# Reduction of Terphenyl Co(II) Halide Derivatives in the Presence of Arenes: Insertion of Co(I) into a C−F Bond

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ⓢ Supporting Information

ABSTRACT: Reduction of $[(3,5-^{i}Pr_2-Ar^*)Co(\mu-Cl)]_2$ $(3,5-^{i}Pr_2-Ar^* = -C_6H-2,6-(C_6H_2-2,4,6-^{i}Pr_3)_2-3,5-^{i}Pr_2)$ with KC_8 in the presence of various arene molecules resulted in the formation of a series of terphenyl stabilized Co(I) half-sandwich complexes $(3,5-^{i}Pr_2-Ar^*)Co(\eta^6\text{-arene})$ (arene = toluene (**1**), benzene (**2**), C_6H_5F (**3**)). X-ray crystallographic studies revealed that the three compounds adopt similar bonding schemes but that the fluorine-substituted derivative **3** shows the strongest cobalt-η^6-arene interaction. In contrast, C−F bond cleavage occurred when the analogous reduction was conducted in the presence of C_6F_6, affording the salt $K[(3,5-^{i}Pr_2-Ar^*)Co(F)(C_6F_5)]$ (**4**), in which there is a three-coordinate cobalt complexed by a fluorine atom, a C_6F_5 group, and the terphenyl ligand Ar*-3,5-$^{i}Pr_2$. This salt resulted from the formal insertion of a putative $3,5-^{i}Pr_2-Ar^*Co$ species as a neutral or anionic moiety into one of the C−F bonds of C_6F_6. Reduction of $[(3,5-^{i}Pr_2-Ar^*)Co(\mu-Cl)]_2$ in the presence of bulkier substituted benzene derivatives such as mesitylene, hexamethylbenzene, *tert*-butylbenzene, or 1,3,5-triisopropylbenzene did not afford characterizable products.
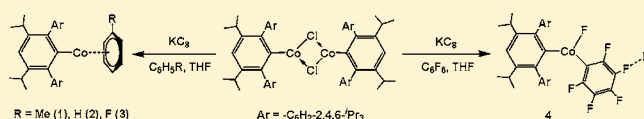
INTRODUCTION

Low-coordinate Co(I) complexes have received increasing attention during the past decade owing to their exceptionally high reactivity toward small molecules, as well as their potential catalytic applications. Various low-coordinate Co(I) compounds bearing different ligand sets have been reported,[1−15] and their synthesis and isolation usually require the use of multidentate ligands to stabilize the unsaturated cobalt center. Recently we reported the synthesis and reactivity of a half-sandwich Co(I) toluene complex $(3,5-^{i}Pr_2-Ar^*)Co(\eta^6-C_7H_8)$ (**1**, $3,5-^{i}Pr_2-Ar^* = -C_6H-2,6-(C_6H_2-2,4,6-^{i}Pr_3)_2-3,5-^{i}Pr_2)$, which was supported by a very bulky monodentate terphenyl ligand.[16] In the solid-state structure of **1**, the cobalt atom is η^6-bound to the aromatic ring of a toluene molecule. Such Co-η^6-arene interactions were not unprecedented and have been observed in several other low-valent cobalt complexes.[13−24] The bonding in **1** is composed of a 15-electron (arene)Co fragment which contains three unpaired spins, one of which becomes paired upon σ-bonding to the terphenyl ligand, to afford a paramagnetic compound with two upaired electrons. Theoretical investigations of model compounds $CH_3M(C_6H_6)$ (M = Cr, Fe, Co) revealed that the interaction energies between the CH_3M fragment and the benzene ring increase substantially between Cr (−9.6 kcal/mol) and Co (−22.1 kcal/mol).[25] This is consistent with our observation that, the monomeric, univalent chromium(I) compounds $(3,5-^{i}Pr_2-Ar^*)Cr(L)$ (L = THF or PMe_3) decompose via rearrangement when reacted with benzene or toluene in attempts to form $(3,5-^{i}Pr_2-Ar^*)Cr(\eta^6\text{-arene})$ complexes.[26] In contrast, the analogous Fe[27] or Co[16] derivatives form stable η^6 complexes with benzene or toluene (**1**), respectively. Furthermore, reactivity studies of complex **1** showed that it had a relatively low

reactivity in comparison to its iron counterpart $(3,5-^{i}Pr_2-Ar^*)Fe(\eta^6-C_6H_6)$. For example, the iron compound reacts readily with N_2O at room temperature to afford a μ-oxo bridged Fe(III) dimer.[28] In contrast, **1** does not react with N_2O even at elevated temperature. This low reactivity may be attributed to the exceedingly strong Co-η^6-arene interaction. Thus we reasoned that the reactivity of **1** might be enhanced by fine-tuning the Co-η^6-arene interaction through modification of the substituents on the arene ring to give weaker bonding to the metal. We hoped to extend the previous work with the aim of synthesizing a series of Co(I) compounds $(3,5-^{i}Pr_2-Ar^*)Co(\eta^6\text{-arene})$ and investigating the effects of the arene substituents on the cobalt-arene interaction. While this work was in progress Holland and his group showed that the unusual Co(I) β-diketiminate $[HC\{C(Bu^t)N(C_6H_3-2,6-^{i}Pr_2)\}_2]Co$, that is, CoL^{tBu}, $(HC\{C(^{t}Bu)N(C_6H_3-2,6-^{i}Pr_2)_2 = L^{tBu})$, in which the L^{tBu} ligand has a masked Co(I) center in the unusual $\kappa N,\eta^6$-arene bonding mode, reacted with fluorobenzene to afford $(L^{tBu}Co(\mu-F))_2$ and $L^{tBu}CoPh$ products.[29]

Herein we report the synthesis and characterization of $(3,5-^{i}Pr_2-Ar^*)Co(\eta^6\text{-arene})$ (arene = C_6H_6 (**2**), C_6H_5F (**3**)), the formation of the latter being in contrast to the insertion behavior of CoL^{tBu} toward C_6H_5F. The solid-state structures of **2** and **3** were determined by X-ray crystallography and compared to **1** to elucidate the strength of the cobalt-arene interactions. We also show that the reduction of $(3,5-^{i}Pr_2-Ar^*)CoCl$ in the presence of C_6F_6 resulted in the formation of the three-coordinate C−F inserted product $K[3,5-^{i}Pr_2-Ar^*Co-(F)C_6F_5]$, (**4**).

■ EXPERIMENTAL SECTION

General Methods. All manipulations were carried out by using modified Schlenk techniques under an atmosphere of N_2 or in a Vacuum Atmospheres OMNI-Lab drybox. All solvents were dried over an alumina column, followed by storage over 3 Å molecular sieves overnight, and degassed three times (freeze−pump−thaw) prior to use. The compound $[(3,5-^iPr_2-Ar^*)Co(\mu-Cl)]_2$ was prepared according to literature procedures.[30] ^{1}H NMR data were obtained on a Varian Mercury 300 MHz spectrometer and referenced to the residual protio benzene in the C_6D_6 solvent. Melting points were measured in glass capillaries sealed under N_2 by using a Mel-Temp II apparatus and are uncorrected. UV−vis data were recorded on a Hitachi-1200 spectrometer.

$(3,5-^iPr_2-Ar^*)Co(\eta^6-C_6H_6)$ (2). A brown solution of $[(3,5-^iPr_2-Ar^*)Co(\mu-Cl)]_2$ (0.98 g, 0.74 mmol) in about 30 mL of benzene was added dropwise to a suspension of KC_8 (0.37 g, 2.76 mmol) at 0 °C in about 20 mL of benzene. The dark mixture was stirred for about 24 h, then the solvent was removed under reduced pressure, and the dark residue was extracted with about 100 mL of hexane. The solution was filtered, and the green filtrate was concentrated to about 20 mL, which afforded X-ray quality green crystals of $2 \cdot C_6H_{12}$ after storage at −18 °C for several days. Yield: 0.77 g (74%). M.p.: 182 °C. Anal. Calcd. for $2 \cdot C_6H_{12}$: C, 82.4; H, 10.12. Found: C, 81.9: H, 9.81. ^{1}H NMR (300.08 MHz, C_6D_6, 20.0 °C): δ 65.84 (br s), 16.17 (s), 14.28 (br s), 8.68 (s), 7.55 (s), 7.42 (s), 6.88 (s), 3.28 (s), 2.91 (s), 2.56 (s), 1.23 (d), 0.26 (d), −0.83 (s), −62.00 (s). UV−vis [hexanes; λ_{max}, nm (ε, $L \cdot mol^{-1} \cdot cm^{-1}$)]: 660 (100).

$(3,5-^iPr_2-Ar^*)Co(\eta^6-C_6H_5F)$ (3). A mixture of $[(3,5-^iPr_2-Ar^*)Co(\mu-Cl)]_2$ (0.97 g, 0.73 mmol) and C_6H_5F (1.5 mL, 16.0 mmol) in about 30 mL of tetrahydrofuran (THF) was added dropwise to a suspension of KC_8 (0.47 g, 3.50 mmol) at 0 °C in about 20 mL of THF. The dark mixture was stirred for about 24 h; then the solvent was removed under reduced pressure and the dark residue was extracted with about 100 mL of hexane. The solution was filtered, and the green filtrate was concentrated to about 20 mL, which afforded X-ray quality green crystals of $3 \cdot C_4H_8O$ after storage at −18 °C for several days. Yield: 0.32 g (30%). M.p.: 165 °C. Anl. Calcd. for $3 \cdot C_4H_8O$: C, 78.75; H, 9.41. Found C, 78.13; H, 9.19. ^{1}H NMR (300.08 MHz, C_6D_6, 25.0 °C): δ 66.00 (br s), 16.17 (s), 14.30 (br s), 8.71 (br s), 7.55 (s), 7.24 (s), 6.88 (s), 3.30 (s), 2.91 (s), 2.56 (s), 1.30 (s), 1.18 (s), 0.31 (s), −0.81 (s), −62.04 (s). UV−vis [hexanes; λ_{max}, nm (ε, $L \cdot mol^{-1} \cdot cm^{-1}$)]: 386 (1000, sh), 664 (120).

$K[(3,5-^iPr_2-Ar^*)Co(F)(C_6F_5)]$ (4). A mixture of $[(3,5-^iPr_2-Ar^*)Co(\mu-Cl)]_2$ (0.90 g, 0.68 mmol) and C_6F_6 (1.5 mL, 13.0 mmol) in about 30 mL of THF was added dropwise to a suspension of KC_8 (0.55 g, 4.09 mmol) at 0 °C in about 20 mL of THF. The dark mixture was stirred for about 24 h; then the solvent was removed under reduced pressure and the dark residue was extracted with about 100 mL of hexane. The solution was filtered, and the green filtrate was concentrated to about 20 mL, which afforded X-ray quality green crystals of $4 \cdot C_6H_{14}$ after storage at −18 °C for several days. Yield: 0.28 g (25%). M.p.: 171 °C. Anal. Calcd for $4 \cdot C_6H_{14}$: C, 69.28; H, 8.08. Found: C, 68.90; H, 7.83. ^{1}H NMR (300.08 MHz, C_6D_6, 25.0 °C): δ 71.09 (s), 52.70 (br), 48.31 (br), 39.97 (s), 36.14 (s), 20.44 (br), 1.26 (m), 0.90 (s), 0.30 (s), −1.20 (br), −16.58 (s), −27.03 (s), −46.74 (s), −47.76 (s), −86.57 (br). UV−vis [hexanes; λ_{max}, nm (ε, $L \cdot mol^{-1} \cdot cm^{-1}$)]: 460 (32), 706 (42).

Reduction of $[(3,5-^iPr_2-Ar^*)Co(\mu-Cl)]_2$ in the Presence of Bulkier Arenes. Representative procedure: a mixture of $[(3,5-^iPr_2-Ar^*)Co(\mu-Cl)]_2$ (0.58 g, 0.44 mmol) and C_6Me_6 (1.61 g, 9.9 mmol) in about 30 mL of THF was added dropwise to a suspension of KC_8 (0.36 g, 2.67 mmol) at 0 °C in about 20 mL of THF. The dark mixture was stirred for about 24 h, and the solvent was removed under reduced pressure. The dark residue was extracted with about 100 mL of hexane. The solution was filtered, and the dark brown filtrate was concentrated to about 10 mL and stored at −18 °C for a week. No characterizable product could be isolated. Other reactions were implemented in a similar fashion by replacing C_6Me_6 with the corresponding arenes (mesitylene, *tert*-butylbenzene or 1,3,5-triisopropylbenzene). A similar

color change was observed, but no characterizable product was isolated.

X-ray Crystallography. Crystals of appropriate quality were removed from a Schlenk tube under a stream of nitrogen and immediately covered with a thin layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber on a copper pin, and quickly placed in the cold N_2 stream on the diffractometer.[31] Data for compound **3** were collected at 90 K on a Bruker APEX DUO diffractometer with Cu Kα radiation (λ = 1.54178 Å). Data for compounds **2** and **4** were collected at 90 K on a Bruker SMART APEX II diffractometer with Mo Kα (λ = 0.71073 Å) radiation and a CCD area detector. Absorption corrections were applied using SADABS program.[32] The crystal structures were solved by direct methods and refined by full-matrix least-squares procedures in SHELXTL.[33] All non-H atoms were refined anistropically. All H atoms were placed at calculated positions and included in the refinement using a riding model.

SQUID Magnetic Studies. The samples for magnetic measurements were sealed under vacuum in 4 mm quartz tubes. The magnetic properties were measured on a Quantum Design MPMSXL7 SQUID on 16.6 mg of **2**, 15.9 mg of **3**, and 14.8 mg of **4**. The sample was initially zero-field cooled to 5 K, and the magnetic susceptibility was then measured from 5 to 300 K in a 0.010 T applied magnetic field. The observed molar magnetic susceptibilities were corrected for the diamagnetic contribution of the constituents by subtracting −0.000509, −0.000512, and −0.000546 emu/mol for **2**, **3**, and **4**, respectively, values that were obtained from tables of Pascal's constants.[34]

■ RESULTS AND DISCUSSION

Synthesis and Characterization. The reduction of $[(3,5-^iPr_2-Ar^*)Co(\mu-Cl)]_2$[30] with KC_8 in benzene afforded green crystals of the half-sandwich complex $(3,5-^iPr_2-Ar^*)Co-(\eta^6-C_6H_6)$ (**2**) in 74% yield (Scheme 1). A similar reduction

Scheme 1. Synthetic Routes of 1−4
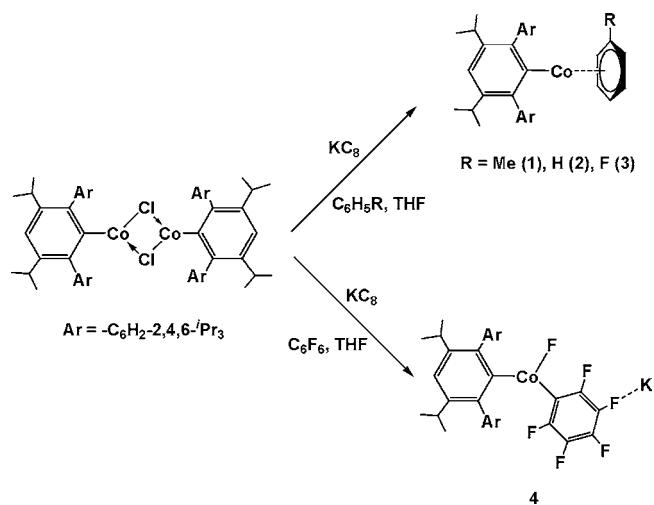
with KC_8 in THF in the presence of C_6H_5F also afforded green crystals of $(3,5-^iPr_2-Ar^*)Co(\eta^6-C_6H_5F)$ (**3**), but in a lower 30% yield (Scheme 1). In contrast, similar reduction in the presence of bulkier arenes (mesitylene, hexamethylbenzene, *tert*-butylbenzene or 1,3,5-triisopropylbenzene) did not yield any characterizable products, possibly a result of instability because of the steric repulsion between the substituents on the arenes and the isopropyl groups on the flanking rings of the terphenyl ligand, which may prevent complex formation. The results of all the attempted reduction in the presence of various arene molecules are summarized in Table 1.

Table 1. Summary of Results Obtained by Reduction in the Presence of Various Arenes

arenes	products
toluene	$(3,5\text{-}^iPr_2\text{-}Ar^*)Co(\eta^6\text{-}C_7H_8)$ (**1**)
benzene	$(3,5\text{-}^iPr_2\text{-}Ar^*)Co(\eta^6\text{-}C_6H_6)$ (**2**)
fluorobenzene	$(3,5\text{-}^iPr_2\text{-}Ar^*)Co(\eta^6\text{-}C_6H_5F)$ (**3**)
hexafluorobenzene	$K[(3,5\text{-}^iPr_2\text{-}Ar^*)Co(F)(C_6F_5)]$ (**4**)
mesitylene	N/A
hexamethylbenzene	N/A
tert-butylbenzene	N/A
1,3,5-triisopropylbenzene	N/A

The ^1H NMR spectra of **2** and **3** showed paramagnetically shifted resonances (see Supporting Information), suggesting high-spin d^8 electron configuration with two unpaired spins for the cobalt atoms in both compounds. This was further confirmed by the study of their magnetic properties in the solid state. The magnetic susceptibilities of **2** and **3** were measured from 5 to 300 K in a 0.010 T applied magnetic field. A plot of the inverse molar magnetic susceptibility of **2** versus temperature is linear and yields a Curie constant of 0.707(3) mol emu^{-1} K^{-1}, a Curie−Weiss temperature of −12.1(4) K, and a corresponding effective magnetic moment of 2.35 μ_B. A plot of the inverse molar magnetic susceptibility of **3** versus temperature is almost linear and yields a Curie constant of 1.00(1) mol emu^{-1} K^{-1}, a Curie−Weiss temperature of −18(1) K, and a corresponding effective magnetic moment of 2.79 μ_B.

Both complexes displayed Curie paramagnetism, and the resulting effective magnetic moment and inverse molar susceptibility were plotted in Figures 1 and 2 for **2** and **3**,
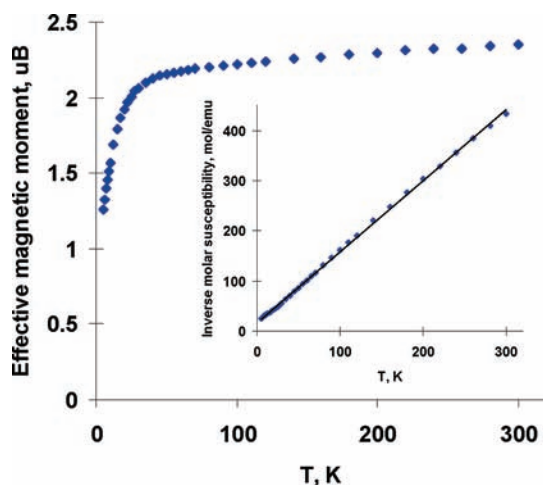
Figure 1. Effective magnetic moment of **2** between 5 and 300 K in a 0.010 T applied field. Inset: the corresponding inverse molar magnetic susceptibility of **2**.

respectively. The magnetic behavior of **2** and **3** conform to the Curie−Weiss law; however, they display somewhat different room temperature effective magnetic moments of 2.35 (**2**) and 2.79 (**3**) μ_B which correspond roughly to the spin-only value of 2.83 μ_B for an $S = 1$ ground state. Thus, the magnetic results are consistent with a high-spin Co(I) electron configuration in each case. The bonding in the Co(I) half sandwich complex and related Fe(I) species and the effects of geometrical distortion on their magnetic properties have been studied experimentally and computationally.[15,25] For Co(I) they are consistent with
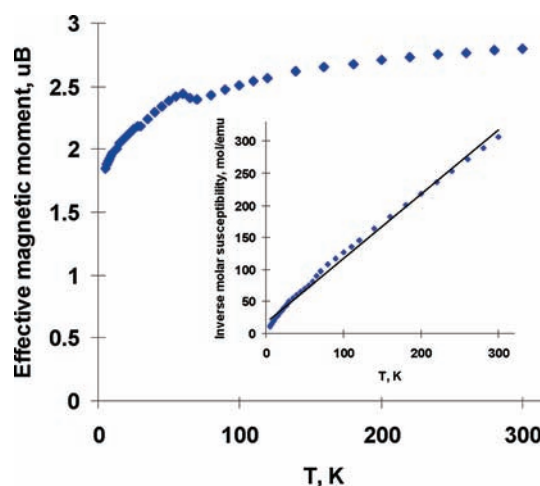
Figure 2. Effective magnetic moment of **3** between 5 and 300 K in a 0.010 T applied field. Inset: the corresponding inverse molar magnetic susceptibility of **3**.

the presence of two unpaired electrons in **1**−**3**. In addition, all three complexes were characterized by UV−vis spectroscopy, and each compound shows a characteristic absorption in the visible region (676 nm (**1**), 660 nm (**2**), 664 nm (**3**)).

The attempted synthesis of $(3,5\text{-}^iPr_2\text{-}Ar^*)Co(C_6F_6)$, to investigate the strong electron-withdrawing effect of the six fluorine atoms on metal-arene bonding, was performed in a similar fashion to that of **2** and **3**, by reduction of $[(3,5\text{-}^iPr_2\text{-}Ar^*)Co(\mu\text{-}Cl)]_2$[30] with KC_8 in THF in the presence of C_6F_6 (Scheme 1). The reaction gave, after workup and crystallization, green crystals of the unexpected C−F activated product $K[(3,5\text{-}^iPr_2\text{-}Ar^*)Co(F)(C_6F_5)]$ (**4**) in 25% yield which is a very rare example of a three coordinate transition metal fluoride complex.[35] Although C−F bond activation by Ni(0) complexes is well documented,[36] for Co(I) complexes it is a rarity.[29,37,38] For example, Li and co-workers demonstrated that a cyclometalation reaction involving C−F activation occurs when N,N'-bis-(2,6-difluorobenzylidene)hydrazone is reacted with $MeCo(PMe_3)_4$, to afford an mono-*ortho*-metalated cobalt(III) fluoride.[37] Holland and co-workers described an unusual, masked two-coordinate cobalt(I) complex, $L^{tBu}Co$ (L^{tBu} = $HC\{C(^tBu)N(C_6H_3\text{-}2,6\text{-}^iPr_2)\}_2$ in which the cobalt atom is bound to one of the ligand nitrogens and η^6 to one of the $C_6H_3\text{-}2,6\text{-}Pr^i_2$ rings, and showed that it cleaves to the C−F bond in fluorobenzene to give $[L^{tBu}Co(\mu\text{-}F)]_2$ and $L^{tBu}CoPh$ products.[29] In this binuclear oxidative addition reaction, the hemilabile β-diketiminate ligand can rearrange from the "masked" $\kappa N,\eta^6$-arene binding mode to the two-coordinate $\kappa^2 N,N'$ ligation mode during reductive cleavage of the C−F bond in fluorobenzene. The mechanism of the formation of **4** remains unknown. The cleavage of the C−F bond in C_6F_6 could be a result of direct reaction of C_6F_6 with KC_8, to produce KC_6F_5, which could then react with the $3,5\text{-}^iPr_2\text{-}Ar^*CoCl$ to generate $3,5\text{-}^iPr_2\text{-}Ar^*CoC_6F_5$ which then forms a complex with KF to generate **4**. The reaction could also proceed via the generation of a neutral, masked intermediate, Co(I) species of formula $3,5\text{-}^iPr_2\text{-}Ar^*Co$ which has a structure that is related to the κ,N,η^6-arene structure of $L^{tBu}Co$[29] that is generated in the reduction process. The neutral $3,5\text{-}^iPr_2Ar^*Co$ may then insert into a C−F bond in C_6F_6 to give the Co(III) species $3,5\text{-}^iPr_2Ar^*Co(C_6F_5)F$ which can be reduced to KC_8 to give **4**. Alternatively, the formation of **4** could result from the

generation of an $[3,5\text{-}^iPr_2\text{-Ar*Co}]^-$ anion from the reduction of $\{3,5\text{-}^iPr_2Ar^*Co(\mu\text{-Cl})\}_2$ with K_8 which then inserts into a C−F bond of C_6F_6 to afford the anion of **4** which can crystallizes with the K^+ cation. However, we note that over reduction of σ-bonded aryl Co(I) to give an anionic Co(0) species has not been described in the literature and that the generation of a neutral $3,5\text{-}^iPr_2Ar^*$ moiety is consistent with the formation of **1**−**3** upon its η^6-complexation with an arene ring.

Compound **4** was also characterized by UV−vis and ^{1}H NMR spectroscopy. It shows broad absorption bands at 460 and 706 nm in its UV−vis spectrum, which may be due to the $^4F \rightarrow {}^4P$ transitions of Co(II) ion in a distorted trigonal ligand field. The ^{1}H NMR spectrum of **4** features shifted and broadened resonances in the region between 71 and −86 ppm, consistent with the paramagnetic nature of the cobalt center in **4**. The magnetic properties of **4** were measured from 5 to 300 K in a 0.010 T applied magnetic field. It shows nearly ideal Curie paramagnetism, and the temperature effective magnetic moment and inverse molar susceptibility are plotted in Figure
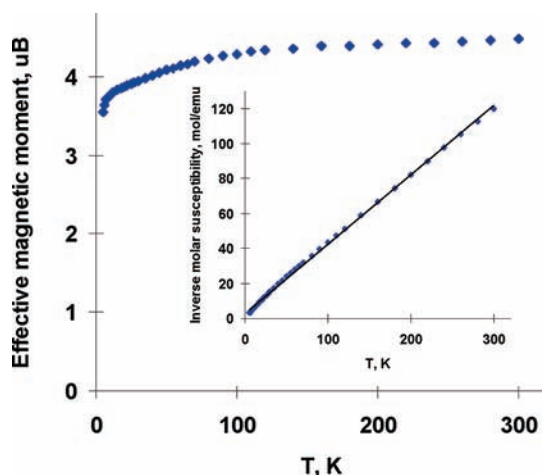
value of 3.87 μ_B for high-spin Co(II) $S = 3/2$ ground state, possibly as a result of spin orbit coupling.[39]

X-ray Crystal Structures. The formulation and solid state structures of **2** and **3** were established by X-ray crystallography (Figure 4 and Table 2). The structures of both compounds are

Table 2. Selected Crystallographic Data and Collection Parameters for 2−4

	$2 \cdot C_6H_{12}$	$3 \cdot C_4H_8O$	$4 \cdot C_6H_{14}$
formula	$C_{54}H_{79}Co$	$C_{52}H_{74}CoFO$	$C_{54}H_{75}CoF_6K$
fw	787.10	793.03	936.17
color	green	green	light green
habit	block	block	block
space group	$Pnn2$	$Pnn2$	$P2_1/c$
a, Å	14.4108(7)	14.4101(4)	16.0295(9)
b, Å	14.8230(7)	14.8119(3)	10.4041(6)
c, Å	10.9922(5)	10.9705(2)	30.7218(18)
α, deg	90	90	90
β, deg	90	90	99.3690(10)
γ, deg	90	90	90
V, Å^3	2348.06(19)	2341.55(9)	5055.2(5)
Z	2	2	4
d_{calcd}, Mg/m^3	1.113	1.126	1.230
θ range, deg	2.31−27.50	4.28−71.57	2.59−25.25
μ, mm^{-1}	0.399	3.154	0.478
no. of obsd data, $I > 2\sigma(I)$	4876	2088	5933
R_1 (obsd data)	0.0467	0.0740	0.0592
wR_2 (all data)	0.1211	0.2246	0.1771

broadly similar to the structure of the toluene analogue $(3,5\text{-}^iPr_2\text{-Ar*})Co(\eta^6\text{-}C_7H_8)$ (**1**) reported earlier.[16] A comparison of the key structural parameters of compounds **1**−**3** is illustrated in Table 3. In the solid state structure, the Co atom is

Figure 3. Effective magnetic moment of **4** between 5 and 300 K in a 0.010 T applied field. Inset: the corresponding inverse molar magnetic susceptibility of **4**.

3. The resulting room temperature effective magnetic moment

of **4** is 4.47 μ_B, which is higher than the expected spin-only

Table 3. Selected Bond Distances (Å) and Angles (deg) for 1−3

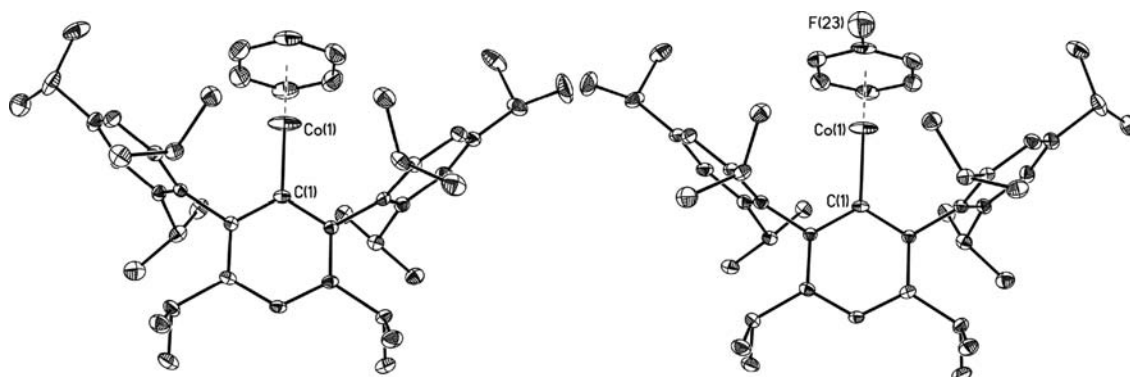|	1	2	3
Co(1)−C(1)	2.021(2)	1.985(3)	2.069(8)
Co(1)−centroid	1.659(1)	1.634(2)	1.557(5)
C(1)−Co(1)−centroid	167.6(2)	180.0	180.0
C(2)−Co(1)−C(6)	117.23(18)	117.0(3)	117.0(7)

Figure 4. Solid-state molecular structure of **2** (left) and **3** (right) (H atoms and solvent molecules are not shown; thermal ellipsoids are shown at 30% probability; F(23) in **3** is distorted over six positions around the ring, only one position is shown). Selected bond distances (Å) and angles (deg) for **2**: Co(1)−C(1) 1.985(3), Co(1)−centroid 1.634(2), C(1)−Co(1)−centroid 180.0; For **3**: Co(1)−C(1) 2.069(8), Co(1)−centroid 1.557(5), C(1)−Co(1)−centroid 180.0.

η^1 bonded to the terphenyl ligand and η^6 bonded to the arene molecule, affording a linear coordination C(ipso)−Co−centroid arrangement that has 180.0° angles in both **2** and **3**. The Co(1)−centroid distance in **2** is 1.634(2) Å, which is slightly shorter than the corresponding distance in **1** (1.659(1) Å). In comparison, **3** has a considerably shorter Co(1)−centroid distance (1.557(5) Å), indicating a much stronger Co-η^6-arene interaction in this case. In contrast, the related dimeric complex Ar′CoCoAr′ (Ar′ = -C$_6$H$_3$-2,6-(C$_6$H$_3$-2,6-^{i}Pr$_2$)$_2$) in which Ar′ behaves as an η^1:η^6-μ_2 bridging ligand, contains a much longer Co−centroid distance (1.7638(16) Å),[15] possibly a result of the steric repulsion between the two Ar′Co fragments. In view of the lower electron density on C$_6$H$_5$F ring because of the electron-withdrawing effect of the fluorine atom, the observed trend of the Co(1)−centroid distances in **1**−**3** implies that the major contribution of the Co-η^6-arene interaction involves backbonding from the cobalt atom to the aromatic ring, which is strengthened by electron withdrawing ring substituents. This is consistent with our previous observation in Ar′CoCoAr′, where the average C−C bond length within the metal-coordinated flanking arene rings is approximately 0.02 Å longer than that in the uncomplexed rings as a result of electron density transferred from the metal into the ring π^* orbitals.[15] The Co(1)−C(1) σ-bond length in **2** (1.985(3) Å) is 0.036 Å shorter than that in **1**. However, the Co(1)−C(1) distance in **3** (2.069(8) Å) is considerably longer. This is in agreement with the fact that **3** has the strongest Co-η^6-arene interaction among compounds **1**−**3**, as a result of which its Co(1)−C(1) σ-bond is weakened. Both the Co−C σ-bond and Co−centroid distances in the toluene complex **1** are slightly larger than those in the benzene complex **2** probably for steric reasons. The Co(1)-C(ipso) bond lengths in **1**−**3** are similar to those found for low-coordinate Co(II) complexes such as CoAr$^\#_2$ (2.001(3) Å, Ar$^\#$ = -C$_6$H$_3$-2,6-(C$_6$H$_2$-2,4,6-Me$_3$)$_2$),[40] Ar′CoN-(H)Ar$^\#$ (1.977(1) Å),[41] [BrCoAr$^\#$(THF)]$_2$ (2.053(8) Å),[42] [Li(OEt$_2$)Ar′CoI$_2$]$_2$ (1.998(5) Å),[29] CoAr′$_2$ (2.014(2) Å),[43] and Ar′CoN(SiMe$_3$)$_2$ (1.9732(16) Å).[43] A feature of the structures is that the difference in oxidation state between Co(I) and Co(II) has only a minor effect on the Co−C(ipso) bond distances. The almost linear C(ipso)−Co−centroid arrangement in **1**−**3** may be contrasted with the bent geometry, C(Ipso)−Co−centroid angle = 143.7(3)°, in Ar′CoCoAr′[15] and the similarly bent 140° angle for N−Co−centroid in $\kappa N, \eta^6$-arene bonded L^{tBu}Co.[29]

The formulation and solid-state structure of **4** was determined by X-ray crystallography (Figure 5 and Table 2). The Co(1) atom is in a three-coordinate planar coordination environment (sum of interligand angles is 360.01°), and is σ-bonded to a terphenyl ligand, a C$_6$F$_5$ group, and a fluorine atom. Three-coordinate cobalt complexes are relatively rare, and their synthesis and isolation requires the employment of bidentate,[13,14,44−48] tridentate,[4,6] or bulky monodentate ligands. Our group has reported several three-coordinate cobalt compounds using monodentate ligands, such as bulky silylamido or alkyloxo groups.[49−53] Compound **4** differs in that it contains three different monodentate ligands attached to the cobalt atom. The wide C(1)−Co(1)−C(43) angle (142.71(14)°) is probably due to the strong steric repulsion between the very bulky terphenyl ligand and the C$_6$F$_5$ group. The Co(1)−C(1) (2.007(3) Å) and Co(1)−C(43) (2.070(4) Å) distances are similar to reported Co−C lengths in other aryl cobalt species, such as CoAr$^\#_2$ (2.001(3) Å),[40] Ar′CoN(H)Ar$^\#$ (1.977(1) Å),[41] [BrCoAr$^\#$(THF)]$_2$ (2.053(8) Å),[42] [Li(OEt$_2$)-
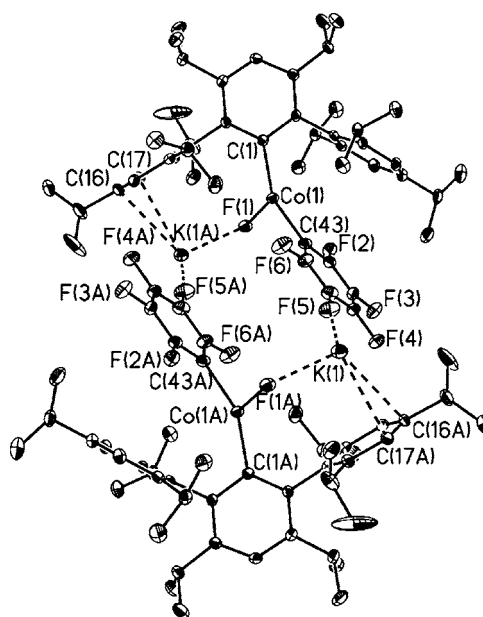

Figure 5. Solid-state molecular structure of **4** (H atoms and solvent molecules are not shown; thermal ellipsoids are shown at 30% probability) shown the K--F interactions with one of its neighbors. Selected bond distances (Å) and angles (deg.): Co(1)−F(1) 1.896(2), Co(1)−C(1) 2.007(3), Co(1)−C(43) 2.070(4), C(1)−Co(1)−F(1) 117.77(12), C(1)−Co(1)−C(43) 142.71(14), F(1)−Co(1)−C(43) 99.53(12).

Ar′CoI$_2$]$_2$ (1.998(5) Å),[29] Ar′CoCoAr′ (2.008(3), 2.019(3) Å),[15] CoAr′$_2$ (2.014(2) Å),[43] and Ar′CoN(SiMe$_3$)$_2$ (1.9732(16) Å).[43] The Co(1)−F(1) bond length (1.896(2) Å) is shorter than those in the fluoride salts [Co(Me)(F){C$_6$H$_3$-2-(C$_6$H$_5$CO)-3-F}(PMe$_3$)$_2$] (1.9316(14) Å),[54] [Co(Me)(F)-{C$_6$H$_3$-2-(CHNNCH-2,6-F$_2$C$_6$H$_3$)-3-F}(PMe$_3$)$_2$] (1.941(1) Å),[54] and {η^3-HB-(3-^{t}Bu-pyrazolyl)$_3$}CoF (2.060(3) Å),[55] which is probably due to the lower coordination number at cobalt in **4**. The potassium ion weakly interacts with two carbon atoms (C(16A) and C(17A)) from one flanking aryl ring of the terphenyl ligand, as well as four fluorine atoms (F(5), F(1A), F(1B), F(2A)). The K(1)···C(16A) (3.225(4) Å) and K(1)···C(17A) (3.080(4) Å) distances are within the range of K···C(arene) distances (3.028−3.303 Å) in the salt KAr′Ge-GeAr′.[56] The K···F distances are in the range of 2.501−3.060 Å. With such K···F and K···C secondary interactions, the K[(3,5-^{i}Pr$_2$-Ar*)Co(F)(C$_6$F$_5$)] unit is repeated in three dimensions in the solid state, thus forms an infinite coordination polymer framework structure.

CONCLUSIONS

In summary, compounds (3,5-^{i}Pr$_2$-Ar*)Co(η^6-arene) (arene = C$_6$H$_6$ (**2**), C$_6$H$_5$F (**3**)) were synthesized by reduction of [(3,5-^{i}Pr$_2$-Ar*)Co(μ-Cl)]$_2$ with KC$_8$ in the presence of the corresponding arene molecules. Both complexes were characterized by UV−vis and ^{1}H NMR spectroscopy, as well as SQUID magnetic study, which confirm the high-spin d^8 electron configuration for the cobalt centers. The solid-state structures of these two compounds in comparison to that of (3,5-^{i}Pr$_2$-Ar*)Co(η^6-C$_7$H$_8$) (**1**) indicate that **3** has the strongest Co-η^6-arene interaction among the three compounds. Furthermore, attempts to reduce [(3,5-^{i}Pr$_2$-Ar*)Co(μ-Cl)]$_2$ with KC$_8$ under the same conditions in the presence of C$_6$F$_6$ afforded the unexpected three-coordinate Co(II) complex

K[(3,5-^{i}Pr$_2$-Ar*)Co(F)(C$_6$F$_5$)] (**4**), which arose from the formal insertion of a 3,5^{i}Pr$_2$-Ar*Co moiety into a C−F bond of C$_6$F$_6$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR spectra and crystallographic information files (CIFs) for **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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