$_{14}$H$_{10}$)(η^4-COD)]. The treatment of 0.100 g of this sample with cryptand-222 (0.05 g) in THF, followed by layering with pentane at 0 °C, provided metallic red-violet plates of **8**, along with some yellow crystals of **9**. A more conventional route to the related salt [K(18-crown-6)][Co(η^4-COD)$_2$] (**11**), which was fully characterized, will be described later. Crystal data for **8** and **9** are shown in Table 1.

[K(18-crown-6)][Co(η^4-C$_{10}$H$_8$)(η^4-COD)] (10). Method 1: From CoBr$_2$ and 1,3-Cyclooctadiene. A clear-blue solution of CoBr$_2$ (0.500 g, 2.29 mmol) and 1,3-COD (0.867 g, 8.03 mmol) in THF (40 mL, −78 °C) was added to a deep-green solution of K[C$_{10}$H$_8$] (6.86 mmol) in THF (40 mL, −78 °C). The resulting reddish-brown solution was warmed slowly to room temperature, at which time it was filtered to remove KBr. The solvent was removed in vacuo, and Et$_2$O (50 mL) was added to extract the product. The reaction mixture was filtered, and 18-crown-6 (0.604 g, 2.29 mmol) in Et$_2$O (20 mL) was added to the filtrate, at which point a bright-red microcrystalline solid formed. The slurry was filtered, and the product was washed with Et$_2$O (20 mL) and dried in vacuo, yielding a magenta microcrystalline solid (0.671 g, 49%). ^{1}H NMR spectra on the bulk sample showed 0.5 equiv of THF per formula unit. Elem anal. Calcd for C$_{32}$H$_{48}$CoKO$_{6.5}$: C, 60.55; H, 7.62. Found: C, 61.15; H, 7.61. Mp: 124−126 °C (dec). ^{1}H NMR (300 MHz THF-d_8, 20 °C, δ, ppm): 5.49 (m, 4H, Np, H$_{5,6,7,8}$), 4.91 (s, 2H, Np, H$_{2,3}$), 4.13 (br, 2H, COD, C*H*), 3.61 (18-crown-6, THF), 2.83 (m, 2H, Np, H$_{1,4}$), 2.44 (m, vbr, 2H, COD, C*H*$_2$), 1.94 (m, vbr, 2H, COD, C*H*$_2$), 1.75 (m, vbr, 2H, COD, C*H*$_2$), 1.73 (THF), 1.25 (m, vbr, 2H, COD, C*H*$_2$), 0.94 (br, 2H, COD, C*H*). ^{13}C NMR (75.5, MHz, THF-d_8, 20 °C, δ, ppm): 149.2 (s, Np, C$_{9,10}$), 118.4 (d, J = 148.0 Hz, Np, C$_{5,8}$ or C$_{6,7}$), 114.7 (d, J = 152.6 Hz, Np, C$_{5,8}$ or C$_{6,7}$), 84.8 (d, J = 164.1 Hz, Np, C$_{2,3}$), 71.3 (t, J = 141.6 Hz, 18-crown-6), 69.9 (d, J = 163.6 Hz, COD, CH), 67.4 (quintet, THF), 60.2 (d, J = 153.8 Hz, Np, C$_{1,4}$), 54.3 (d, J = 144.5 Hz, COD, CH), 33.4 (t, J = 122.4 Hz, COD, CH$_2$), 25.4 (quintet, THF). Assignments were confirmed by HMQC and COSY 2D NMR experiments. The X-ray structural characterization of **10** was previously reported.[18] Also, a new polymorph of **10** was obtained as red-brown plates. Crystal data: triclinic, $P\bar{1}$; cell constants a = 10.040(2) Å, b = 10.195(2) Å, c = 30.618(5) Å, α = 82.405(3)°, β = 88.299(3)°, and γ = 68.125(3)°; V = 2882.2(9) Å^3; Z = 4; T = 173(2) K; 13089 reflections (9905 for $[I > 2\sigma(I)]$); R1 = 0.0491 $[I > 2\sigma(I)]$; wR2 = 0.1301 (all data). This crystal structure was of inferior quality and will not be described further herein.[24]

Method 2: From CoBr$_2$ and 1,5-Cyclooctadiene. The above procedure was followed, except exactly 1 equiv of 1,5-COD was added in lieu of 1,3-COD (final yields generally around 20%). This product was spectroscopically identical with bona fide complex **10** obtained from 1,3-COD.

Method 3: From Cobaltocene and 1,5-Cyclooctadiene. A solution of C$_{10}$H$_8$ (0.678 g, 5.29 mmol) and 1,5-COD (0.572 g, 5.29 mmol) in THF (40 mL, −78 °C) was transferred to a precooled flask (in a −78 °C bath) containing freshly cut potassium metal (0.620 g, 15.9 mmol) and cobaltocene (1.000 g, 5.29 mmol). The reaction mixture warmed slowly to room temperature with the following color observations: at −78 °C, red-orange; at −60 °C, deep green; at −20 °C, bright red. The solution was recooled to −78 °C, and the stirring was stopped for 1 h to allow deposition of KC$_5$H$_5$. The solution was filtered through a jacketed frit[25] and maintained below −60 °C, and 18-crown-6 (1.398 g, 5.29 mmol) in THF (20 mL) was added to the filtrate. After the solvent was removed in vacuo, Et$_2$O (50 mL) was added and the resulting slurry was filtered. The product was washed with Et$_2$O (20 mL) and dried in vacuo (2.877 g, 91%). Except for a small resonance due to C$_5$H$_5^-$, the NMR spectra for **10** prepared by method 3 were identical with those of samples prepared by methods 1 and 2. The minor Cp impurity was characterized by X-ray diffraction to be a double salt of composition [K(18-crown-6)(THF)$_2$][{K(18-crown-6)}$_2$(C$_5$H$_5$)][Co(η^4-C$_{10}$H$_8$)(η^4-COD)]$_2$. Thus, the unit cell contains equal amounts of a normal [K(18-crown-6)(THF)$_2$)]$^+$ cation and another cation consisting of one C$_5$H$_5^-$ anion sandwiched between two [K(18-crown-6)]$^+$ cations. (The latter cation has recently been observed and structurally characterized in a salt containing [Co(COD)$_2$]$^-$.[27]) Dark-red-orange blocks were grown from a pentane-layered THF solution at 0 °C. Crystal data: triclinic, $P\bar{1}$; cell constants a = 9.7377(8) Å, b = 10.0468(8) Å, c = 22.625(2) Å, α = 85.758(1)°, β = 79.304(1)°, and γ = 87.193(1)°; V = 2167.6(3) Å^3, Z = 2; T = 173(2) K; 9840 reflections (7569 for $[I > 2\sigma(I)]$); R1 = 0.0369 $[I > 2\sigma(I)]$; wR2 = 0.0887 (all data).

[K(18-crown-6)][Co(η^4-COD)$_2$] (11). Method 1: From 10. Excess 1,5-COD was added to a slurry of **10** (0.300 g, 0.501 mmol) in Et$_2$O (35 mL) at 20 °C. Within minutes, the reddish color turned pale yellow. After stirring for 4 h, the slurry was filtered, and the product was washed with Et$_2$O (20 mL) and dried in vacuo, yielding a light-yellow powder (0.247 g, 85%). Elem anal. Calcd for KCoC$_{28}$H$_{48}$O$_6$: C, 58.11; H, 8.36. Found: C, 57.82; H, 8.62. ^{1}H NMR (300 MHz, THF-d_8, 20C, δ, ppm): 3.63 (s, 24H, 18-crown-6), 2.20 (br, 8H, C*H*$_2$), 1.87 (br, 4H, C*H*), 1.73 (THF). ^{13}C NMR (75.4 MHz, THF-d_8, 20 °C, δ, ppm): 71.3 (t, J = 141.7 Hz, 18-crown-6), 69.7 (d, J = 156.6 Hz, CH), 67.5 (quintet, THF), 34.7 (t, J = 121.2 Hz, CH$_2$), 25.4 (quintet, THF). X-ray-quality yellow blocks were grown from a pentane-layered THF solution at 0 °C. Crystal data: triclinic, $P\bar{1}$; cell constants a = 9.862(1) Å, b = 10.114(1) Å, c = 16.143(2) Å, α = 83.911(2)°, β = 81.953(2)°, and γ = 64.969(2)°; V = 1442.7(3) Å^3; Z = 2; T = 173(2) K; 6538 reflections (5827 for $[I > 2\sigma(I)]$); R1 = 0.0254 $[I > 2\sigma(I)]$; wR2 = 0.0634 (all data).

Method 2: From Cobaltocene. The published procedure was followed for the synthesis of [K(THF)$_{0.5}$][Co(COD)$_2$][26] from 1.000 g (5.29 mmol) of CoCp$_2$, *except* 1 equiv of 18-crown-6 was added (yield 2.863 g, 94%). The ^{1}H NMR spectrum showed a slight C$_5$H$_5^-$ impurity but was otherwise identical with that of bona fide complex **11**. X-ray-quality yellow blocks of **11** were obtained by the same procedure as that shown in method 1. A few yellow plates also formed.

X-ray diffraction data established that these were the sources of $C_5H_5^-$ and had composition $[\{K(18\text{-crown-}6)\}_2(C_5H_5)][Co(COD)_2]\cdot 3THF$. These crystals showed structural units essentially identical with those recently reported for an otherwise analogous bis(tetrahydrofuran) solvate.[27] Crystal data for the tris(tetrahydrofuran) solvate: monoclinic, $P2_1/c$; cell constants a = 9.3632(12) Å, b = 25.726(3) Å, c = 25.887(3) Å, and β = 90.971(4)°; V = 6234.6(13) Å^3; Z = 4, T = 173(2) K.

Method 3: From $CoBr_2$. A clear-blue solution of $CoBr_2$ (0.500 g, 2.29 mmol) in THF (60 mL, −78 °C) was added to a deep-green solution of K[$C_{10}H_8$] (6.86 mmol) and excess 1,5-COD in THF (60 mL, −78 °C). The resulting reddish-yellow solution was warmed slowly to room temperature, at which time it was filtered to remove KBr. To the filtrate was added 18-crown-6 (0.604 g, 2.29 mmol) in THF (20 mL). The solvent was removed in vacuo, and Et_2O (50 mL) was added. As the product was stirred in Et_2O, the reddish color faded. The resulting cream-colored slurry was filtered, and the product was washed with Et_2O (2 × 20 mL) and dried in vacuo, yielding a pale-yellowish-tan solid (1.019 g, 77%). Elem anal. Calcd for $KCoC_{28}H_{48}O_6$: C, 58.11; H, 8.36. Found: C, 57.43; H, 8.10. *Products made by this method contain paramagnetic impurities that cause NMR spectral peaks to be too broad for interpretation.* Removal of the paramagnetic component from **11** proved to be very difficult without significantly reducing the yield of product. However, the slightly impure **11** prepared by this route is a useful source of $[Co(COD)_2]^-$ in chemical reactions.

[K(18-crown-6)][Co(η^4-$C_{14}H_{10}$)(η^4-COD)] **(12)**. THF (30 mL) was added to a flask containing **10** (0.250 g, 0.418 mmol) and $C_{14}H_{10}$ (0.095 g, 0.533 mmol) at room temperature. The solution turned blue-green almost immediately and was stirred for 1 h. After the solvent was removed in vacuo and Et_2O (50 mL) was added, the resulting slurry was filtered. The product was dried in vacuo, yielding a deep-blue solid (0.217 g, 80%). Products crystallized from Et_2O contain no cocrystallized THF molecules. Mp: ~120 °C (slumps). ^{1}H NMR (300 MHz, THF-d_8, 20 °C, δ, ppm): 6.31 (m, 2H, An, $H_{5,8}$ or $H_{6,7}$), 6.26 (m, 2H, An, $H_{5,8}$ or $H_{6,7}$), 5.27 (s, 2H, An, $H_{9,10}$), 4.68 (m, 2H, An, $H_{2,3}$), 3.74 (br, 2H, COD, CH), 3.58 (THF), 3.55 (s, 24H, 18-crown-6), 3.43 (m, 2H, An, $H_{1,4}$), 2.49 (br, 2H, COD, CH_2), 1.89 (br, 4H, COD, CH_2), 1.73 (THF), 1.32 (br, 2H, COD, CH_2), 1.12 (br, 2H, COD, CH). ^{13}C NMR (75.5 MHz, THF-d_8, 20 °C, δ, ppm): 146.7 (s, An, $C_{13,14}$), 136.1 (s, An, $C_{11,12}$), 122.9 (d, J = 153.8 Hz, An, $C_{5,8}$ or $_{6,7}$), 120.5 (d, J = 163.5 Hz, An, $C_{5,8}$ or $C_{6,7}$), 104.8 (d, J = 151.5 Hz, An, $C_{9,10}$), 84.2 (d, J = 164.7 Hz, An, $C_{2,3}$), 74.6 (d, J = 150.9 Hz, COD CH), 71.2 (t, J = 141.6 Hz, 18-crown-6), 67.5 (quintet, THF), 63.9 (d, J = 157.8 Hz, An, $C_{1,4}$), 54.4 (d, J = 152.6 Hz, COD, CH), 33.3 (t, J = 117.2 Hz, COD, CH_2), 25.4 (quintet, THF). Assignments were confirmed by HMQC and COSY 2D NMR experiments. Satisfactory elemental analyses were obtained on the closely related **7** vide supra. Single-crystal X-ray crystallography was carried out on the analogous [K(cryptand-222)]salt, **8** (Table 1).

[K(18-crown-6)][Co(η^4-COD)(η^4-C_4H_6)] **(13)**. Argon was removed in vacuo from a room temperature slurry of **10** (0.500 g, 0.835 mmol) in Et_2O (40 mL) and replaced with butadiene (~1 atm, tank attached to line), with the system open to a mercury bubbler. *This reaction generates a lot of heat; therefore, a water bath is recommended for cooling!* The reaction mixture, which turned orange almost immediately, was stirred for 2 h. The butadiene atmosphere was replaced with argon, and the slurry was filtered. The product was washed with Et_2O (20 mL) and dried in vacuo, yielding a bright-orange solid (0.383 g, 87%). Elem anal. Calcd for $KCoC_{24}H_{42}O_6$: C, 54.95; H, 8.07; Found: C, 54.89; H, 8.99. Mp 135−136 °C (dec). ^{1}H NMR (300 MHz, THF-d_8, 20 °C, δ, ppm): 3.63 (18-crown-6), 3.58 (THF), 3.55 (m, 2H, But, $H_{2,3}$), 2.76 (s, br, 4H, COD, CH), 2.14 (m, br, 4H, COD, CH_2), 1.73 (THF), 1.63 (m, 4H, COD, CH_2), 1.53 (m, 2H, But, *exo*-$H_{1,4}$), −0.99 (m, 2H, But, *endo*-$H_{1,4}$). ^{13}C NMR (75.5 MHz, THF-d_8, 20 °C, δ, ppm); 82.4 (d, J = 160.7 Hz, But, $C_{2,3}$), 71.2 (t, J = 141.6 Hz, 18-crown-6), 67.5 (quintet, THF), 57.8 (d, J = 148.5 Hz, COD, CH), 36.9 (splitting unresolved, But, $C_{1,4}$), 34.7 (t, J = 121.5 Hz, COD, CH_2), 25.4 (quintet, THF). Assignments were confirmed by HMQC and COSY 2D NMR experiments. Suitable orange blocks were grown from a pentane-layered THF solution at 0 °C. Crystal data: triclinic, $P\bar{1}$; cell constants a = 8.6632(7) Å, b = 10.9612(9) Å, c = 14.924(1) Å, α = 90.252(1)°, β = 93.574(1)°, and γ = 112.826(1)°; V = 1302.3(2) Å^3; Z = 2; T = 173(2) K; 5670 reflections (4613 for $[I > 2\sigma(I)]$); R1 = 0.0392 $[I > 2\sigma(I)]$; wR2 = 0.0988 (all data). Owing to disorder of the butadiene ligand, the structure of anion **13** will not be discussed herein.[24] However, it is extremely similar to that of **14** and unambiguously confirms its nature.

[K(18-crown-6)][Co(η^4-COD)(2,3-Me_2-C_4H_4)] **(14)**. A solution of 2,3-dimethyl-1,3-butadiene (Dmbd; 0.029 g, 0.356 mmol) in THF (15 mL) was added to a solution of **10** (0.213 g, 0.356 mmol) in THF (25 mL) at room temperature. As it was stirred for 12 h, the color changed from bright red to bright red-orange. After the solvent was removed in vacuo and Et_2O (30 mL) was added, the resulting slurry was filtered. The product was dried in vacuo, yielding a yellow-orange solid (0.141 g, 72%). ^{1}H NMR spectra on the bulk sample showed 0.5 equiv of THF per formula unit. Elem anal. Calcd for $KCoC_{28}H_{50}O_{6.5}$: C, 57.12; H, 8.56. Found: C, 56.91; H, 9.52. ^{1}H NMR (300 MHz, THF-d_8, 20 °C, δ, ppm): 3.63 (18-crown-6), 3.58 (THF), 2.45 (br, 4H, COD, CH), 2.13 (m, br, 4H, COD, CH_2), 1.73 (THF), 1.68 (s, 2H, COD, CH_2), 1.66 (s, 2H, COD, CH_2), 1.58 (s, 6H, But, CH_3), 1.29 (s, 2H, But, *exo*-$H_{1,4}$), −1.22 (s, 2H, But, *endo*-$H_{1,4}$. ^{13}C NMR (75.5 MHz, THF-d_8, 20 °C, δ, ppm): 87.1 (s, But, $C_{2,3}$), 71.3 (t, J = 141.6 Hz, 18-crown-6), 67.5 (quintet, THF), 59.3 (d, J = 147.9 Hz, COD, CH), 41.0 (t, J = 148.0 Hz, But, $C_{1,4}$), 34.8 (t, J = 120.9 Hz, COD, CH_2), 25.4 (quintet, THF), 19.6 (q, J = 123.4 Hz, But, CH_3). Assignments were confirmed by HMQC and COSY 2D NMR experiments. Suitable orange blocks were grown from a pentane-layered THF solution at 0 °C (Table 1).

[K(18-crown-6)][Co(η^4-COD)(bipy)] **(15)**. THF (20 mL) was added to a flask containing bipy (0.261 g, 1.67 mmol) and **10** (0.500 g, 0.835 mmol) at room temperature. The initial bright-red solution became blue within seconds and was stirred for 1 h. The solvent was removed in vacuo, and pentane (40 mL) was added. The resulting slurry was filtered, and the product was washed with pentane (20 mL) and dried in vacuo, yielding a dark-purple solid (0.485 g, 93%). Elem anal. Calcd for $KCoC_{30}H_{44}N_2O_6$: C, 57.49; H, 7.08; N 4.47. Found: C, 57.32; H, 7.09; N, 4.97. ^{1}H NMR (300 MHz, THF-d_8, 20 °C, 15 mg in 0.75 mL, external reference $SiMe_4$ at 0.00 ppm, δ ppm): 10.81 (d, 2H, bipy, H_1), 6.78 (d, 2H, bipy, H_4), 6.42 (m, 2H, bipy, H_2), 6.30 (m, 2H, bipy, H_3), 3.31 (s, THF), 3.00 (s, 18-crown-6), 2.43 (m, 4H, COD, CH_2), 1.86 (m, 4H, COD, CH), 1.46 (s, THF), 0.69 (m, 4H, COD, CH_2), ^{13}C NMR (75.5 MHz, THF-d_8, 20 °C, δ ppm): 156.2 (d, J = 170.4 Hz, bipy), 136.3 (s, bipy), 120.1 (d, J = 153.8 Hz, bipy), 114.3 (d, J = 159.5 Hz, bipy), 109.3 (d, J = 158.4 Hz, bipy), 70.2 (t, J = 141.7 Hz, 18-crown-6), 66.7 (quintet, THF), 56.5 (d, J = 145.7 Hz, COD, CH), 337 (t, J = 119.7 Hz, COD, CH_2), 24.6 (quintet, THF). Assignments were confirmed by HMQC and COSY 2D NMR experiments. X-ray-quality red-violet plates were grown from a pentane-layered THF solution at 0 °C (Table 1).

[K(18-crown-6)(THF)$_2$][Co(CNtBu)$_4$] **(16)**. A solution of CN*t*Bu (0.278 g, 3.34 mmol) in THF (~15 mL, −78 °C) was added to a deep-bright-red solution of **10** (0.500 g, 0.835 mmol) in THF (30 mL, −78 °C). As the reaction mixture warmed, the solution became orange-red. Upon solvent reduction to ~20 mL, orange crystals precipitated. The contents of flask were layered with pentane (80 mL) and placed in the dark at −6 °C for 12 h. The solvent was carefully removed via cannula, and the orange crystals were dried in vacuo, during which time they became a yellow powder (0.304 g, 43%). The product appeared to be stable in a THF solution (below 0 °C), but the isolated solid became reddish-brown within hours at room temperature under argon [the IR spectrum of which showed no ν_{CN} absorptions due to anion **16**]. IR (ν_{CN}, THF, cm^{-1}): 1832 sh, 1778 vs br. IR (ν_{CN}, Nujol mull, cm^{-1}): 1823 sh, 1764 vs br, 1735 sh. ^{1}H NMR (300 MHz, THF-d_8, 20 °C, δ, ppm): 3.73 (br, 24H, 18-crown-6), 3.58 (s, 8H, THF), 1.73 (s, 8H, THF), 1.27 (s, 36H, CH_3). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 20 °C, δ, ppm): 71.4 (18-crown-6), 67.4 (THF), 54.1 ($CNC(CH_3)_3$), 32.6 ($CNC(CH_3)_3$), 25.4 (THF). The resonance for the metal-coordinated carbon atom could not be resolved. No elemental analyses were obtained for this

Table 1. Crystal Data Summary for Structures 2, 3, 5, 8, 9, and 14−16

	2	3	5	8	9	14	15	16
formula	$C_{20}H_{36}CoKO_6$	$CoF_{12}KP_4$	$C_{56}H_{124}CoKO_{20}P_4$	$C_{40}H_{58}CoKN_2O_6$	$C_{34}H_{60}CoKN_2O_6$	$C_{26}H_{46}CoKO_6$	$C_{30}H_{44}CoKN_2O_6$	$C_{44}H_{84}CoKN_4O_9$
fw	470.52	449.91	1339.46	760.91	690.87	552.66	626.70	911.18
T (K)	173(2)	223(2)	173(2)	173(2)	173(2)	173(2)	173(2)	223(2)
cryst syst	monoclinic	orthorhombic	monoclinic	triclinic	orthorhombic	triclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$Pnma$	$P2_1/c$	$P\bar{1}$	$Pccn$	$P\bar{1}$	$P2_1/n$	$Pnnm$
a (Å)	11.1122(9)	12.625(1)	24.2720(17)	12.1042(10)	17.889(2)	8.764(1)	9.776(1)	18.5263(14)
b (Å)	13.5440(11)	8.5070(7)	17.8466(12)	13.1580(11)	11.8653(13)	11.2048(13)	19.690(2)	25.4164(19)
c (Å)	15.2768(13)	10.8490(9)	17.2666(12)	14.4109(13)	16.562(2)	15.863(2)	16.0969(16)	11.4747(8)
α (deg)	90	90	90	108.664(2)	90	81.571(2)	90	90
β (deg)	94.778(2)	90	90.545(1)	107.142(2)	90	79.646(2)	99.094(2)	90
γ (deg)	90	90	90	106.915(2)	90	67.214(2)	90	90
V (Å^3)	2291.2(3)	1165.22(16)	7479.1(9)	1880.3(3)	3515.4(7)	1407.7(3)	3059.7(5)	5403.1(7)
Z	4	4	4	2	4	2	4	4
ρ_{calcd} (g cm^{-3})	1.364	2.565	1.190	1.344	1.305	1.304	1.360	1.120
μ (mm^{-1})	0.961	2.512	0.432	0.616	0.651	0.793	0.741	0.443
color, shape	red, block	colorless, block	colorless, block	red-violet, plate	yellow, block	orange, block	red-violet, plate	orange, block
reflns collected	19531	13136	66211	20765	24924	15563	32445	51512
indep reflns	5182	1428	17158	8487	4024	6375	7011	5041
R_{int}[a]	0.0367	0.0221	0.0660	0.0355	0.0430	0.0310	0.0475	0.0273
reflns obsd	3920	1336	11159	6724	3185	4894	5339	4134
no. of param	301	106	815	483	213	357	377	320
GOF[b] on F^2	1.049	1.088	1.023	1.022	1.024	1.028	1.034	1.065
R1 [$I > 2\sigma(I)$][c]	0.0357	0.0242	0.0493	0.0355	0.0424	0.0398	0.0473	0.0541
wR2[d]	0.0816	0.0555	0.1375	0.0955	0.0815	0.1024	0.0873	0.1516

[a] $R_{int} = \sum|F_o^2 - \langle F_o^2\rangle|/\sum F_o^2$. [b] GOF = $S = [\sum w(F_o^2 - F_c^2)^2/(m - n)]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = {}^1/_3 \max(0, F_o^2) + {}^2/_3 F_c^2$, m = number of independent reflections, and n = number of parameters. [c] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^2]^{1/2}$.

compound because of its thermal instability at room temperature. X-ray-quality orange blocks of **16** were grown from a pentane-layered solution at 0 °C (Table 1).

X-ray Crystallographic Data Collection and Refinement of the Structures. Single crystals were placed onto the tip of a 0.1-mm-diameter glass capillary and mounted on a Bruker SMART Platform diffractometer, equipped with a CCD area detector, for data collection at 173(2) K, or 223(2) K, for **16**. The data collection was carried out using Mo Kα radiation (graphite monochromator). The intensity data were corrected for absorption (*SADABS*).[93] Final cell constants were obtained from least-squares fits of ~4000 reflections. The structures were solved using *SHELXS-97* and refined using *SHELXL-97*.[94] A direct methods solution was calculated that provided most non-hydrogen atoms from the *E* map. Full-matrix least-squares/difference Fourier cycles were performed to locate the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. When possible, hydrogen atoms on metal-coordinated carbon atoms were found from the difference Fourier map, and their positional and isotropic displacement parameters were refined independently from those of their bonded carbon atoms. All other hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Crystallographic data are listed in Table 1. More information on the data collection and refinement of individual structures is included in the Supporting Information.

RESULTS AND DISCUSSION

Alkali-Metal Polyarene Reductions of Cobalt Halides and Cobaltocene. Reactions of cobalt halides and other transition-metal halides with alkali-metal polyarenes[28] were first examined over 70 years ago and found to afford highly reactive metal powders. Thus, Scott and Walker disclosed in a 1939 duPont patent this basic reaction,[29] which, as Seyferth stated in a Cover Essay,[30] "was rediscovered for cobalt in 1955 by Chu and Friel,[31] and rediscovered once again by Rieke et al in 1981,[32] who have used it to prepare what they call 'Rieke metal powders'...." Also, reduction of $CoCl_2$ or $CoBr_2$ by sodium naphthalene in THF at room temperature under an atmosphere of carbon monoxide was established by IR spectra to afford solutions of $Na[Co(CO)_4]$, albeit no yields were reported for either halide precursor.[33−35] We investigated the reactions of anhydrous $CoCl_2$ with alkali-metal polyarenes under a variety of conditions and solvents and found this halide worked poorly in attempts to obtain labile Co^- species; i.e., invariably pyrophoric cobalt metal was the major product. The poor solubility of $CoCl_2$ in THF, DME, and similar ether solvents appears to prevent facile coordination of polyarenes to cobalt during reduction and thereby promotes the formation of cobalt metal, in what appears to be mainly a heterogeneous redox reaction. In contrast, when we switched to $CoBr_2$, which has a much higher solubility in ethers, our fortunes improved dramatically. In this respect, $CoBr_2$ is similar to cobaltocene, which also has good solubility in these solvents. However, reductions of cobaltocene often provide higher yields of analogous products than those of $CoBr_2$, such as $[Co(CO)_4]^-$, owing to the much greater ability of Cp^-, compared to the bromide ion, to stabilize labile cobalt(I) and cobalt(0) intermediates. Effectively, the critical difference between Cp^- and Br^- is that the former ligand binds more tightly to low-valent cobalt and is thereby a poorer leaving group in these reductions. Thus, Geiger discovered the remarkable stability of the cobaltocene anion, $[CoCp_2]^-$, in DME at 20 °C, in which it survives "for at least 30 sec,"[36] but there is no evidence for the existence of "$[CoBr_2]^-$" under similar conditions. Jonas has emphasized the important role of the Cp group as a "support ligand" in metallocene reductions.[6a] Although economics is a major reason for favoring $CoBr_2$ over cobaltocene as the precursor to the low-valent cobalt complexes presented herein,[37] removal of Cp^- from reduction products of cobaltocene can sometimes be problematic, as others have also discovered.[27] However, in the case of $CoBr_2$ reductions, very finely divided, and perhaps colloidal, cobalt metal appears to form. This paramagnetic impurity can be difficult to remove entirely from certain products, e.g., $[Co(COD)_2]^-$; see the Experimental Section.

Synthesis of 1. The addition of bright-blue solutions of anhydrous $CoBr_2$ in THF at −78 °C to deep-blue solutions of 3.0 equiv of KAn, potassium anthracene, in THF at −78 °C resulted within minutes in the formation of deep-red solutions of highly air-sensitive $[Co(\eta\text{-An})_2]^-$. To obtain well-defined and reproducibly solvated potassium salts, the solutions were treated with effective potassium ion complexants, including 18-crown-6, cryptand-222,[38] and triglyme.[38] In this fashion, the respective $[K(18\text{-crown-6})(THF)_2]^+$, $[K(cryptand\text{-}222)]^+$, and $[K(triglyme)_2]^+$ salts of $[Co(\eta\text{-An})_2]^-$ were obtained as thermally stable (at 20 °C), deep-brown-black to red-black microcrystals in 60−80% isolated yields, eq 1, where L = 18-crown-6 ($x = 2$), cryptand-222 ($x = 0$), and 2(triglyme) ($x = 0$).

$$CoBr_2 + 3KC_{14}H_{10} \xrightarrow[-78\ °C]{THF} \xrightarrow[-2KBr]{L} [KL(THF)_x][Co(C_{14}H_{10})_2] + C_{14}H_{10} \qquad (1)$$

All were characterized by single-crystal X-ray structure analyses and shown to contain essentially identical anions. The latter are well-separated from counterions, which are unexceptional, including the previously known $[K(triglyme)_2]^+$ cation, wherein the potassium shows normal 8-fold oxygen coordination.[39,40] Details of the structure of anion **1**, as well as its NMR spectra in solution, have been discussed previously.[17] The important conclusions are that the anion is the anticipated 18-electron species with distorted tetrahedral geometry about the metal, appropriate for d^{10} Co^{I-}. Also its structure appears to be identical in solution and the solid state and is independent of the counterions examined to date.

The same reduction, as shown in eq 1, was also carried out in THF without the addition of an effective potassium ion complexant. X-ray-quality red-black blocks of product were grown from a pentane-layered THF solution at 0 °C and were identified as $[K(THF)_4][Co(\eta^4\text{-}C_{10}H_8)_2]$,[41] which contained the identical cobaltate present in **1**. Unfortunately, all attempts to isolate a pure bulk sample have failed. Removal of THF in vacuo resulted in a solid that was gray-black in color, suggesting partial decomposition and the formation of cobalt metal. Elemental analysis invariably had low carbon values, and NMR spectra of different samples always showed ^1H NMR resonances for uncoordinated $C_{14}H_{10}$.

In view of Jonas' success in obtaining other cobalt(1−) species from cobaltocene, the synthesis of **1** from this reagent was examined. Thus, $CoCp_2$ was reduced by the same procedure as that employed in the synthesis of **1**, except a low-temperature (−78 °C) filtration was employed to remove KCp, which is poorly soluble in THF, especially at low temperature. The addition of 18-crown-6, followed by a standard workup, provided 62% yield of a homogeneous brown solid, established by single-crystal X-ray crystallography to be $[\{K(18\text{-crown-6})\}_2(\mu\text{-}C_5H_5)][Co(\eta^4\text{-}C_{14}H_{10})_2]\cdot 2.5THF$.[42] The asymmetric unit contained a normal anion, essentially identical with that present in the prior [K(18-

crown-6)(THF)$_2$]$^+$ salt, **1**,[17] but, unexpectedly, the counterion was a previously described "sandwich cation",[27] consisting of two normal [K(18-crown-6)]$^+$ units symmetrically flanking a cyclopentadienyl anion. In the above synthesis, only 1 h at −78 °C was allowed for KCp deposition from THF vide infra. As a result, significant amounts of KCp were still present in the filtrate, which was then treated with 18-crown-6. Thus, mixtures of [K(18-crown-6)],$^+$ cyclopentadienyl anions, and other large anions, X$^-$, often combine to form this or related sandwich cations, which appear to be effective "thermodynamic sinks" in the solid state. To the best of our knowledge, the first example of an analogous sandwich counterion, [{K(18-crown-6)}$_2$(*t*BuCp)]$^+$, was discovered nearly 20 years ago in an unsuccessful attempt to isolate a simple [K(18-crown-6)]$^+$ salt of [(*t*BuCp)$_3$UH]$^-$ in the presence of K(*t*BuCp).[43]

Synthesis and Structural Characterization of 2. Bis(butadiene)cobaltate(1−) is significant as the initial example of an isolable late-transition-metal homoleptic 1,3-butadiene complex, the synthesis of which followed the discovery of the first complexes of the type M(C$_4$H$_6$)$_3$, where M = Mo and W.[44] The cobaltate was originally obtained by the reaction of [Co(COD)$_2$]$^-$ or [Co(C$_2$H$_4$)$_4$]$^-$ with 1,3-butadiene, as mentioned only in review articles.[6] However, details of its synthesis/isolation have not been published in the primary literature.[45] Although Cloke and co-workers reported that [Co(η-C$_4$H$_4$*t*Bu$_2$)$_2$]^z, with z = 0 and 1−, containing the 1,4-di-*tert*-butyl-1,3-butadiene ligand, were the first homoleptic butadiene complexes of cobalt,[46] evidence for the prior existence of [Co(η-C$_4$H$_6$)$_2$]$^-$ was the presentation of its ^{13}C NMR spectrum, cited as "unpublished results", for the respective [Li(TMEDA)]$^+$ salt, in a review article.[47]

The treatment of dark red **1** with excess 1,3-butadiene in Et$_2$O at 20 °C over a 5 h period resulted in the formation of a pale-red solid **2**, isolated in 91% yield as a satisfactorily pure material. The previously unreported ^{1}H NMR spectrum of [Co(η-C$_4$H$_6$)$_2$]$^-$ at 20 °C shows the expected three resonances of equal intensities at −1.13, 1.02, and 3.92 ppm (in THF-d_8), assigned as the endo- and exo-terminal hydrogen atoms (H$_{1,4}$) and the internal hydrogen atoms (H$_{2,3}$), respectively. This pattern is very similar to those previously reported for [M(η-C$_4$H$_6$)$_3$]^z, with z = 0, M = Mo and W,[48] and z = 1−, M = Nb and Ta.[49] Also, the observed ^{13}C{^{1}H} NMR spectrum of anion **2** is in good agreement with the one previously reported for [Li(TMEDA)][Co(η-C$_4$H$_6$)$_2$].[47]

Confirmation of the nature of anion **2** was provided by a single-crystal X-ray structure (Figure 1). The asymmetric unit in **2** is comprised of a normal [K(18-crown-6)]$^+$ cation of approximately D_{3d} symmetry.[50] Axial positions of the macrocyclic cations are occupied by equivalent anions in an infinite linear alternating chain of cation (potassium) and anion (cobalt), a common structural motif in unsolvated [K(18-crown-6)]$^+$ salts.[51] The closest potassium-anion contacts are with the internal C$_{2,3}$ cations of the butadiene ligands, with K−C distances of 4.54 and 5.42 Å, respectively. By comparison, in [K(18-crown-6)][η^5-C$_5$H$_5$], the mean K−C(C$_5$H$_5$) distance is significantly shorter, 3.06(7) Å.[51b] Because the [K(18-crown-6)]$^+$ structure in **2** is not significantly altered by the anion and the latter has C−C bond lengths that are statistically identical with corresponding ones present in **1**, we conclude that the anionic unit in **2** is largely unperturbed by the cation in the crystalline lattice.

Anion **2** contains two structurally equivalent and discrete η^4-1,3-butadiene groups bound to the cobalt. The environment about the metal is distorted tetrahedral, with a twist angle of 62.1°,[95] similar to the corresponding value of 62.4° present in **1**.[17] The Co−C and C−C bond distances in anion **2** follow the usual pattern observed in other late-transition-metal 1,3-butadiene complexes, in which metal-to-π*(diene) back-bonding is relatively weak. For example, the average outer and inner Co−C distances in anion **2**, 2.05(1) and 1.97(1) Å, respectively, show the same long−short−short−long pattern as that present in the related 17-electron [Fe(η-C$_4$H$_6$)$_2$]$^-$, for which corresponding Fe−C distances are 2.08(2) and 2.02(1) Å,[52] respectively. In contrast, analogous average Ta−C distances in [Ta(η-C$_4$H$_6$)$_3$]$^-$, i.e., 2.30(1) and 2.406(9) Å, respectively,[49] exhibit the reverse short−long−long−short pattern indicative of significant metal-to-π*(diene) back-bonding, often observed in early-transition-metal 1,3-butadiene complexes. This back-bonding interaction imparts substantial metallacyclopentene character to the butadiene−tantalum bonding and is evident in the pronounced long−short−long pattern in the average C−C distances of the butadiene groups [i.e., C1−C2, 1.44(1) Å; C2−C3, 1.36(1) Å] in the tantalum complex.[49] However, the corresponding average butadiene C−C distances in anion **2**, 1.42(1) and 1.407(4) Å, and [Fe(η-C$_4$H$_6$)$_2$]$^-$, 1.422(5) and 1.412(4) Å, show no significant variations and are statistically identical with analogous values present in Fe(η-C$_4$H$_6$)(CO)$_3$, 1.419(1) and 1.414(2) Å, respectively.[53] On the basis of these structural data, anion **2** is regarded as a normal metal butadiene π complex formally containing d^{10} Co^{I-}.

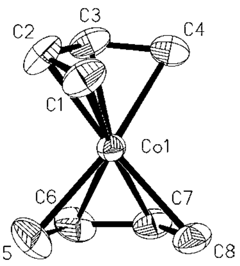

Figure 1. Molecular structure of anion **2**. Thermal ellipsoids are set at the 50% probability level, with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Co−C1 2.043(2), Co−C2 1.966(2), Co−C3 1.983(2), Co−C4 2.059(2), Co−C5 2.045(3), Co−C6 1.986(2), Co−C7 1.964(2), Co−C8 2.048(2), C1−C2 1.435(3), C2−C3 1.408(4), C3−C4 1.416(4), C5−C6 1.413(4), C6−C7 1.407(4), C7−C8 1.434(4), Co−centroid(η^4) 1.573; centroid−Co−centroid 167.0.

Synthesis and Structural Characterization of 3. Anion **3** is of interest as the first reported noncarbonyl homoleptic complex containing a transition metal in a formally negative oxidation state.[14] However, unlike the carbonyl analogue, [Co(CO)$_4$]$^-$, the chemical properties of [Co(PF$_3$)$_4$]$^-$ remain little explored because of its prior poorly accessible nature. Kruck et al. originally reported on the synthesis of **3** via the treatment of HCo(PF$_3$)$_4$ with potassium amalgam.[19] Several other salts of [Co(PF$_3$)$_4$]$^-$ were later described, but all were prepared from the hydride precursor.[54,55] Unfortunately, gram quantities of the hydride can only be accessed presently by difficult (and dangerous) high-pressure reactions, requiring a large excess of the very toxic PF$_3$. Thus, Kruck et al. obtained HCo(PF$_3$)$_4$ as a pure substance in high yields (and large quantities) by the reduction of CoX$_2$, where X = Br and I, with copper powder or directly from cobalt powder under high pressures of PF$_3$ (50−300 atm) and H$_2$ (30−80 atm) at 170 °C

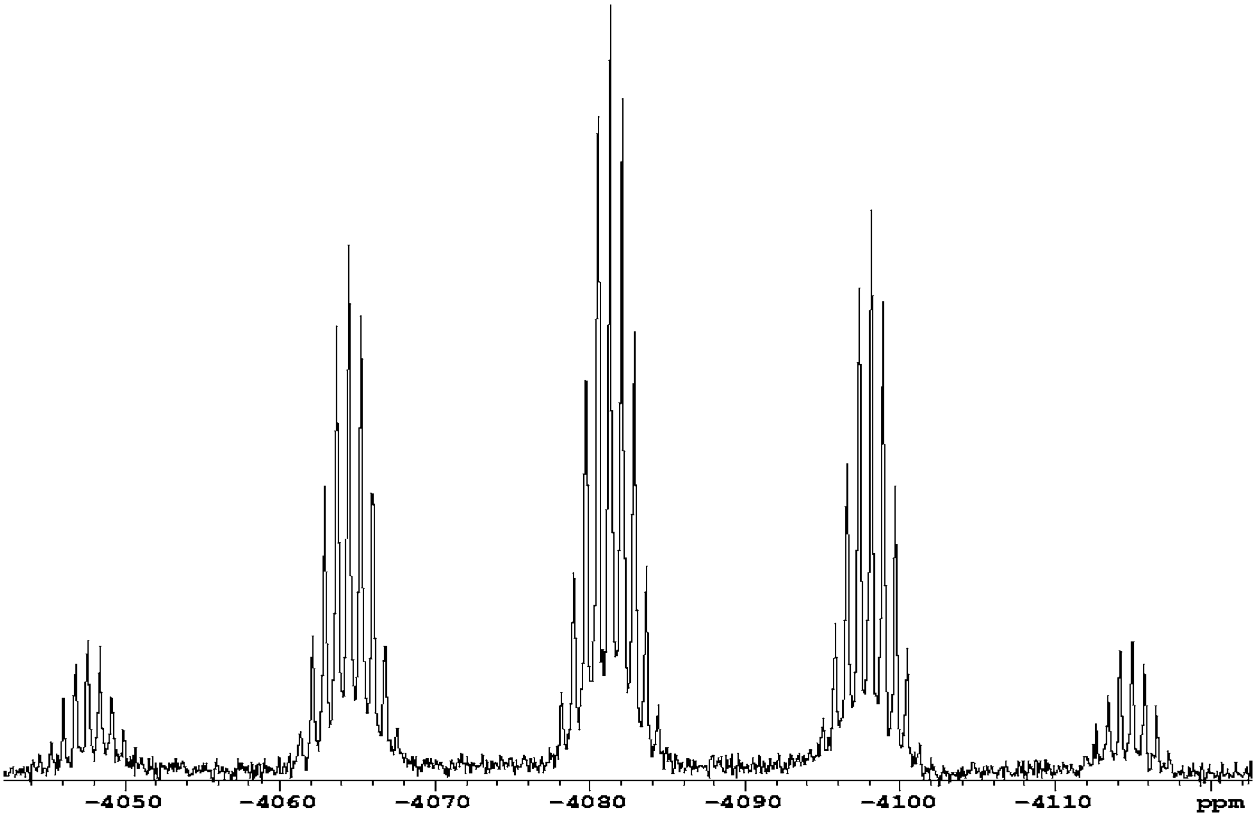

Figure 2. 71.1 MHz ^{59}Co NMR spectrum of **3** in THF at 20 °C, δ_{Co} −4081; $^1J_{PCo}$ = 1199 Hz, $^2J_{FCo}$ = 56 Hz (external reference 0.1 M $K_3[Co(CN)_6]$ in D_2O, δ_{Co} 0.00).

(for CoX_2) or 250 °C (for Co).[54] The treatment of thermally labile $HCo(CO)_4$ with excess PF_3 also provides $HCo(PF_3)_4$ (in unreported yields), but separation of the tetrasubstituted hydride from mixed carbonyl−PF_3 species, $HCo(PF_3)_n(CO)_{4-n}$, with n = 1−3, requires preparative glpc, which lends itself only to relatively small-scale syntheses.[56] However, the availability of $HCo(PF_3)_4$ by the latter method was confirmed by a single-crystal X-ray structural characterization.[57] Small quantities of $HCo(PF_3)_4$ have also been obtained by Timms' classic metal vaporization technique.[58]

Our prior atmospheric pressure syntheses of $[M(PF_3)_6]^-$, where M = V,[59] Nb,[60] and Ta,[61] which are generally conducted with only a slight excess of PF_3, suggested that $[Co(PF_3)_4]^-$ should be available directly from the reaction of PF_3 with anion **1**. The treatment of $[K(THF)_x][Co(C_{14}H_{10})_2]$, prepared in situ, with about 6 equiv of PF_3 afforded an initially pale-pink solid in an unoptimized 20% yield that proved to be spectroscopically pure **3**. As expected for a tetrahedral diamagnetic complex, the ^{59}Co NMR spectrum of **3** (Figure 2) shows a well-resolved quintet, owing to the coordination of four equivalent PF_3 groups, $^1J(^{31}P-^{59}Co)$ = 1199 Hz, further split into multiplets by $^{19}F-^{59}Co$ coupling, $^2J(^{19}F-^{59}Co)$ = 56 Hz. The ^{59}Co NMR chemical shift of **3**, δ −4081 (THF), is in satisfactory agreement with that reported previously, δ −4220 (H_2O), relative to 0.1 M aqueous $K_3[Co(CN)_6]$,[62] although the prior spectrum is of much lower resolution, undoubtedly because of earlier-generation instrumentation. Interestingly, the ^{59}Co δ value for **3** appears to be the most upfield shift known for a diamagnetic cobalt complex[63] (cf. $[Co(P(OMe)_3)_4]^-$, δ −3756 (quintet) in CD_3CN, and $[Co(CO)_4]^-$, δ −3016 in CD_3CN, both values from this work). Previously unreported ^{31}P and ^{19}F NMR spectra for **3** are also given in the Experimental Section. Chemical shifts and $^1J(^{31}P-^{19}F)$ values are similar to those previously reported for $[M(PF_3)_6]^-$, where M = V, Nb, and Ta.[59−61]

X-ray structural characterization of **3** was desirable because, to the best of our knowledge, molecular structures of homoleptic PF_3 metal complexes have only been available previously for neutral and cationic species, including $Ni(PF_3)_4$,[64] $Pt(PF_3)_4$,[65−67] $[Pt(PF_3)_4]^{2+}$,[67] and $[Au(PF_3)_2]^{+}$[68] in the primary literature.[69] Also, a comparison of the molecular geometry and interatomic distances of $[Co(PF_3)_4]^-$ with those of the previously examined parent hydride $HCo(PF_3)_4$[57] promised to be of fundamental interest. Colorless blocks of **3** were grown by the slow evaporation of an acetone/hexane solution at room temperature in air; i.e., unlike the extremely O_2-sensitive $K[Co(CO)_4]$,[70] **3** is stable in air for days, as a solid or in solution. The X-ray structure of **3** (Figure 3) shows an approximate tetrahedral arrangement of phosphane ligands, twist angle = 88.0°,[71] appropriate for formally d^{10} Co^{I-}. The potassium cation has close contacts to 10 fluorine atoms, where only two are depicted in Figure 3. The K−F distances range from 2.736(2) to 3.344(9) Å, where the shortest K−F contacts, 2.736(2) and 2.796(2) Å, are similar to those observed in $K[BF_4]$.[72] A crystallographic mirror plane coincides with atoms K1, Co1, P2, F4, P3, and F6; thus, half of the anion is unique. Atoms of one PF_3 ligand (P3, F6, F7, and F8) are disordered slightly over the mirror plane (50:50) and are modeled as such.

In contrast to the neutral $M(PF_3)_4$, where M = Ni[64] and Pt,[65−67] which possess regular tetrahedral MP_4 units, slightly distorted CoP_4 tetrahedra are present in **3**, likely owing to cation−anion interactions. Thus, P−Co−P angles of 107.9−

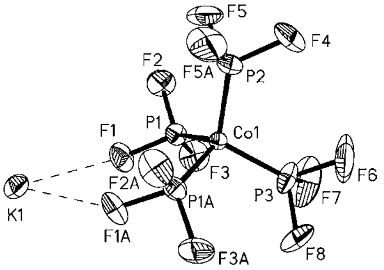

Figure 3. Molecular structure of **3**, showing two close K−F contacts. Thermal ellipsoids are set at the 50% probability level. A crystallographic mirror plane runs through the salt; thus, half of it is unique. Selected distances (Å) and angles (deg): Co−P1 2.0096(6), Co−P2 2.0183(8), Co−P3 2.0094(10), K−F1 2.994(2), K−F2 2.796(2), K−F3 2.736(2), av P−F 1.572(4); P1−Co−P1A 107.87(4), P1−Co−P2 108.79(2), P1−Co−P3 111.1(2), P2−Co−P3 112.06(5), av F−P−F 95.1(5). Note: Average P−F and F−P−F values exclude a disordered PF_3 group, defined by P3.[73].

112.4° are present, and Co−P distances range from 2.0096(6) to 2.0183(8) Å, av Co−P = 2.012(4) Å. With the exclusion of the aforementioned disordered PF_3 group,[73] the average P−F distance and F−P−F angle are 1.572(4) Å and 95.1(5)°, respectively. A comparison of the structure of anion **3** with $HCo(PF_3)_4$[57] reveals significant differences. The neutral hydride complex, with P−Co−P angles ranging from 101.8 to 118.0°, contains a more distorted CoP_4 environment, strongly suggesting that the hydrogen atom occupies a definite coordination site on cobalt, as was observed for the related complex $HCo(P(OEt)_2Ph)_4$.[74] Although the hydrogen ligand in $HCo(PF_3)_4$ could not be detected in the final difference Fourier map,[57] the presence of a direct Co−H bond is also indicated by its ^1H NMR spectrum, which shows a high-field resonance, δ −12.5,[19] similar to the value observed for $HCo(P(OEt)_2Ph)_4$, δ −14.5.[74] Consistent with the excellent π-acceptor ability of PF_3,[75] the average M−P distance in anion **3**, 2.012(4) Å, is substantially shorter than corresponding distances present in the isoelectronic neutral compounds $HCo(PF_3)_4$, 2.052 Å,[57] and $Ni(PF_3)_4$, 2.099(3) (Å).[64] As expected, anion **3** has a slightly larger average P−F distance, 1.572(4) Å, compared to those in $HCo(PF_3)_4$, 1.549(12) Å,[52] and $Ni(PF_3)_4$, 1.561(3) Å, corresponding to a greater degree of metal ($d\pi$)-to-PF_3 (σ^*) back-bonding in the anion.[75−77] Thus, anion **3** has longer and likely weaker P−F bonds than $HCo(PF_3)_4$ and $Ni(PF_3)_4$. Solution IR spectra of **3** in polar solvents, including acetone and water, are qualitatively consistent with the X-ray results in that the P−F stretching frequencies are about 60−80 cm^{-1} lower than the corresponding ones for $HCo(PF_3)_4$ and $Ni(PF_3)_4$.[78]

The robust nature of **3** is strongly reminiscent of the main-group salt $K[B(CF_3)_4]$, wherein the anion has been established to be more weakly coordinating than $[B(C_6F_5)_4]^-$ or the carborane anion $[HCB_{11}Cl_{11}]^-$, based on its relatively weak interaction with n-octyl$_3$NH$^+$ in CCl_4;[79] i.e., "the infrared νNH scale for weakly basic anions."[80] However, unlike the tetraorganoborate anions, which are unstable at normal temperatures as unsolvated conjugate acids, pure $HCo(PF_3)_4$ is easily obtained in high yields by the treatment of **3** with sulfuric acid.[54] Solution pK_a values of the quite thermally stable $HCo(PF_3)_4$, decomposition ~250 °C, appear to be unknown, but the gas-phase acidity of this species has been determined to exceed that of triflic acid.[81] On this basis and in view of the now facile availability of $[Co(PF_3)_4]^-$, exploration of the use of this species as a weakly coordinating anion and $HCo(PF_3)_4$ as a potential transition-metal "super-acid" will be of considerable interest. Although PF_3 is now quite expensive from commercial sources, it is relatively easy to prepare in multigram quantities from readily available and fairly inexpensive SbF_3 and PCl_3 in the presence of $SbCl_5$.[82]

Synthesis and Structural Characterization of 5. Shortly after Kruck et al. established the existence of several homoleptic PF_3 metalates,[83] Muetterties and Hirsekorn reported on the first phosphite analogues, $[Co(P(OR)_3)_4]^-$, where R = Me and Et.[84] These were obtained by treatment of the corresponding hydrides, $HCo(P(OR)_3)_4$, with KH in THF, as potassium salts, $K[Co(P(OR)_3)_4]$, which were reported to be insoluble in all nonreactive solvents.[85] The hydrides were prepared by sodium borohydride reduction of $CoCl_2$ in the presence of excess phosphite,[85] where only the yield for R = ethyl, ca. 40%, has been reported.[86] However, similar protocols have provided $HCo(P(OPh)_3)_4$[87] and $HCo(P(OEt)_2Ph)_4$[74] in 65−80% isolated yields. Although no yield data were originally provided for either potassium salt,[85] Theopold et al. later reported that the reaction was essentially quantitative. He also solubilized the salt with cryptand-222 and obtained a crystal structure of the product **4**.[22] Compound **4** was also obtained in 92% yield by the direct reaction of anion **1**, as the [K(cryptand-222)] salt, with excess $P(OMe)_3$. The structure of **4** was confirmed by single-crystal X-ray diffraction on a polymorph of the one described by Theopold et al.[22] Noteworthy is the significantly longer average Co−P distance in anion **4**, 2.064(2) Å, compared to that in $[Co(PF_3)_4]^-$, 2.012(4) Å, owing to both the poorer acceptor character and the slightly larger size[88] of $P(OMe)_3$ versus PF_3.

Rakowski and Muetterties later prepared a homoleptic phosphitecobaltate with $P(OiPr)_3$. In contrast to the very poor solubilities of sodium or potassium salts of $[Co(P(OMe)_3)_4]^-$, the sodium salt of the analogous triisopropylphosphitecobaltate was very soluble in THF, as well as in hydrocarbons. Most surprisingly, the isolated sodium salt had the composition $Na^+CoL_5^-$, where L = $P(OiPr)_3$. Because ^1H NMR data showed two sets of phosphite resonances in a 4:1 ratio, it was proposed that the salt contained a normal CoL_4^- unit, with the additional phosphite complexed only to the sodium cation. Unfortunately, all attempts to obtain suitable crystals for X-ray analysis failed, so the rather enigmatic character of this "$Na^+CoL_5^-$" species was not fully resolved.[20] To help shed some light on the nature of the cobaltate, an independent synthesis by the reaction of **1** with excess $P(OiPr)_3$ was carried out. A yellowish-white solid was initially obtained in 57% yield. Recrystallization from THF/pentane afforded colorless block-shaped crystals of composition [K(18-crown-6)(THF)$_2$][$Co(P(OiPr)_3)_4$] (**5**). The X-ray structure of anion **5** (Figure 4) shows a distorted tetrahedral arrangement of phosphite ligands, with P−Co−P angles ranging from 104.0 to 117.4°, av = 109.5°, and a twist angle of 82.4°, defined by the intersection of planes P1−Co−P2 and P3−Co−P4. The Co−P distances range from 2.0694(8) to 2.0767(8) Å, av =2.073(4) Å, which is about 0.01 Å longer than the value for anion **4**, consistent with the larger size of $P(OiPr)_3$, cone angle of 130°, compared to $P(OMe)_3$.[88] Average P−O and C−O distances of $P(OiPr)_3$ are statistically identical with corresponding distances of $P(OMe)_3$ in anion **4**. Also, anion **5** is well separated from [K(18-crown-6)(THF)$_2$]$^+$, which has a normal structure with K−O distances within the ranges previously observed for this cation.[89] Our conclusion is that the original proposal of

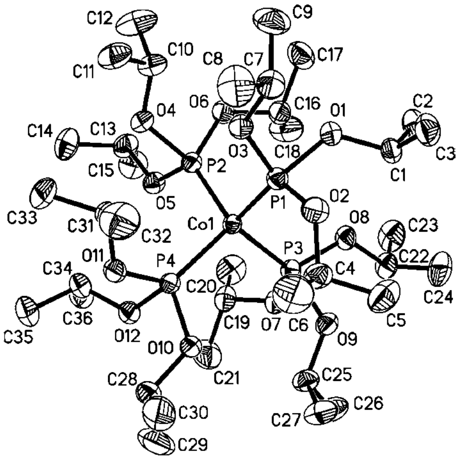

Figure 4. Molecular structure of anion **5**. Thermal ellipsoids are set at the 50% probability level, with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Co−P1 2.0693(7), Co−P2 2.0757(8), Co−P3 2.0769(7), Co−P4 2.0712(8), av P−O 1.65(1), av C−O 1.439(8); P1−Co−P2 104.02(3), P1−Co−P3 106.55(3), P1−Co−P4 117.35(3), P2−Co−P3 116.66(3), P2−Co−P4 106.94(3), P3−Co−P4 105.84(3); av O−P−O 96(2).

Rakowski and Muetterties for the formulation of the product $Na^+CoL_5^-$, where L = $P(OiPr)_3$, is substantially correct, where effective solvation of Na^+ by both the "free" $P(OiPr)_3$ and anion **5** is likely responsible for the unusually high solubility of this species in hydrocarbons. A related "inverted micelle" cation−anion interaction has also been proposed to account for the excellent solubility of Kläui's salt, $Na[C_5H_5Co\{P(O)(OC_2H_5)_2\}_3]$, in pentane.[90]

Reactions of 1 with 1,2-Bis(diphenylphosphano)ethane, dppe, and Trimethylphosphine. To test the generality of the reactions of **1** with PX_3 (or PR_3) reagents, its reactions with dppe and trimethylphosphine were examined. As described previously, **1** reacted with 2 equiv of dppe in a normal fashion to afford about 75% isolated yields of $[Co(dppe)_2]^-$, which was the first structurally authenticated homoleptic triorganophosphanecobaltate(1−).[17] However, the reaction of **1** with excess PMe_3 provided entirely different products, as depicted in eq 2. Thus, the formal cobalt(I−) precursor, **1**, was converted to a previously known cobalt(0)

$$[Co(C_{14}H_{10})_2]^- + 3PMe_3 \xrightarrow[-78\text{ to }+20\ °C]{THF} Co(C_{14}H_{10})(PMe_3)_3 + [C_{14}H_{10}]^- \qquad (2)$$

anthracene complex **6**[12] and the anthracene radical anion salt, $[K(18\text{-crown-}6)(THF)_2][C_{14}H_{10}]$. These products were both isolated in 50−60% yield and unambiguously identified by unit cell comparisons.[12,23] Although no intermediate in the reaction of **1** with PMe_3 has been identified, the initial formation of a very strongly reducing anthracene/trimethylphosphanecobaltate(1−) seems likely. This transient species then must reduce coordinated or free anthracene to afford **6** and $C_{14}H_{10}^-$.

At the outset of this study, it was known that $[Co(PMe_3)_4]^-$ would not be accessible from this reaction, because Klein and co-workers had previously shown this species to be an exceedingly strong reducing agent.[12,91] For example, it rapidly reduces free naphthalene to a naphthalene radical anion (eq 3). Also, because $C_{10}H_8^-$ is more strongly reducing than $C_{14}H_{10}^-$

$$K[CoPMe_3)_4] + C_{10}H_8 \xrightarrow[20°C]{Et_2O} \bullet Co(PMe_3)_4 + K[C_{10}H_8] \qquad (3)$$

by about 0.5 V,[92] $[Co(PMe_3)_4]^-$ is also expected to reduce anthracene to $C_{14}H_{10}^-$. *In this study, we have highlighted an obvious but significant limitation to the use of homoleptic poly(arenemetalates) as sources of "naked" atomic metal anions; i.e., the desired products must be redox-compatible.* For example, we previously reported on a similar reaction of bis(anthracene)ferrate(1−) with excess $P(OMe)_3$. The final products were the neutral iron(0) complex $Fe(\eta^4\text{-}C_{14}H_{10})(P(OMe)_3)_3$ and $C_{14}H_{10}^-$ rather than an anticipated anionic iron(I−) complex and neutral anthracene.[52]

Reactions of 1 with 1,5-Cyclooctadiene, COD, and Ethylene. It was of interest to determine whether **1** would react with COD to produce $[Co(COD)_2]^-$, Jonas' original "naked" cobalt(I−) complex.[4] However, the treatment of dark-red solutions of **1** with excess COD in THF rapidly produced a bright-blue-green solution rather than the pale-yellow color of $[Co(COD)_2]^-$. From this reaction, a 69% yield of a satisfactory pure blue-violet salt, **7**, containing the mixed-ligand cobaltate was obtained (eq 4). NMR spectra of anion **7** are identical with those shown in the Experimental Section for the closely related salt **12**, the synthesis

$$[Co(C_{14}H_{10})_2]^- + \text{excess 1,5-COD} \xrightarrow[20\ °C]{THF} [Co(C_{14}H_{10})(COD)]^- + C_{14}H_{10} \qquad (4)$$

of which will be described below. Dichroic red-violet (to reflected light) plates of **7** were analyzed by X-ray diffraction to verify the formulation of the salt. However, owing to severe disorder of both cation and anion in **7**, the analogous [K(cryptand-222)] salt of **8** was prepared. Single crystals were grown and provided a successful structural characterization. Anion **8** (Figure 5) is well separated from an unexceptional cation and contains a nonplanar anthracene, coordinated as a η^4-conjugated diene, and a η^4-COD group, both bound in a distorted tetrahedral array about cobalt, with a twist angle of 79.8°.[95]

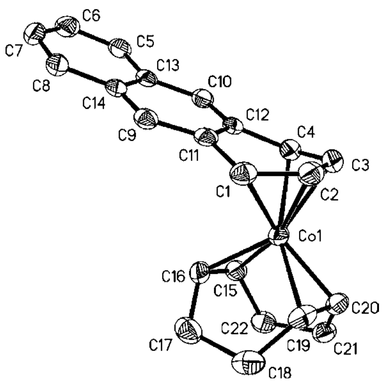

Figure 5. Molecular structure of anion **8**. Thermal ellipsoids are set at the 50% probability level, with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Co−C1 2.146(2), Co−C2 2.023(2), Co−C3 2.043(2), Co−C4 2.187(2), Co−C15 2.023(2), Co−C16 2.016(2), Co−C19 2.012(2), Co−C20 2.028(2), C1−C2 1.421(3), C2−C3 1.410(3), C3−C4 1.409(3), C15−C16 1.395(3), C19−C20 1.414(3), Co−centroid(C1−C4) 1.69, Co−centroid(COD) 1.31; centroid−Co−centroid 175.7.

The Co−C and C−C bond lengths of the η^4-diene (coordinated anthracene) and η^4-COD groups are statistically identical with corresponding values previously reported for the naphthalene analogue, $[Co(\eta^4\text{-}C_{10}H_8)(\eta^4\text{-COD})]^-$.[18] Pertinent interatomic data for these structures, along with that of $[Co(\eta^4\text{-COD})_2]^-$, will be compared and discussed below.

The reaction of **1** with excess ethylene was also examined briefly. A brown slurry of **1** in Et_2O was stirred under an atmosphere of ethylene gas at 20 °C and resulted in the formation of a bright-purple solid within 1 h. Attempts to isolate this product as the [K(18-crown-6)] salt were unsuccessful, but the analogous reaction conducted with the [K(cryptand-222)] salt of anion **1** provided a more thermally stable species. When the bright-purple solid was dissolved in THF and *immediately* layered with pentane at 20 °C, square red prisms with a metallic sheen formed. A single-crystal X-ray diffraction study established the formulation $[K(\text{cryptand-222})][Co(\eta^4\text{-}C_{14}H_{10})(\eta^2\text{-}C_2H_4)_2]$, wherein the anionic component had a molecular structure very similar to that observed for anion **8**.[24,96] No other characterization of this mixed anthracene−ethylene cobaltate was pursued.

Synthesis of 10. Prior to this study, naphthalene−cobalt complexes were quite rare, represented only by the cobalt(III) metallocarborane, $Co(\eta^6\text{-}C_{10}H_8)(CB_{10}H_{11})$,[97] and two cobalt(I) species, $(C_5Me_5)Co(\eta^4\text{-}C_{10}H_8)$,[98] and $[Co(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-COD})][BF_4]$.[99] The existence of the latter cation strongly suggested that previously unknown naphthalenecobaltates should be accessible as $[Co(\eta^4\text{-}C_{10}H_8)(\eta^4\text{-COD})]^-$ anion **10**. As mentioned previously, the reduction of $CoBr_2$ or cobaltocene by 3 equiv of potassium naphthalene afforded extremely thermally unstable deep-red species that defied all attempts at isolation or characterization.[18] However, the addition of 1 equiv of 1,5-cyclooctadiene per cobalt to these solutions afforded low (20%, unoptimized from $CoBr_2$) or high (typically 85−90% from cobaltocene) yields of **10**, which contains about 0.5 equiv of THF in the bulk sample. Neither of these reactions can be carried out in the presence of excess 1,5-COD because anion **10** readily reacts with additional 1,5-COD to produce $[Co(COD)_2]^-$ anion **11**; see below. Indeed, the poor yield of **10** from $CoBr_2$ arises because of the significant formation of anion **11** in this reaction. Analogous potassium naphthalene reductions of $CoBr_2$ in the presence of an excess of 1,3-COD, ca. 3.5 equiv, have also been examined and shown to provide about 50% isolated yields of bona fide **10**.[100] No evidence for the formation of the unknown complex $[Co(C_{10}H_8)(1,3\text{-COD})]^-$ was observed in this reaction. Although no further information is presently available for this interesting transformation, the isomerization of 1,3-COD to 1,5-COD by group 9 metal complexes has been known since at least 1964,[101] including a well-defined conversion of CpCo(1,3-COD) to CpCo(1,5-COD).[102] In contrast to other syntheses reported herein, cobaltocene appears to be a much better precursor to this particular cobaltate than $CoBr_2$. However, the removal of traces of KCp from the cobaltocene reaction can be problematic.

Reactions of 10 with 1,5-COD and Anthracene. The treatment of magenta **10** in Et_2O or THF with equimolar or excess amounts of 1,5-COD or anthracene at 20 °C causes full displacement of naphthalene within minutes and the formation of pale-yellow or bright-blue-green products, respectively. From these reactions, about 80% yields of $[K(\text{18-crown-6})]^+$ salts of $[Co(COD)_2]^-$, **11**, or $[Co(C_{14}H_{10})(COD)]^-$, **12**, were obtained. Although the $[K(\text{18-crown-6})]^+$ salt of anion **11** has not been described, as mentioned previously, the closely related salt $[\{K(\text{18-crown-6})\}_2(Cp)][Co(COD)_2]\cdot 2THF$ has been isolated recently from the direct reduction of cobaltocene by potassium naphthalene in the presence of excess 1,5-COD, followed by treatment with 18-crown-6.[27] Formation of the sandwich counterion in this reaction indicates that significant amounts of KCp were present when the reaction mixture containing $K[Co(COD)_2]$ was treated with 18-crown-6. It is useful here to emphasize Jonas' prior observations that quantitative precipitation of KCp from potassium metal or potassium naphthalene reductions of metallocenes in THF requires cooling of the reaction mixture to −78 °C for up to 2 days.[103] Thus, when we prepared relatively pure $[K(THF)_{0.5}][Co(COD)_2]$ by the potassium metal reduction of cobaltocene in the presence of 1,5-COD, as originally described by Jonas,[26] it was treated with 18-crown-6 and the major product was **11**, as verified by NMR and X-ray diffraction. However, traces of cyclopentadienide ion were still evident by ^1H NMR spectra. Also, contamination of **11** by small amounts of $[\{K(\text{18-crown-6})\}_2(Cp)][Co(COD)_2]\cdot 3THF$, was confirmed by X-ray diffraction. Thus, crops of single crystals from this reaction invariably contained two types of yellow crystals that were readily distinguishable under a microscope: blocks (major, **11**) and plates (minor, containing $[\{K(\text{18-crown-6})\}_2(Cp)][Co(COD)_2]\cdot 3THF$); see Experimental Section.

Solution ^1H and ^{13}C NMR spectra of anion **11** in THF-d_8 at 20 °C are similar to those reported by Jonas and co-workers for $[Li(THF)_2][Co(COD)_2]$.[4] For example, the ^1H NMR spectrum of anion **11** consisted of two broad resonances of 2:1 relative intensities at δ 2.20 and 1.87, due to the CH_2 and CH groups, respectively. Jonas reported analogous broad resonances at δ 2.43 and 2.1 for the lithium salt.[104] Corresponding ^{13}C NMR spectra of anion **11** showed two signals at δ 69.7 (d, CH) and 34.7 (t, CH_2), essentially identical with analogous resonance positions, δ 69.1 and 34.7, observed by Jonas.[4] Structural characterizations were carried out on **9** and **11**, i.e., the $[K(\text{cryptand-222})]^+$ and $[K(\text{18-crown-6})]^+$ salts of $[Co(COD)_2]^-$, respectively, to verify their nature. Unlike the anion in Jonas' salt $[Li(THF)_2][Co(COD)_2]$,[4] or the anion in **11**, anion **9** is well separated from and is relatively unperturbed by the counterion. In **9**, the cation $[K(\text{cryptand-222})]^+$ is ordered and has metrical properties in good agreement with those previously reported for the corresponding iodide salt.[105] Figure 6 shows the molecular structure of anion **9**. The cobalt and potassium atoms in the asymmetric unit are located on different 2-fold axes (both parallel to the *c* axis); thus, half of each molecule is unique. Anion **9** contains two equivalent η^4-1,5-COD groups bound in a distorted tetrahedral fashion about cobalt, with a twist angle of 67.3°,[95] which is similar to the corresponding value, 73°, observed in the isoelectronic $Ni(COD)_2$.[106] It is useful to note key differences in the interatomic distances of these classic organometallics. For example, despite the fact that nickel and cobalt have nearly identical atomic and covalent radii,[107] the average M−C distance in anion **9**, 2.052(5) Å,[108] is 0.07 Å shorter than the corresponding distance for $Ni(COD)_2$, 2.124(9) Å.[106] Also, the average C−C(diene) distance in anion **9**, 1.414(3) Å, is 0.02 Å longer than the corresponding value for $Ni(COD)_2$, 1.391(2) Å.[106]

The above data indicate that d^{10} Co^{I-} is substantially more effective in metal ($d\pi$)-to-alkene (π^*) back-bonding than d^{10} Ni^0, in accordance with the Dewar−Chatt−Duncanson model.[109] The closer approach of the COD groups to the

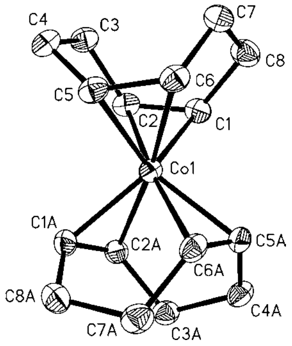

Figure 6. Molecular structure of anion **9**. Thermal ellisoids are set at the 50% probability level, with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Co−C1 2.048(2), Co−C2 2.055(2), Co−C5 2.047(2), Co−C6 2.057(2), C1−C2 1.415(3), C2−C3 1.523(3), C3−C4 1.539(3), C4−C5 1.520(3), C5−C6 1.412(3), C6−C7 1.524(3), C7−C8 1.541(3), Co−centroid(COD) 1.362; centroid−Co−centroid 179.4.

metal center in $[Co(COD)_2]^-$ than those in $Ni(COD)_2$ also indicates that the M−COD bond energy is likely to be greater for cobalt than for nickel in these complexes. This observation, in addition to its anionic nature and the presence of counterions, which should inhibit the approach of potential nucleophiles, likely explains why it is more difficult to displace COD groups from $[Co(COD)_2]^-$, compared to $Ni(COD)_2$, in nonredox nucleophilic substitution reactions. For example, $Ni(COD)_2$ has been shown to readily react with $P(OMe)_3$ or PMe_3 to produce the homoleptic complexes NiL_4, where L = $P(OMe)_3$ or PMe_3,[110] but surprisingly **11** failed to give a perceptible reaction with these phosphorus ligands in THF at 20 °C. In contrast, as mentioned above, **1** reacts with $P(OMe)_3$ to provide **4** under identical conditions. Also, the naphthalene−COD cobaltate **10** provided 70% isolated yields of $[K(18\text{-crown-}6)(THF)_{0.5}][Co(\eta^4\text{-}COD)(PMe_3)_2]^-$, a product characterized exclusively by X-ray diffraction[111] (eqs 5 and 6). Jonas has mentioned in review articles that the highly labile ethylene complex $[Co(C_2H_4)_4]^-$ reacts with excess 1,2-bis(dicyclohexylphosphano)ethane (dcpe) to afford $[Co(C_2H_4)_2(dcpe)]^-$,[6] but to the best of our knowledge, no reactions of $[Co(COD)_2]^-$ with phosphanes (or phosphites) have been described to date.

$$[Co(COD)_2]^- + \text{excess } PMe_3 \xrightarrow[20\ °C]{THF} \text{no reaction} \tag{5}$$

$$[Co(C_{10}H_8)(COD)]^- + \text{excess } PMe_3 \xrightarrow[20\ °C]{THF} [Co(COD)(PMe_3)_2]^- + C_{10}H_8 \tag{6}$$

In view of the nonreactivity of **11** with $P(OMe)_3$ or PMe_3 at 20 °C, it is not surprising that **11** also fails to react with naphthalene, unlike $[Co(C_2H_4)_4]^-$.[18] However, although **11** shows no reaction with anthracene for several hours at 20 °C in THF, rapid formation of the blue-green complex $[Co(C_{14}H_{10})(COD)]^-$, anion **12**, occurred when the reaction was heated to 60 °C (eq 7). However, the best routes to **12** involve reactions of 1,5-COD with **1** (see eq 4) or anthracene with **10** (eq 8). The latter reaction involves the displacement of coordinated naphthalene by anthracene, which is now a well-precedented reaction in early-transition-metal chemistry.[112] However, to the best of our knowledge, the only prior report on a related conversion involving a late-transition-metal complex is the reaction of the (2-naphthyl)hydrideiron(II) complex, *cis*-$HFe(2\text{-}C_{10}H_7)(dmpe)_2$, where dmpe = 1,2-bis(dimethylphosphano)ethane, with anthracene to afford the formal iron(0) complex, $Fe(\eta^4\text{-}C_{14}H_{10})(\kappa^2\text{-dmpe})(\kappa^1\text{-dmpe})$, bearing a dangling phosphane.[113] An important component of the driving force for the reaction of **10** with anthracene shown, in eq 8, is undoubtedly the production of free naphthalene, which has a higher resonance stabilization per ring than anthracene.[114] However, formation of the anthracene complex may also make the reaction more favorable energetically because anthracene is usually regarded as a better acceptor ligand than naphthalene and, on this basis, should bind more strongly to cobalt.[115] A computational study may be useful in sorting out the relative importance of these factors and the identification of others, such as the influence of the COD ligand and steric effects on the energetics of the reaction.

$$[Co(COD)_2]^- + C_4H_{10} \xrightarrow[60\ °C]{THF} [Co(C_{14}H_{10})(COD)]^- + COD \tag{7}$$

$$[Co(C_{10}H_8)(COD)]^- + C_{14}H_{10} \xrightarrow[20\ °C]{THF} [Co(C_{14}H_{10})(COD)]^- + C_{10}H_8 \tag{8}$$

^1H and ^{13}C NMR spectra of anion **12** in solution are unexceptional and entirely consistent with its formulation. They exhibit resonances characteristic of 1−4-η^4-anthracene[17] and η^4-1,5-cyclooctadiene groups[4] bound in a 1:1 ratio to an electron-rich cobalt center. These spectra are also very similar to those of the naphthalene analogue **10**. Both show the presence of inequivalent methine groups of coordinated COD ligands in ^1H and ^{13}C NMR spectra. This feature is consistent with the molecular structures of the anions, as previously reported for **10**[18] and shown in Figure 5 for $[Co(C_{14}H_{10})(COD)]^-$ in the $[K(\text{cryptand-}222)]^+$ salt **8**, which will be denoted as anion **12** in the discussion below.

Anions **10** and **12** have extremely similar coordination environments and contain distorted tetrahedral cobalt with twist angles of 84.5 and 79.8°, respectively, consistent with the presence of d^{10} Co^{I-}. The average outer and inner Co−C(1−4) distances in anion **12** are 2.17(2) and 2.03(1) Å, respectively, which are statistically identical with those of anion **10**.[18] Thus, the Co−C(1−4-anthracene) distances in **12** have a distinct long−short−short−long pattern similar to that in **1**[17] and characteristic of a predominantly π^2-1,3-diene−metal interaction. The cobalt−COD interactions in **10** and **12** are also essentially identical with the respective average Co−C(COD) distances of 2.019(8) and 2.020(7) Å. Most interesting, however, is the significantly longer average Co−C(COD) distance of 2.052(5) Å present in $[Co(COD)_2]^-$, anion **9**. The closer approach of the COD ligand to the cobalt center in **10** or **12**, compared to that in **9**, appears to be more electronic than steric in origin because replacement of one COD group in $[Co(COD)_2]^-$ by a bulkier η^4-polyarene ligand should have the opposite effect; i.e., the average Co−C(COD) distance would increase. However, if one takes into account the synergy of the mixed COD−polyarene ligand sets in **10** or **12**, where the nonconjugated diene 1,5-COD is expected to be both a stronger π donor and weaker π^* acceptor than the η^4-polyarenes, the rather close approach of the COD ligand to cobalt in these mixed-ligand cobaltates seems reasonable. Although this statement is consistent with expectations based on the Dewar−Chatt−Duncanson model for metal−alkene/

diene interactions,[109] certain interatomic data for **10** and **12** are not in support of this simple explanation. For example, the reaction of bis(anthracene)cobaltate **1** with COD to provide **12** actually causes a slight increase in the average Co−C(1−4-η^4-anthracene) distance, as measured by the different Co−centroid(C1−C4) values in **1**, 1.64 Å, and **12**, 1.69 Å. This may be due to sterics; i.e., the close approach of the η^4-COD ligand to the cobalt center in **12** may cause repulsion of the anthracene ligand. Also, the average C−C distances of the 1−4-η^4-anthracene groups in **1**, 1.417(7) Å, and **12**, 1.41(1) Å, are statistically identical, suggesting that if the anthracene group in **12** is functioning as a better acceptor ligand than the two groups are in **1**, the effect is small at best. Concern has been previously expressed that interatomic parameters from X-ray diffraction studies may be rather insensitive measures of metal−diene/arene binding in very similar systems.[18] Thus, a computational study comparing the electronic/molecular structures and ligand bond dissociation in energies in anions **1**, **9**, and **12** (or $[\mathrm{Co}(\eta^4\text{-naphthalene})_2]^-$,[18] **9**, and **10**) would be of substantial interest.

Reactions of 10 with 1,3-Butadiene and 2,2′-Bipyridine. Whereas the reaction of **1** with excess 1,3-butadiene, as described above, affords high isolated yields of the homoleptic 1,3-butadienecobaltate, **2** (eq 9), the corresponding reaction of **10**, carried out under nearly identical conditions, provided only the mixed-ligand complex $[\mathrm{Co}(\eta^4\text{-C}_4\mathrm{H}_6)(\eta^4\text{-COD})]^-$, anion **13**, in 87% isolated yield, as the bright-orange $[\mathrm{K}(18\text{-crown-}6)]^+$ salt (eq 10).[116] Equimolar amounts of Dmbd and **10** also reacted

$$[\mathrm{Co}(\mathrm{C}_{14}\mathrm{H}_{10})_2]^- + \text{excess } 1{,}3\text{-C}_4\mathrm{H}_6 \xrightarrow[20\,°\mathrm{C}]{\mathrm{Et_2O}} [\mathrm{Co}(\mathrm{C}_4\mathrm{H}_6)_2]^- + 2\mathrm{C}_{14}\mathrm{H}_{10} \qquad (9)$$

$$[\mathrm{Co}(\mathrm{C}_{10}\mathrm{H}_8)(\mathrm{COD})]^- + \text{excess } 1{,}3\text{-C}_4\mathrm{H}_6 \xrightarrow[20\mathrm{C}]{\mathrm{Et_2O}} [\mathrm{Co}(\mathrm{C}_4\mathrm{H}_6)(\mathrm{COD})]^- + \mathrm{C}_{10}\mathrm{H}_8 \qquad (10)$$

at 20 °C in THF to provide a 72% isolated yield of the closely related $[\mathrm{K}(18\text{-crown-}6)][\mathrm{Co}(\eta^4\text{-C}_4\mathrm{H}_4\mathrm{Me}_2)(\mathrm{COD})]$ (**14**).[117] Both **13** and **14** have unexceptional ^{1}H and ^{13}C NMR spectra consistent with the assigned formulations. Single-crystal X-ray diffraction studies also confirmed their compositions. Unfortunately, the butadiene ligand in **13** was disordered over two positions (58% and 42%), resulting in unreliable Co−C and C−C bond distances. In contrast, both cation and anion are well-ordered in **14**, the anion of which is shown in Figure 7. One methylene group, C9, of the COD ligand and C3 and C4 of the butadiene ligand weakly interact with neighboring potassium cations, thereby completing the potassium coordination sphere. The net result is a pseudopolymeric structure in one dimension along the *b* axis. A very similar cation−anion interaction was described above for **2**. In both cases, the anions appear to be largely unperturbed by essentially identical and unexceptional $[\mathrm{K}(18\text{-crown-}6)]^+$ units. Anion **14** contains η^4-Dmbd and η^4-COD groups bound in a distorted tetrahedral fashion about cobalt, with a twist angle of 71.0°.[95] As in the case of anion **12**, the average Co−C(COD) distance in **14**, 2.009(6) Å, is significantly shorter than the value for $[\mathrm{Co}(\mathrm{COD})_2]^-$, anion **9**, 2.052(5) Å. The average C−C(diene) distances in **14**, 1.421(8) Å, and **9**, 1.414(3) Å, are not significantly different. The Co−C distances for the Dmbd group appear to be normal, with average outer, C1,4, and inner, C2,3, distances of 2.09(1) and 2.021(2) Å, respectively. Although the average C1−C2 distance, 1.416(4) Å, is normal and similar to the value in anion **2**, 1.42(1) Å, the inner C2−C3 distance, 1.434(3) Å, is unexpectedly longer, 0.027 Å (>6σ), than the unexceptional value observed in anion **2**, 1.407(4) Å. We have no explanation for the resulting anomalous short−long−short pattern in the coordinated C−C bond lengths, particularly because the Co−C2 and Co−C3 distances are normal, the cation−anion interactions are very weak, and the structure (R1 = 4%) is of good quality. A survey of iron and cobalt Dmbd complexes (27 total with R1 values < 7.5%) provided mean values of 1.415 Å for the outer C−C bond lengths and 1.411 Å for the inner one.[118]

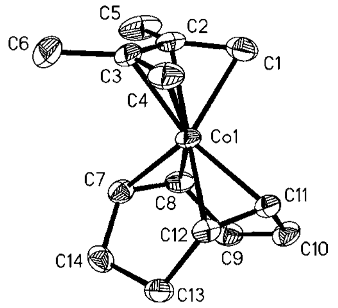

Figure 7. Molecular structure of anion **14**. Thermal ellipsoids are set at the 50% probability level, with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Co−C1 2.106(2), Co−C2 2.023(2), Co−C3 2.019(2), Co−C4 2.080(2), Co−C7 2.004(2), Co−C8 2.017(2), Co−C11 2.010(2), Co−C12 2.006(2), C1−C2, 1.418(4), C2−C3 1.437(3), C3−C4 1.414(3), C7−C8 1.427(3), C11−C12 1.416(3), Co−centroid(butadiene) 1.63, C-centroid-(COD) 1.30; centroid−Co−centroid 174.2.

Earlier we had established that **1** reacted with 2 equiv of 2,2′-bipyridine (bipy) to afford the long known $[\mathrm{Co}(\mathrm{bipy})_2]^-$[24] (eq 11), so it was of interest to examine the corresponding reaction with **10**. However, the reaction provided the mixed-ligand complex $[\mathrm{Co}(\mathrm{COD})(\mathrm{bipy})]^-$ (**15**) rather than the homoleptic (bipy)cobaltate. Dark-purple microcrystalline **15** was isolated in 93% yield as a satisfactorily $[\mathrm{K}(18\text{-crown-}6)]^+$ salt (eq 12). Anion **15** was previously prepared from the reaction of $[\mathrm{Li}(\mathrm{tmeda})_2][\mathrm{Co}(\mathrm{COD})_2]$, where tmeda = *N,N,N′,N′*-tetramethylethylenediamine, with bipy.[119] Interestingly, the latter salt was characterized only by elemental analysis and found

$$[\mathrm{Co}(\mathrm{C}_{14}\mathrm{H}_{10})_2]^- + 2\mathrm{bipy} \xrightarrow[-78\text{ to }20\,°\mathrm{C}]{\mathrm{THF}} [\mathrm{Co}(\mathrm{bipy})_2]^- + 2\mathrm{C}_{14}\mathrm{H}_{10} \qquad (11)$$

$$[\mathrm{Co}(\mathrm{C}_{10}\mathrm{H}_8)(\mathrm{COD})]^- + \mathrm{bipy} \xrightarrow[20\,°\mathrm{C}]{\mathrm{THF}} [\mathrm{Co}(\mathrm{COD})(\mathrm{bipy})]^- + \mathrm{C}_{10}\mathrm{H}_8 \qquad (12)$$

to be weakly paramagnetic, μ_{eff} (20 °C) = 1.15 μ_{B}. Our NMR studies confirm its paramagnetism. However, ^{1}H and ^{13}C NMR spectra for **15** are well-resolved and corroborate the formulation of this substance. Both ^{1}H and ^{13}C NMR spectra of the coordinated bipy ligand showed resonances in positions similar to those previously observed for $\mathrm{Co}(\eta^5\text{-C}_5\mathrm{Me}_5)(\mathrm{bipy})$.[120] Chemical shifts of the methylene and methine resonances of the COD ligand in **15** were similar to those for **9**. X-ray-quality red-violet plates of **15** were grown and confirmed the nature of the salt, where the structure of anion **15** is shown in Figure 8. The $[\mathrm{K}(18\text{-crown-}6)]^+$ counterion is normal and

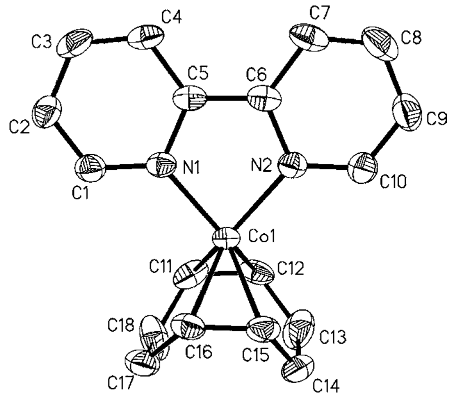

Figure 8. Molecular structure of anion **15**. Thermal ellipsoids are set at the 50% probability level, with hydrogen atoms omitted for clarity. Selected bond distances (Å): Co−N1 1.919(2), Co−N2 1.934(2), Co−C11 2.011(3), Co−C12 1.996(2), Co−C15 1.995(2), Co−C16 1.989(2), C5−C6 1.412(3), N1−C1 1.370(3), N1−C5 1.398(3), N2−C10 1.361(3), N2−C6 1.402(3), C11−C12 1.397(4), C15−C16 1.413(4).

has essentially the same metrical parameters as those found for **2**. As in the case of **2**, we believe that anion **15** is relatively unperturbed by its interaction with the counterion. Thus, the closest K−C(anion) contacts are with a C14, C15, and C16 of the COD group and range from 3.374(3) to 3.477(3) Å. These are significantly longer than the mean K−C(η^5-C_5H_5) distance, 3.06(7) Å, in [K(18-crown-6)][C_5H_5], in which cation−anion interactions are weak and are believed to be relatively nonperturbing.[51b] The coordination environment about cobalt is distorted tetrahedral, with a twist angle of 89.1°.[45] Metrical parameters of the COD ligand in **15** are quite similar to those in anion **14**; i.e., the average Co−C(COD) distances are 1.998(9) and 2.009(6) Å, respectively, while the average C−C(diene) distances in **15** and **14** are 1.41(1) and 1.421(8) Å, respectively. Of most interest is the bipy group, where the inter-ring C5−C6 distance of 1.412(3) Å, as well as other C−C and C−N distances, is diagnostic for the presence of a coordinated bipy radical anion, bipy$^{\bullet-}$.[121,122] Very closely related formal "18-electron" complexes Co(η^5-C_5Me_5)(bipy)[120] and Fe(η^6-toluene)(bipy)[123] have essentially identical bipy inter-ring C−C distances of 1.419(3) and 1.417(3) Å, respectively. These and several other transition-metal bipy complexes were recently definitively established by a computational study to contain coordinated bipy$^{\bullet-}$.[124] On this basis, anion **15** most likely contains d^9 Co^0 and coordinated bipyridyl radical anion, i.e., [Co(η^4-COD)(bipy$^{\bullet-}$)]$^-$. Unlike Co(η^5-C_5Me_5)(bipy) and Fe(η^6-toluene)(bipy), which appear to be diamagnetic at 20 °C, anion **15** is weakly paramagnetic, which indicates that the singlet ($S = 0$) and triplet ($S = 1$) states must be very similar in energy. Clearly, a further study will be necessary for an unambiguous description of the electronic properties of **15**.

Synthesis of 16, the First Structurally Characterized Homoleptic Alkylisocyanometalate. Interestingly, alkylisocyanides predate CO as ligands in transition-metal chemistry. Although the first metal carbonyls, including $PtCl_2(CO)_2$ and $[PtCl_2(CO)]_2$, were reported by Schützenburger in 1868−1870,[125] alkylisocyanide complexes apparently date back to 1854, with the synthesis of an iron cyanide complex of composition $(CH_3)_4Fe(CN)_6$.[126] More than 80 years later, this species was established to be a mixture of isomeric methylisocyanide complexes, *cis*- and *trans*-Fe$(CNCH_3)_4(CN)_2$.[127] Homoleptic neutral and anionic metal carbonyls[128] were established long before corresponding metal isocyanide complexes,[129] but it is of interest that the opposite is true for analogous cationic species. Thus, a compound of composition $(CH_3)_6Fe(CN)_6Cl_2$, referred to as "hexamethylferrocyanogen chloride", was originally reported in 1910[130] and structurally characterized as the dichloride salt of $[Fe(CNCH_3)_6]^{2+}$ in 1945,[131] long before the first homoleptic metal carbonyl cations, $[M(CO)_6]^+$, where M = Mn and Re, were established in 1961.[132]

Warnock and Cooper announced the first homoleptic isocyanometalate, $[Co(CNXyl)_4]^-$, where Xyl = 2,6-dimethylphenyl, in 1989.[133] The cobaltate was originally prepared by the treatment of $K[Co(C_2H_4)_4]$ with 4 equiv of CNXyl (eq 13).[10,133] Much later we discovered that **1** also reacted with CNXyl to provide the identical anion in similar high yield (eq 14).[17,24] Several other homoleptic isocyanometalates have been

$$[Co(C_2H_4)_4]^- + 4CNXyl \xrightarrow[-20\ ^\circ C]{THF} [Co(CNXyl)_4]^- + 4C_2H_4 \tag{13}$$

$$[Co(C_{14}H_{10})_2]^- + 4CNXyl \xrightarrow[-78\ to\ 20\ ^\circ C]{THF} [Co(CNXyl)_4]^- + 2C_{14}H_{10} \tag{14}$$

isolated and structurally characterized,[134,135] including Figueroa's novel $[Co(CNR^*)_4]^-$, which employs a very bulky *m*-terphenylisocyanide ligand, R* = ArMes2, where Mes = 2,4,6-trimethylphenyl.[136] However, all of these prior isocyanometalates contain arylisocyanides, which are generally considered to be better π-acceptor ligands than alkylisocyanides.[137] On this basis, arylisocyanides should be more effective than alkylisocyanides in the stabilization of homoleptic complexes containing transition metals in formal negative oxidation states. Thus, although evidence has been presented for the existence of homoleptic alkylisocyanometalates, including $[Ru(CNtBu)_4]^{2-}$,[138] and $[Fe(CNtBu)_4]^{2-}$,[135] neither species has been isolated or unequivocally observed because of their substantial thermal instabilities. Indeed, the only well-established dianion of this type is $[Fe(CNXyl)_4]^{2-}$.[135]

Several years ago, the reduction of $[Co(CNtBu)_5][PF_6]$ by potassium naphthalene in THF was examined,[138b] and more recently the reaction of **1** with CN*t*Bu, with the hope of obtaining $[Co(CNtBu)_4]^-$. Although IR spectra of the reaction mixtures showed intense absorptions at about 1790−1720 cm^{-1}, suggestive of the presence of an isocyanocobaltate species, no product could be isolated. However, isolation of a stable and well-characterized triphenyltin derivative, $Ph_3SnCo(CNtBu)_4$, provided evidence for the existence of the cobaltate.[138b] In contrast, the treatment of a bright-red solution of **10** in THF at −78 °C with 4 equiv of CN*t*Bu, followed by workup, afforded orange crystals of composition $[K(18\text{-crown-}6)(THF)_2][Co(CNtBu)_4]$ (**16**), isolated in about 40% yield. Although the solid proved to be too thermally unstable at 20 °C to obtain elemental analyses on the bulk sample, ^1H and ^{13}C NMR spectra are consistent with its formulation.[139] IR spectra of **16** and $[K(18\text{-crown-}6)][Co(CNXyl)_4]$ (**17**) in THF in the isocyanide ν_{CN} region, ca. 2300−1600 cm^{-1}, show nearly identical spectral signatures, but the most intense absorptions occur at 1778 vs br and 1826 vs br cm^{-1}, respectively;[140−143] i.e., the alkylisocyanidecobaltate absorbs at nearly 50 cm^{-1} *lower* than the arylisocyanidecobaltate. In contrast, free alkyl isocyanides generally have a slightly higher ν_{CN} value than arylisocyanides. For example, neat CN*t*Bu and CNPh have CN stretching frequencies at 2134 and 2116 cm^{-1}, respectively.[144] Less electron-rich isocyanide metal complexes also show this "normal" trend for the ν_{CN} values. For example, the homoleptic cations, $[Mn(CNR)_6]^+$ have their most intense IR ν_{CN} absorptions at 2094 cm^{-1} for R = *t*Bu and at 2084 cm^{-1} for R = Ph.[145] In the past, observations that arylisocyanides almost invariably had lower ν_{CN} absorptions than alkylisocyanides in analogous complexes, especially in isocyanide-substituted metal carbonyls,[146] were presented as evidence that arylisocyanides were better acceptor ligands than alkylisocyanides. However, a careful analysis of IR and Raman spectra of $[Mn(CNR)_6]^z$, with z = 1 and 2 for R = alkyl and aryl, led to the conclusion that IR ν_{CN} data effectively underestimate the degree of back-bonding for arylisocyanides because they are relatively insensitive to the additional delocalization of the metal electron density into aryl π^* orbitals,[145] which is of key importance in making arylisocyanides better acceptors than alkyl isocyanides.[147] Indeed, for homoleptic isocyanide complexes of zerovalent metals, $M(CNR)_x{}^0$, generally, the IR ν_{CN} absorptions for given alkylisocyanide complexes occur at lower energies than those for corresponding arylisocyanides. Examples of this "anomalous" trend, as observed for **16** and **17**, will now be presented.

As expected, the isoelectronic nickel complexes $Ni(CNR)_4$ have corresponding, most intense IR ν_{CN} peaks at considerably higher energies than **16** and **17**, i.e., 2000 cm^{-1} for R = *t*Bu,[148−153] 2029 cm^{-1} for R = Xyl,[143] and 2031 cm^{-1} for R = Ph,[143] owing to the less basic or weaker π-donor ability of Ni^0 versus Co^-. However, they show the same, albeit much less pronounced, "anomalous" trend in IR ν_{CN} values as those observed for **16** and **17**.[154−156]

The differences in the IR spectra of the two iron(0) complexes $Fe(CNR)_5$, where R = *t*Bu and Xyl, are more dramatic and have been briefly discussed.[157] In hexane, the *t*BuNC complex shows two intense ν_{CN} peaks at 2005 and 1830 cm^{-1}, whereas the XylNC complex shows only one intense broad absorption at 1978 cm^{-1}.[158] Both molecules have distorted trigonal-bipyramidal geometry in the solid state (X-ray), but the axial and equatorial isocyanides show substantial differences in the two complexes. Thus, for $Fe(CNtBu)_5$, the isocyanides in the axial positions are close to linear, mean C−N−C = 163°, while those in the equatorial positions are appreciably bent, mean C−N−C = 146°.[159] Basset and coworkers attributed the unusually low energy band at 1830 cm^{-1} to the significantly bent equatorial isocyanides, which are expected to participate more than the axial groups in metal ($d\pi$)-to-isocyanide (π^*) back-bonding.[160] In contrast, they suggested that the absence of a similar low-energy IR ν_{CN} bond for $Fe(CNXyl)_5$ must indicate that all of the isocyanide ligands in this complex are relatively linear, for electronic and possibly steric reasons.[161,162] A recent single-crystal X-ray structure of $Fe(CNXyl)_5$ supports their proposal, where the mean axial and equatorial C−N−C angles were found to be 172° and 163°, respectively.[163] Mixed-ligand complexes of the type $Fe(PMe_3)_2(CNR)_3$ have been reported and also show very low ν_{CN} values, e.g., 1960 and 1720 cm^{-1} for R = phenyl, and quite bent isocyanides, e.g., mean C−N−C = 146(2)° for R = neopentyl.[164] Similar features are also exhibited by several electron-rich heteroleptic *tert*-butylisocyanide complexes.[157,169]

Single-crystal X-ray analysis of **16** revealed a well-defined cobaltate, shown in Figure 9, with some disorder in atom N1 and *tert*-butyl groups of four discrete isocyanides. The counterions, [K(18-crown-6)(THF)$_2$], are normal, albeit with disordered axial THF groups. They are well-separated from and do not appear to significantly perturb the anions. The cobalt atom lies on a mirror plane, resulting in the equivalence of two isocyanides, designated as C1, C1A, etc., and has a slightly distorted tetrahedral geometry, as defined by the four ligated isocyanide carbon atoms, where the twist angle is 81.6°. The average Co−C and C−N distances are 1.782(4) and 1.206(5) Å, respectively, which are within the range of corresponding values previously reported for $[Co(CNXyl)_4]^-$, 1.78(1) and 1.20(1) Å,[10] and $[Co(CNArMes_2)_4]^-$ for the $[PPN]^+$ salt, 1.783(4) and 1.206(8) Å, and the Na^+ salt, 1.800(8) and 1.192(4) Å,[136] respectively. In this context, it is interesting that the average Co−C distance in [K(cryptand-222)][Co(CO)$_4$], 1.766(5) Å,[24] is only slightly shorter than the corresponding values of the isocyanocobaltates, despite the larger size of the isocyanides versus CO. This comparison attests to the outstanding acceptor ability of the isocyanides in these complexes. Also noteworthy is that, although **16** has a significantly lower CN stretching frequency, ca. 1780 cm^{-1}, for the most intense absorption, than the arylisocyanocobaltates, where the values range from about 1812 to 1826 cm^{-1},[10,24,136] corresponding Co−C and C−N distances appear to be relatively insensitive to IR spectral differences. Similar comments have been made concerning nickel isocyanides.[143] In contrast, for metal carbonyls, the M−C and carbonyl C−O distances are generally quite sensitive functions of IR or Raman CO stretching frequencies.[165] However, as noted below, there are significant differences in the M−C and isocyanide C−N distances for $[Co(CNR)_4]^-$, where R = aryl, *t*Bu, and $[Fe(CNXyl)_4]^{2-}$.[135]

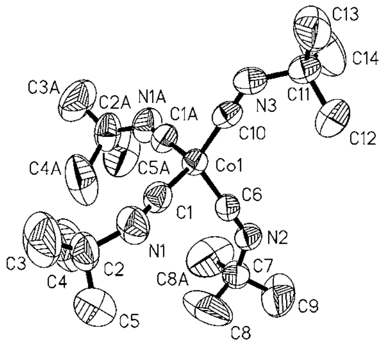

Figure 9. Molecular structure of anion **16**. Thermal ellipsoids are set at the 50% probability level, with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Co−C1 1.781(3), Co−C6 1.784(4), Co−C10 1.781(4), C1−N1 1.205(4), C6−N2 1.203(5), C10−N3 1.211(5), N1−C2 1.459(5), N2−C7 1.452(5), N3−C11 1.469(5); C1−N1−C2 138.4(5), C6−N2−C7 135.9(4), C10−N3−C11 134.1(3).

The major surprise in the structure of anion **16** was the high degree of bending observed for the isocyanide groups, with an average C−N−C angle of 137(2)°. For homoleptic isocyanide complexes, only $[Fe(CNXyl)_4]^{2-}$ comes close, with a corresponding angle of 144(3)°. However, the ferrate dianion has a significantly shorter average M−C distance, 1.765(3) Å, where the covalent radii of iron and cobalt are essentially identical,[107] a longer average C−N distance, 1.237(7) Å, and a much lower IR ν_{CN} absorption, ca. 1675 cm^{-1}[135] than anion **16**. These comparisons underscore prior observations that arylisocyanides usually show a lesser tendency to bend about nitrogen than alkylisocyanides, despite their better acceptor ability, in a given coordination environment, and this is likely due to an interplay of the electronic and steric effects.[155b,157] Indeed, the most strongly bent isocyanides reported to date occur in the heteroleptic methylisocyanidetantalum(I) complex $\mathrm{Ta(CNMe)_2(dmpe)_2Cl}$, which has an average C−N−C angle of 122.0(7)°. This species also has a long average C−N distance, 1.228(9) Å, similar to the value of 1.237(7) Å found in $[\mathrm{Fe(CNXyl)_4}]^{2-}$[135] and quite low IR ν_{CN} values of 1737 and 1695 cm^{-1}.[166] Interestingly, reduction of $\mathrm{Ta(CNMe)_2(dmpe)_2Cl}$ has been reported to afford a thermally unstable species, possibly $[\mathrm{Ta(CNMe)_2(dmpe)_2}]^-$, which undergoes facile reductive coupling of coordinated isocyanides in the presence of electrophiles. It seems likely that the strongly bent alkylisocyanide ligands are of key importance in facilitating this transformation.[155b,167] Indeed, it is possible that the thermal instabilities of $[\mathrm{Co(CN}t\mathrm{Bu)_4}]^-$, and species proposed to be $[\mathrm{Fe(CN}t\mathrm{Bu)_4}]^{2-}$[135] and $[\mathrm{Ru(CN}t\mathrm{Bu)_4}]^{2-}$,[138] may arise from analogous alkali-metal cation-mediated reductive coupling of the coordinated *tert*-butylisocyanide ligands.

■ CONCLUSION

Full details of the syntheses, isolation, and characterization of bis(anthracene)cobaltate(1−) (**1**) and (naphthalene)(1,5-cyclooctadiene)cobaltate(1−) (**10**) are presented. These reagents are useful storable sources of atomic $\mathrm{Co^-}$ because of the lability of the coordinated hydrocarbons in the cobaltates. Interestingly, whereas **1** readily reacts with organophosphites, $\mathrm{P(OR)_3}$, where R = Me and *i*Pr, to afford the homoleptic complexes $[\mathrm{Co(P(OR)_3)_4}]^-$, Jonas' classic $[\mathrm{Co(COD)_2}]^-$ fails to react for hours at 20 °C (as the potassium salt in THF) with these phosphites. However, we have not explored other possible differences in the reactivities of these two cobaltates, which may well depend on the temperature, counterion, and solvent. Interestingly, good use of the lability of **1** and the closely related bis(anthracene)ferrate(1−)[52] has been made in a recent examination by Wolf and co-workers of their reactions with phosphaalkynes RCP, where R = *t*Bu and adamantyl. The products are novel diphosphacyclobutadiene complexes $[\mathrm{M}(\eta^4\text{-}\mathrm{P_2C_2R_2})_2]^z$, with $z = 0$ and 1−, where M = Co and Fe, which have been isolated, characterized, and extensively evaluated.[168] Independent syntheses and applications of **1** and the iron analogue provide evidence that these species promise to be useful storable sources of atomic anions of cobalt (and iron) for many future endeavors.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format and single-crystal X-ray crystallography including crystal structure reports. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Professor Wolfgang Beck on the occasion of his 80th birthday.

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(40) Single crystals of [K(triglyme)$_2$][**1**] from THF invariably contain 0.5 equiv of cocrystallized free anthracene. Crystal data: $C_{51}H_{61}CoKO_8$, monoclinic, $P2_1/c$; cell constants a = 12.511(1) Å, b = 28.183(3) Å, c = 14.023(1) Å, and β = 105.816(2)°; V = 4757.5(8) Å^3; Z = 4; T = 173(2) K; 8427 reflections (6341 for $[I > 2\sigma(I)]$); R1 = 0.0340 $[I > 2\sigma(I)]$; wR2 = 0.0853 (all data).

(41) Crystal data: $C_{44}H_{52}CoKO_4$, monoclinic, $C2/c$; cell constants a = 20.170(2) Å, b = 16.421(2) Å, c = 13.2241(15) Å, and β = 120.527(2)°; V = 3772.8(7) Å^3; Z = 4; T = 173(2) K; 4298 reflections (3577 for $[I > 2\sigma(I)]$); R1 = 0.0476 $[I > 2\sigma(I)]$; wR2 = 0.1410 (all data).

(42) Crystal data: $C_{67}H_{93}CoK_2O_{14.5}$, monoclinic, $C2/c$; cell constants a = 27.534(3) Å, b = 9.7976(9) Å, c = 49.465(5) Å, and β = 96.106(2)°; V = 13268(2) Å^3; Z = 8; T = 173(2) K; 11749 reflections (5887 for $[I > 2\sigma(I)]$); R1 = 0.0635 $[I > 2\sigma(I)]$, wR2 = 0.1814 (all data).

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(140) Ideal tetrahedral $[Co(CNR)_4]^-$ species, with essentially linear isocyanides, are expected to show only one IR-active ν_{CN} band (of T_2 symmetry), but solution IR spectra of **16** and **17** also show well-defined shoulder spikes of medium intensity at 1832 and 1886 cm^{-1}, respectively.[24] Although ion pairing could perturb the anion and result in the additional peak, the IR spectrum of [K(cryptand-222)] $[Co(CNXyl)_4]$ in THF shows very similar features, ν_{CN} 2005 vw, 1900 m sh, 1815 vs br cm^{-1}.[10] However, the weakly coordinating and highly symmetric $[K(cryptand\text{-}222)]^+$ counterion appears unlikely to cause significant distortion of the geometry of the anion in solution, as is true for carbonylmetalate salts.[141] Most likely, the additional ν_{CN} bands, as well as the substantial width of the most intense peak, are due to the nonlinearity of the CNR groups; i.e., the true symmetry of these $[Co(CNR)_4]^-$ species is expected to be substantially lower than tetrahedral. Indeed, over 50 years ago, in a classic paper, Cotton and Zingales discussed this "breakdown of the infrared selection rules for the NC stretching modes" in neutral isocyanide complexes, such as $Ni(CNPh)_4$. They attributed the phenomenon to significant bending of the ligated isocyanides, which "spoils" the T_d symmetry of the formally tetrahedral complexes.[142] A recent X-ray structural characterization of $Ni(CNPh)_4$ has confirmed the presence of slightly nonlinear isocyanides, with an average C−N−C angle of 168.4(4)°.[143]

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(159) For two independent Fe(CN*t*Bu)$_5$ molecules in the asymmetric unit, axial C−N−C angles range from 151.6(9) to 177.1(8)°, while equatorial C−N−C angles range from 133.1(8) to 169.2(8)°. For each independent molecule, two of the three equatorial isocyanides are especially nonlinear, with a mean C−N−C angle of 135°.[157]

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