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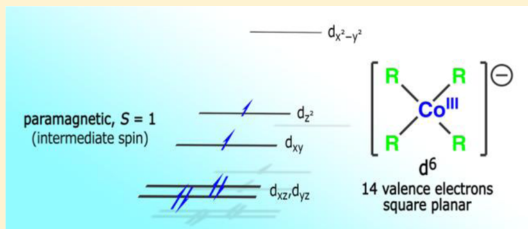
Homoleptic Organocobalt(III) Compounds with Intermediate Spin

M. Angeles García-Monforte,[†] Irene Ara,[†] Antonio Martín,[†] Babil Menjón,*[,†] Milagros Tomás,[†] Pablo J. Alonso,*[,‡] Ana B. Arauzo,[‡] Jesús I. Martínez,[‡] and Conrado Rillo[‡]

[†]Instituto de Síntesis Química y Catálisis Homogénea (iSQCH) and [‡]Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC−Universidad de Zaragoza, C/Pedro Cerbuna 12, E-50009 Zaragoza, Spain

Ⓢ *Supporting Information*

ABSTRACT: Homoleptic organocobalt(III) compounds with formula $[NBu_4][Co^{III}(C_6X_5)_4]$ [X = F (**3**), Cl (**4**)] were obtained in reasonable yields by chemical oxidation of the corresponding divalent species $[NBu_4]_2[Co^{II}(C_6X_5)_4]$ [X = F (**1**), Cl (**2**)]. The $[Co^{III}(C_6X_5)_4]^-/[Co^{II}(C_6X_5)_4]^{2-}$ couples are electrochemically related by quasi-reversible, one-electron exchange processes at moderate potential: $E_{1/2} = -0.29$ (X = F) and −0.36 V (X = Cl) versus saturated calomel electrode. The $[Co^{III}(C_6X_5)_4]^-$ anions in salts **3** and **4** show an unusual square-planar geometry as established by single-crystal X-ray diffraction methods. According to their stereochemistry, these Co^{III} derivatives (d^6) are paramagnetic non-Kramers systems with a large zero-field splitting contribution and no observable electron paramagnetic resonance (EPR) spectrum. The thermal dependence of their magnetic susceptibilities can be explained in terms of a spin-Hamiltonian formalism with *S* = 1 ground state (intermediate spin) and substantial spin−orbit contribution. The magnetic properties of the square-planar d^7 parent species $[NBu_4]_2[Co^{II}(C_6X_5)_4]$ were also thoroughly studied both at microscopic (EPR) and macroscopic levels (alternating current and direct current magnetization measurements). They behave as *S* = 1/2 (low spin) systems with mainly $(d_{z^2})^1$ electron configuration and a certain degree of s-orbital admixture that has been quantified. The electronic structures of all four open-shell $[Co(C_6X_5)_4]^{q-}$ compounds (*q* = 1, 2) accounting for their respective magnetic properties are based on a common orbital energy-level diagram.



■ INTRODUCTION

Cobalt(III) compounds played a key role in the development of Werner's coordination theory on "complex" species.[1] As in any other d^6 metal species, Co^{III} coordination compounds show a sharply marked tendency to adopt octahedral (*OC*-6) structures. The ligand field of octahedral geometry causes the d orbitals to split into the t_{2g}/e_g manifolds, whereby the six d electrons of the metal center are paired at the lower t_{2g} level (or those derived thereof by symmetry lowering). This results in diamagnetic species with coordinative and electronic saturation (18 valence electrons). The stability and chemical inertness derived from this 2-fold saturation enabled the preparation and isolation of different isomers and stereoisomers for the same stoichiometry (including enantiomers), which were instrumental in the inception of Werner's stereochemical model as well as in its later confirmation. The vast majority of the thousands of Co^{III} coordination compounds prepared since then show in fact *OC*-6 structures.[2]

Organocobalt(III) compounds are no exception to this general trend,[3] as they typically exhibit *OC*-6 or pseudo-(*OC*-6) structures, depending on the σ or π nature of the coordinated organic group. Important examples of these closed-shell, 18-electron species are given by the homoleptic $[Co^{III}(C{\equiv}CR)_6]^{3-}$ anions (R = H, Me,[4] and $SiMe_3$[5]) and some hexacarbene derivatives[6] of Co^{III} as well as by the classic sandwich cation $[Co^{III}Cp_2]^+$ and the like.[7] However, unsaturated organocobalt(III) species with open-shell electronic structure[8] are much less common. Thus, just a handful of 16-electron square-pyramidal (*SPY*-5) compounds have been structurally characterized,[9] and, as far as we know, the presumably tetrahedral (*T*-4) complex $[Li(THF)_4]$-$[Co^{III}(\text{norborn-1-yl})_4]$ (THF = tetrahydrofuran) appears to be the only example of 14-electron species to have been isolated.[10] Compounds with formula $[Co^{III}(NHC)_4]^{3+}$ (NHC = 1,3-dialkyl-4,5-dimethylimidazole-2-ylidene)[11] have been suggested to arise by electrochemical oxidation of the $[Co^{II}(NHC)_4]^{2+}$ precursors in THF solution ($E_{1/2}$ = 1.2−1.5 V vs saturated calomel electrode (SCE)), but no spectroscopic or structural information seems yet to be available for the oxidized species. To the best of our knowledge, no well-established organocobalt(III) compound with *SP*-4 structure has been reported so far.

The organometallic chemistry of Co^{III} receives continued attention given the involvement of organocobalt(III) species in certain biological processes.[12] Furthermore, there is a special interest in the preparation of nonoctahedral Co^{III} compounds due to the close relationship between spin state and the stereochemistry of a given d^n metal complex with partially occupied d orbitals ($1 < n < 9$).[13]

We now report the synthesis and characterization of the four-coordinate organocobalt(III) derivatives $[NBu_4][Co^{III}(C_6X_5)_4]$ [X = F (**3**), Cl (**4**)]. According to their square-planar (*SP*-4) structure, they exhibit an interesting and rather unusual

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intermediate-spin behavior ($S = 1$). Full details of the synthesis of the organocobalt(II) precursors $[NBu_4]_2[Co^{II}(C_6X_5)_4]$ [X = F (**1**), Cl (**2**)], which had been briefly outlined,[14] are also given together with their spectroscopic, structural, and magnetic characterization.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of the Organocobalt(II) Precursors. Anhydrous cobalt(II) halides, CoX_2, or solvates thereof, are known to react with a number of Grignard reagents, RMgX, giving rise to organocobalt(II) compounds of general formula "CoR_2".[15] The precise formulation of the resulting compounds is largely dependent on the reaction conditions and on the nature of the R group but, in most cases, they may be considered as solvates $CoR_2(solv)_x$[16] or higher aggregates $(CoR_2)_n$.[17] Except for extremely bulky R groups,[18] organocobalt(II) compounds with higher R contents can be obtained by treatment of the same precursors with organolithium reagents, LiR. Thus, homoleptic derivatives with formulæ $[Li(THF)_4][Co^{II}(Mes)_3]$ (Mes = mesityl),[19] $[Li(THF)_2]_2[Co^{II}\{(o\text{-}C_6H_4)_2O\text{-}\kappa^2C\}_2]$,[20] $Li_2[Co^{II}\{C_6H_3(OMe)_2\text{-}2,6\}_4]\cdot 3THF$,[21] and $[Li(tmen)]_2[Co^{II}R_4]$ (R = Me, CH_2SiMe_3; tmen = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-amine)[22] were obtained by reaction of CoX_2 with the corresponding LiR in excess.[23] Compounds with even higher degree of substitution are achieved using sodium or potassium alkynyls, QC≡CR, a method used to prepare different salts of the apparently six-coordinate $[Co(C{\equiv}CR)_6]^{4-}$ anions (R = H, Me, Ph,[4,24] Cy[25]).

The organolithium method also proves to be useful in the case where R is a perhalophenyl group: C_6F_5 or C_6Cl_5. Thus, the homoleptic $[NBu_4]_2[Co^{II}(C_6X_5)_4]$ compounds [X = F (**1**), Cl (**2**)] are conveniently prepared (eq 1) by low-temperature treatment of the halo-complex precursor $[NBu_4]_2[CoCl_2Br_2]$ with the corresponding organolithium reagent.

$$[NBu_4]_2[CoCl_2Br_2] + LiC_6X_5 \rightarrow [NBu_4]_2[Co^{II}(C_6X_5)_4] \quad \mathbf{1}(X = F), \mathbf{2}(X = Cl) \tag{1}$$

Compounds **1** and **2** are isolated as highly colored solids in more than 80% yield. They were characterized by analytical and spectroscopic methods. Their IR spectra are similar to those corresponding to the isoleptic nickel derivatives $[NBu_4]_2[Ni^{II}(C_6X_5)_4]$.[26] Compound **1** shows strong, sharp absorptions at 1483 and 945 cm^{-1}, respectively, which are attributable to C−C and C−F stretching modes of the C_6F_5 ring. A medium-sized absorption at 754 cm^{-1} is assigned to the so-called X-sensitive mode with mainly ν(M−C) character.[27] This vibration appears as a weak absorption at 810 cm^{-1} in the perchlorophenyl derivative **2**. In this compound, a double band of unequal intensity at 579 and 595 cm^{-1} is attributed to ν(M−C). All the referred vibration modes are sensitive to the metal oxidation state (see below).[27a]

Four-substituted Co^{II} compounds are known to face a structural dichotomy between tetrahedral (*T*-4) and square-planar (*SP*-4) geometries. For instance, an *SP*-4 structure was described for the cyano complex $[N(PPh_3)_2][Co^{II}(CN)_4]\cdot 4DMF$,[28] (DMF = dimethylformamide), whereas a *T*-4 structure was reported for the homoleptic "ate" compound $[Li(tmen)]_2[Co^{II}(CH_2SiMe_3)_4]$.[29] In the latter case, important covalent cation/anion interactions were observed, which might possibly effect the molecular geometry found for this compound.

To resolve this dichotomy, the crystal and molecular structures of the perfluorophenyl compound **1** were established by X-ray diffraction methods on single crystals of the $\mathbf{1}\cdot 0.3CH_2Cl_2$ solvate, which was found to be isostructural with $[NBu_4]_2[Ni^{II}(C_6F_5)_4]\cdot 0.3CH_2Cl_2$.[26] The lattice is made of separate cations and anions with interstitial solvent molecules interspersed. The metal within the $[Co^{II}(C_6F_5)_4]^{2-}$ anion exhibits an *SP*-4 coordination environment (Figure 1), as evidenced by the very small continuous shape measure (CShM) value obtained for that geometry: $S(SP\text{-}4) = 0.12$.[30] The C_6F_5 rings are arranged almost perpendicularly to the coordination plane (ca. 80° tilt angles) with a helical disposition around the metal center. They are also considerably swung with different Co−C^{ipso}−C^{ortho} angles within each ring, the largest difference being 118.6(7)° versus 127.8(7)°. Accordingly, different Co···F distances are observed for the corresponding F^{ortho} substituents: 304 versus 328 pm in the case of the greatest difference. All of these distances are, however, too long to denote the existence of any bonding interaction in the axial direction. Acute C^{ortho}−C^{ipso}−$C^{ortho'}$ angles are observed in the aryl rings (113.6(9)° average) as usually found when electron-withdrawing perhalophenyl groups are bound to more electropositive centers.[31]

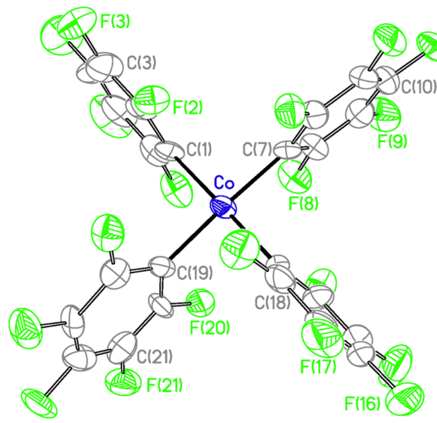

Figure 1. Thermal ellipsoid diagram (50% probability) of the $[Co^{II}(C_6F_5)_4]^{2-}$ anion in $\mathbf{1}\cdot 0.3CH_2Cl_2$. Selected bond lengths (pm) and angles (deg) with estimated standard deviations: Co−C(1) 195.6(9), Co−C(7) 196.7(9), Co−C(13) 196.9(9), Co−C(19) 195.6(9), C(1)−Co−C(7) 90.9(3), C(1)−Co−C(13) 176.9(4), C(1)−Co−C(19) 90.1(4), C(7)−Co−C(13) 90.2(3), C(7)−Co−C(19) 175.2(4), C(13)−Co−C(19) 89.0(3), Co−C(1)−C(2) 121.5(7), Co−C(1)−C(6) 125.2(8), Co−C(7)−C(8) 118.6(7), Co−C(7)−C(12) 127.8(7), Co−C(13)−C(14) 123.5(8), Co−C(13)−C(18) 122.4(8), Co−C(19)−C(20) 121.7(7), Co−C(19)−C(24) 124.6(8), average C^{ortho}−C^{ipso}−$C^{ortho'}$ 113.6(9).

The average Co^{II}−C(sp^2) distance in **1** (196.2(9) pm) is considerably shorter than the Co^{II}−C(sp^3) distance in the *T*-4 compound $[Li(tmen)]_2[Co^{II}(CH_2SiMe_3)_4]$ (215.1(8) pm average)[29] and longer than the Co^{II}−C(sp) distance in the *SP*-4 cyano complex $[N(PPh_3)_2][Co^{II}(CN)_4]\cdot 4DMF$ (187(1) pm average),[28] in line with the different hybridization of the C-donor atom in each case. The slightly shorter Co^{II}−C(sp^2) distance found in the carbene derivative $[Co(NHC\text{-}Et)_4][BF_4]_2$ (193.0(3) pm average; NHC-Et = 1,3-diethyl-4,5-dimethylimidazole-2-ylidene)[11] can be attributed to its cationic nature. The average M^{II}−C(sp^2) distance in **1** is slightly longer than that found in the isoleptic and isostructural species $[NBu_4]_2[Ni^{II}(C_6F_5)_4]$ (Ni^{II}−C 192.3(5) pm)[26] in keeping

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with the slight contraction of the radii along each transition series.[32]

The structure of the perchlorophenyl compound **2** could not be directly established due to a lack of suitable single crystals for X-ray diffraction purposes. Nevertheless, a comparison of the magnetic properties of compounds **1** and **2** (see below) will allow us to assign to the latter a similar structure to that actually found for the former.

Magnetic Properties of the Organocobalt(II) Precursors. Compounds **1** and **2** show rich electron paramagnetic resonance (EPR) spectra from room temperature to 4.2 K. The X- and Q-band spectra of a polycrystalline powder sample of **1** measured at 77 K are shown in Figure 2, and those

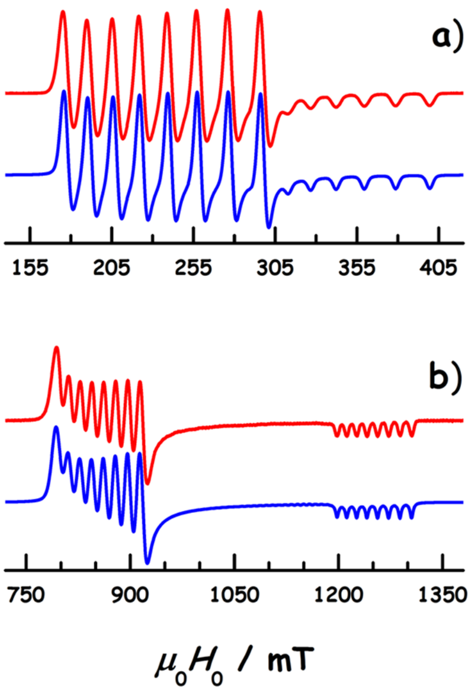

Figure 2. EPR spectra (red traces) of a polycrystalline powder sample of **1** measured at 77 K in X-band (a) and in Q-band (b). The blue traces correspond to calculated spectra (see text for details). No better resolution was attained at 4.2 K.

corresponding to compound **2** are depicted in Supporting Information, Figure S1. The spectra of CH_2Cl_2 solutions of **1** and **2** show no significant difference from those obtained on solid samples. This invariance indicates that both compounds preserve the same structure in CH_2Cl_2 solution as in the solid state. In all these cases, the spectra consist of two octets associated with the hyperfine interaction with the ^{59}Co nucleus (I = 7/2; 100% natural abundance),[33] which are partially overlapped in the X-band and clearly separated in the Q-band. The shape of the low-field features indicates that the metal is in an axial local environment; hence, the following spin-Hamiltonian is used to describe the observed spectra:

$$\mathcal{H} = \mu_B H_0\{(g_\perp \sin\theta)S_x + (g_\parallel \cos\theta)S_z\} + \{A_\perp(S_xI_x + S_yI_y) + A_\parallel S_z\} \quad (2)$$

In this Hamiltonian, $S = 1/2$, H_0 stands for the intensity of the applied magnetic field making an angle θ with the axis of the paramagnetic entity, and the rest of symbols have the usual meanings. Calculated spectra for compounds **1** and **2** using this axial model and the spin-Hamiltonian parameters given in Table 1 are depicted in Figure 2 and Supporting Information, Figure S1, respectively. They show satisfactory agreement with the experimental spectra.

Table 1. Magnetic Parameters for the Organocobalt(II) Compounds 1 and 2[a]

compound	$[NBu_4]_2[Co^{II}(C_6X_5)_4]$		$[NBu_4][Ni^{III}(C_6X_5)_4]$[b]	
X	F (**1**)	Cl (**2**)	F	Cl
$g_\parallel$	1.935(5)	1.955(5)	1.910(5)	1.935
$g_\perp$	2.828(2)	2.747(2)	2.940(5)	2.874
$\lvert A_\parallel \rvert$ (MHz)	418(2)	453(2)		
$\lvert A_\perp \rvert$ (MHz)	680(3)	660(3)		
C (emu·mol^{-1})	0.617(1)	0.591(1)	0.654(1)	0.633
μ_{eff} (μ_B)[c]	2.22	2.17	2.29	2.25

[a]A first estimate of the principal values of the $\tilde{g}$ and $\tilde{A}$ tensors can be directly read from the spectra. These parameters were subsequently refined by fitting the calculated spectra (ref 67) to the experimental ones. [b]For the sake of comparison, the values from ref 26 that correspond to the isoelectronic organonickel(III) complexes are also included. [c]Calculated magnetic moment for a doublet spin system (S = 1/2) with spin-only contribution: μ_{eff} = 1.73 μ_B.

The thermal dependence of the magnetic susceptibility, $\chi(T)$, of compounds **1** and **2** was measured between 1.8 and 275 K, and the results obtained are shown in Figure 3 and Supporting

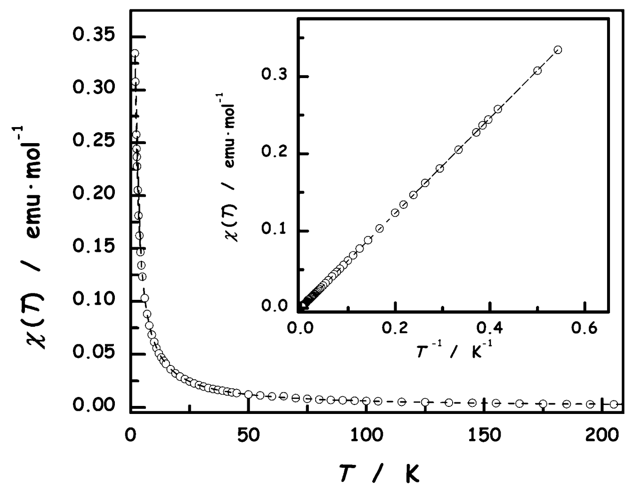

Figure 3. Thermal dependence of the magnetic susceptibility, $\chi(T)$, of a polycrystalline powder sample of **1**. Open circles represent measured values, whereas the dashed line corresponds to the calculated thermal dependence using a Curie law with the Curie constant given in Table 1. (inset) Dependence of $\chi(T)$ as a function of $1/T$.

Information, Figure S2, respectively. Such dependence can be described by a simple Curie law, $\chi(T) = \chi_0 + C/T$, where χ_0 accounts for the temperature-independent contributions — mainly due to the diamagnetism of the organic framework— and where the Curie constant, C, can be determined from the EPR data (Table 1). Dashed lines in Figure 3 and Supporting Information, Figure S2 correspond to the thermal dependence of $\chi(T)$ calculated in this way. Additional representations of both experimental and calculated $\chi(T)$ values against T^{-1} are depicted as insets to emphasize the linear dependence predicted by the Curie law. Excellent agreement is obtained between calculated values and experimental data for compound **1** (Figure 3). For compound **2** just a slight misfit is observed in

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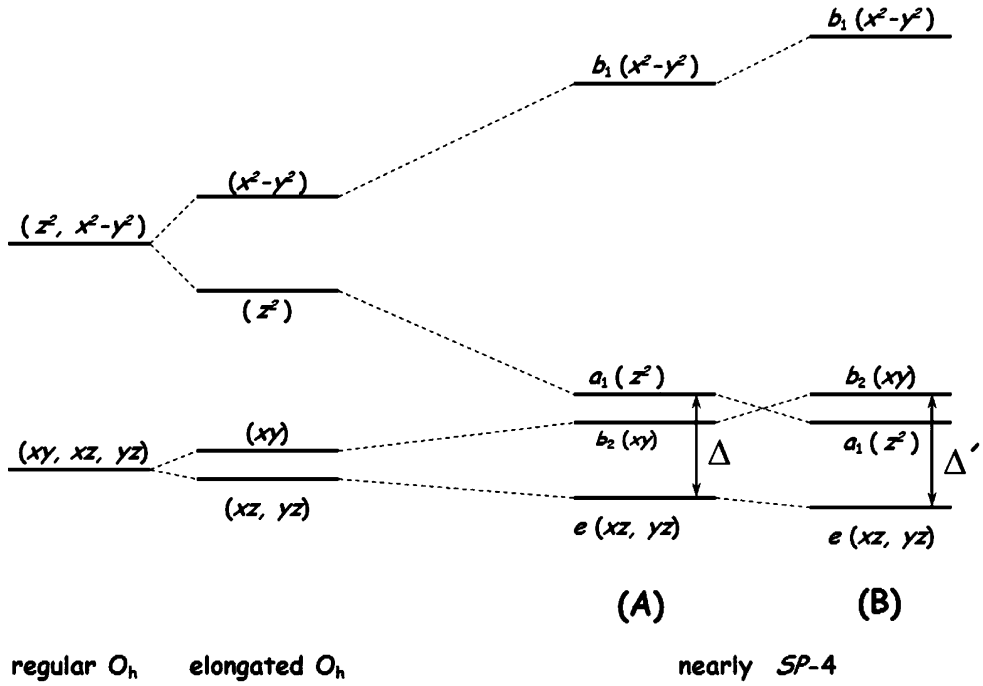

Figure 4. Single-electron energy levels in regular octahedral and tetragonally elongated octahedral environments (left) and their correlation with those in an *SP*-4 environment (right). In the latter case, levels are labeled according to their transformation properties under D_4 symmetry operations. The two possible orderings of the $a_1(z^2)$ and $b(xy)$ levels for mainly σ-donor ligands are labeled **A** and **B**.

the low-temperature region due to an extra contribution at ca. 6 K (Supporting Information, Figure S2), the intensity of which depends on the preparation batch and is thus likely due to an impurity. This contribution is negligible above 15 K, as indicated by the good match shown by the susceptibility values at higher temperature, regardless of the relative intensity of the low-temperature anomaly. After much effort, we succeeded in largely reducing the amount of impurity but failed to completely remove it.

Low-temperature magnetization values per formula unit measured as a function of the reduced magnetic field, $\mu_B H/k_B T$, for both compounds **1** and **2** are shown in Supporting Information, Figure S3. They show saturation trends corresponding to $S = 1/2$ systems, in keeping with the EPR data and the magnetic susceptibility results just discussed. Excellent agreement with the calculated evolution is observed using a Brillouin function and taking into account the anisotropy of the $\tilde{g}$ tensor.[34] The effective magnetic moment thus derived, μ_{eff}, is in agreement with the *g*-factors obtained from EPR measurements (Table 1). In view of the closely similar overall magnetic behavior of the organocobalt(II) compounds **1** and **2**, it can be inferred that they should also have similar structures.

The electronic properties of an *SP*-4 metal complex with D_4 local symmetry at the metal and mainly σ-donor ligands can be described with the single-electron energy scheme depicted in Figure 4. Whereas the orbital doublet $e(d_{xz},d_{yz})$ is invariably the lowest energy level[35] and the $b_1(d_{x^2-y^2})$ orbital is the highest one, the actual ordering of the $a_1(d_{z^2})$ and $b_2(d_{xy})$ orbitals depends on the strength of the ligand field, the two possibilities being shown in Figure 4. It is worth noting that the principal *g* values obtained for compounds **1** and **2** are similar (Table 1) to those reported for the isoelectronic species $[Ni^{III}(C_6X_5)_4]^-$ (X = F, Cl). Considering this close relationship, it can be concluded that the unpaired electron in the cobalt derivatives **1** and **2** is also mainly in the $a_1(d_{z^2})$ orbital (**A** in Figure 4) based on the same arguments used in the nickel case (see Supporting Information for details).[26]

To analyze the magnetic properties of our Co^{II} compounds we started using the model introduced by McGarvey to deal with low-spin d^7 systems.[36] We also adhere to the approximation adopted by Nishida and Kida that neglects any contribution of the $(d_{x^2-y^2})^1$ spin doublet.[37] It is worth noting that this approximation becomes strictly true in axial systems with the unpaired electron in a z^2-like orbital.[38] This approach is therefore particularly suited to our case given the $(d_{z^2})^1$ electron configuration and the axial character of the paramagnetic $[Co^{II}(C_6X_5)_4]^{2-}$ entities (X = F, Cl).

To describe the electronic structure of the Co^{II} ion (d^7) it is convenient to use the hole formalism. A Slater determinant characterizing the three-particle system will have the form $\|d_{x^2-y^2}\alpha, d_{x^2-y^2}\beta, \chi\|$, where α and β, respectively, indicate the m_s = +1/2 and m_s = −1/2 spin states for the corresponding one-electron orbital function. This determinant will hereinafter be denoted simply by $|\chi\rangle$, where χ stands for the wave function of the unpaired electron. A pair of Kramers conjugate wave functions that spans the ground state is given by

$$\phi^{(+} = c_z|\varphi^{(z}\alpha\rangle + c_s\frac{1}{\sqrt{2}}\{|d_{xz}\beta\rangle + i|d_{yz}\beta\rangle\}$$

$$\phi^{(-} = c_z|\varphi^{(z}\beta\rangle - c_s\frac{1}{\sqrt{2}}\{|d_{xz}\alpha\rangle - i|d_{yz}\alpha\rangle\} \quad (3)$$

with c_z and c_s being real coefficients, such that $c_z^2 + c_s^2 = 1$. In the widely used approach of Nishida and Kida,[37] the $\varphi^{(z}$ orbital is a pure d_{z^2} one. However, severe misfit is frequently found when analyzing the hyperfine coupling $\tilde{A}$ tensor in low-spin Co^{II} systems.[39] Even in our homoleptic $[Co^{II}(C_6X_5)_4]^{2-}$ derivatives with axial symmetry, the analysis of the $\tilde{A}$ tensor using the expression derived by Minin and co-workers[38] yields unacceptable results. A plausible source of disagreement was already pointed out by Mabbs and Gerloch and their co-workers,[40] as well as by McGarvey,[36] who indicated that a certain contribution of the 4s orbital—which also transforms as a_1 in tetragonal symmetry—would have a negligible contribution to the $\tilde{\mathbf{g}}$ tensor, but would strongly modify the contact contribution to the $\tilde{\mathbf{A}}$ tensor.

In line with this suggestion, we developed an extension of Nishida and Kida's approach[37] by allowing some d−s admixture. The 4s-orbital contribution can be quantified as follows: $\varphi^{(z} = a\mathrm{d}_{z^2} - b\mathrm{s}$ with a and b being real numbers such that $a^2 + b^2 = 1$ (see Supporting Information for details). Assuming this proposal, the principal g values show the following dependence on the ground-state wave functions given in eq 3:

$$g_{\parallel} = 2{c_z}^2 - 2(1 - k){c_s}^2$$
$$g_{\perp} = 2{c_z}^2 - 2\sqrt{6}\,akc_zc_s \tag{4}$$

where the k parameter accounts for the orbital momentum modification due to covalency effects. Moreover, the principal values of the hyperfine coupling tensor are given by the following expressions:

$$\begin{aligned} A_{\parallel} = {} & K({c_z}^2 - {c_s}^2) + \frac{2}{7}P\{2{c_z}^2 + (7k - 1){c_s}^2 + \sqrt{6}\,c_zc_s\} - \\ & -\frac{2}{\sqrt{5}}Pb\{2{c_z}^2 + \sqrt{6}\,c_zc_s\} - \\ & -\frac{2}{7}Pb^2\left\{2{c_z}^2 + \frac{\sqrt{6}}{1 + a}c_zc_s\right\} + \frac{4}{\sqrt{5}}P\frac{b^3}{1 + a}{c_z}^2 \\ A_{\perp} = {} & K{c_z}^2 - \frac{1}{7}P\{2{c_z}^2 + 6{c_s}^2 + (14k + 1)\sqrt{6}\,c_zc_s\} + \\ & +\frac{1}{\sqrt{5}}Pb\{2{c_z}^2 + \sqrt{6}\,c_zc_s\} + \\ & +\frac{1}{7}Pb^2\left\{2{c_z}^2 + \frac{(14k + 1)\sqrt{6}}{1 + a}c_zc_s\right\} - \frac{2}{\sqrt{5}}P\frac{b^3}{1 + a}c_z^2 \end{aligned} \tag{5}$$

In these expressions $P = g_N\mu_Ng_e\mu_B\langle r^{-3}\rangle$, with $\langle r^{-3}\rangle$ being the expected value of r^{-3} for the orbitals involved in the ground-state Kramers doublet,[41] K describes the Fermi-contact contribution, $g_N(^{59}\mathrm{Co}) = 1.318$, and the other symbols have the usual meanings. In the case of the free Co^{II} ion, $\langle r^{-3}\rangle_0 = 6.0593$ ua, as derived from the Clementi and Roetti radial wave functions,[42] and consequently $P_0 = 762$ MHz. Moreover, K is the sum of two terms: $K = K_{4s} + K_{3d}$,[43] where K_{3d} accounts for the inner s-orbital polarization due to the spin in the d orbitals, and K_{4s} is due to the nonzero spin density in the metal nucleus due to the mixing of the 4s orbital into the d_{z^2} one.

Starting out with the principal values of the $\tilde{\mathbf{g}}$ and $\tilde{\mathbf{A}}$ tensors given in Table 1, and using eqs 4 and 5, estimates of the parameters describing the ground-state Kramers doublet for the unpaired electron were obtained for both compounds **1** and **2** (see Supporting Information for details). The values obtained are given in Table 2. Note that, taking into account the constraints between the different parameters in eqs 4 and 5, only four of them are actually independent, which is exactly the number of experimentally obtained parameters. It is therefore possible to obtain fairly safe estimates from the experimental data. In addition to the relationships already mentioned, the spin density in the 4s orbital is given by $\rho_{4s} = (c_zb)^2$, the spin density in the 3d orbital is estimated as the P/P_0 ratio,[44] and the spin density delocalized onto the ligands is readily calculated as $\rho_L = 1 - (\rho_{4s} + \rho_{3d})$. This analysis enables us to quantify the extent of the d−s admixture. Furthermore, it suggests that roughly one-half of the unpaired electron spin density is spread over the ligands due to the covalent component of the Co−C bond.

Table 2. Values of the Relevant Parameters in the Description of the Ground State Kramers Doublet of Compounds 1 and 2 Deduced from the Analysis of Their EPR Spectra

compound	**1**	**2**
k	1.081(20)	1.124(34)
c_z	0.982(1)	0.987(10)
c_s	−0.188(5)	−0.160(6)
a	0.919(1)	0.917(1)
b	0.395(1)	0.399(1)
Δ/ζ	5.1(3)	6.2(3)
P (MHz)	250(4)	210(4)
K (MHz)	464(3)	496(3)
ρ_{3d}	0.328(5)	0.275(5)
ρ_{4s}	0.150(1)	0.155(1)
ρ_L	0.521(5)	0.569(7)

The model presented here has also been applied to analyze the EPR spectra of a number of other related low-spin Co^{II} systems with $(\mathrm{d}_{z^2})^1$ electron configuration and axial symmetry reported in the literature (see Supporting Information). The relationship of experimental $g_{\perp}$ versus $g_{\parallel}$ literature values is graphically represented in Supporting Information, Figure S8, and the pairwise relationships of the principal values of the $\tilde{\mathbf{g}}$ and $\tilde{\mathbf{A}}$ tensors ($g_{\perp}$ vs $A_{\perp}$ and $g_{\parallel}$ vs $A_{\parallel}$) are shown in Supporting Information, Figure S9. The parameters resulting from their analysis are given in Supporting Information, Table S2. In all these cases there seems to be a significant 4s-orbital contribution in the ground-state configuration (ρ_{4s} ranging from 0.10 to 0.27). The large spectroscopic changes experimentally observed for some chemical species, depending on the crystal environment in which they are embedded, can be attributed to charge transfer between the ligand and the 3d orbitals, as quantified by the corresponding ρ_{3d} and ρ_L values.

Synthesis and Characterization of the Organocobalt(III) Compounds. The electrochemical behavior of compounds **1** and **2** in CH_2Cl_2 solution was studied in the −1.6 to +1.6 V range by cyclic voltammetry. Single redox waves at moderate potentials are observed in both cases (Figure 5). In

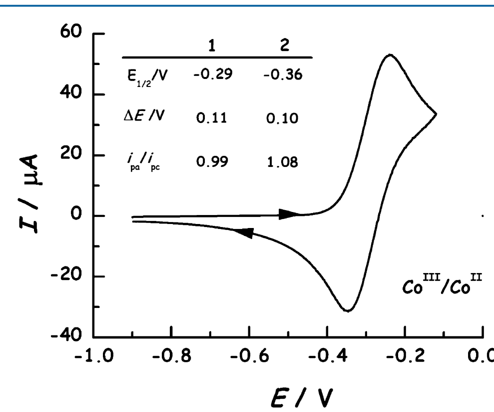

Figure 5. Cyclic voltammogram (CV) of **1** in CH_2Cl_2 solution scanned at 100 mV s^{-1}. The CV of **2** under similar conditions is qualitatively similar and is, therefore, not reproduced.

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view of these electrochemically reversible electron-exchange processes, we aimed to prepare by chemical methods the oxidized species involved. Indeed, the homoleptic organocobaltate(III) derivatives $[NBu_4][Co^{III}(C_6X_5)_4]$ [X = F (**3**), Cl (**4**)] are cleanly obtained by treatment of the corresponding $[NBu_4]_2[Co^{II}(C_6X_5)_4]$ precursor with bromine diluted in CCl_4 (eq 6). Both compounds were isolated as deep blue solids in good yields and gave satisfactory elemental analyses.

$$[NBu_4]_2[Co^{II}(C_6X_5)_4] + Br_2 \rightarrow [NBu_4][Co^{III}(C_6X_5)_4] \quad \mathbf{3}(X = F), \mathbf{4}(X = Cl) \qquad (6)$$

Compound **3** is moderately stable, whereas compound **4** is thermally labile. However, both compounds decompose upon heating with formation of the corresponding perhalogenated biphenyl $C_6X_5{-}C_6X_5$. To avoid decomposition they should be kept at low temperature (−30 °C) under inert atmosphere.

In the IR spectrum of the perfluorophenyl compound **3**, the C−C and C−F stretching modes of the C_6F_5 ring appear as strong, sharp absorptions at 1501 and 956 cm^{-1} respectively, whereas the X-sensitive mode[27] appears as a medium-sized absorption at 782 cm^{-1}. In the IR spectrum of the perchlorophenyl compound **4**, the X-sensitive mode appears as an absorption of medium intensity at 827 cm^{-1}, whereas the ν(M−C) stretching mode gives rise to a weak band at 601 cm^{-1}. All these significant IR absorptions appear shifted toward higher frequencies with respect to those corresponding to the organocobalt(II) precursors (see above). These higher-energy shifts are in keeping with the oxidation undergone by the metal center.[27a]

The crystal and molecular structures of both organocobalt(III) compounds were established by X-ray diffraction methods on single crystals of **3** and **4**·2.5CH_2Cl_2. Crystals of **3** (d^6) are isomorphous with those of the isoleptic organonickel(III) derivative $[NBu_4][Ni^{III}(C_6F_5)_4]$ (d^7),[26] both $[M^{III}(C_6F_5)_4]^-$ anions being isostructural (M = Co, Ni). The $[Co^{III}(C_6X_5)_4]^-$ anions are depicted in Figure 6 (X = F) and Figure 7 (X = Cl). In both cases, the local coordination environment of the Co^{III} center can be described as slightly distorted *SP*-4, following the

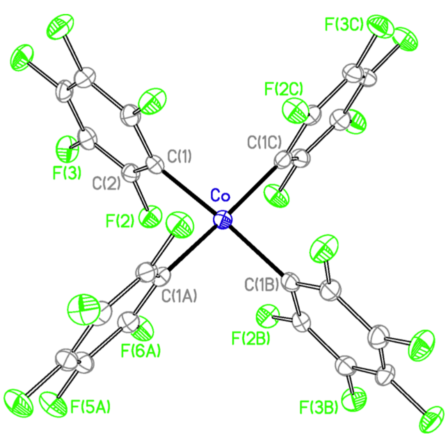

Figure 6. Thermal ellipsoid diagram (50% probability) of the $[Co^{III}(C_6F_5)_4]^-$ anion in **3**. Selected bond lengths (pm) and angles (deg) with estimated standard deviations: Co−C(1) 198.50(15), C(1)−Co−C(1′) 90.329(7), C(1)−Co−C(1′′) 171.31(9), Co−C(1)−C(2) 120.07(12), Co−C(1)−C(6) 124.54(12), $C^{ortho}{-}C^{ipso}{-}C^{ortho\prime}$ 115.39(15).

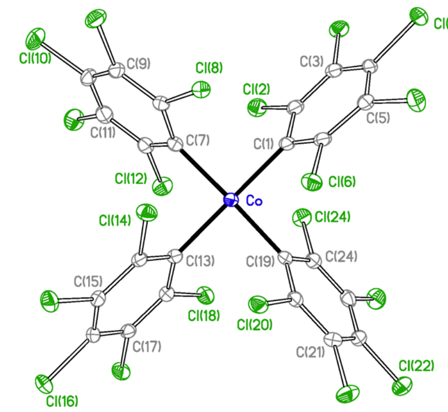

Figure 7. Thermal ellipsoid diagram (50% probability) of one of the two enantiomeric $[Co^{III}(C_6Cl_5)_4]^-$ anions present in the centrosymmetric single crystals of **4**·2.5CH_2Cl_2. Selected bond lengths (pm) and angles (deg) with estimated standard deviations: Co−C(1) 203.7(4), Co−C(7) 204.2(4), Co−C(13) 204.2(4), Co−C(19) 204.6(4), C(1)−Co−C(7) 90.15(16), C(1)−Co−C(13) 174.12(17), C(1)−Co−C(19) 92.12(16), C(7)−Co−C(13) 90.36(16), C(7)−Co−C(19) 174.76(17), C(13)−Co−C(19) 87.87(16), Co−C(1)−C(2) 127.1(3), Co−C(1)−C(6) 118.0(3), Co−C(7)−C(12) 118.5(3), Co−C(7)−C(8) 126.6(3), Co−C(13)−C(14) 118.3(3), Co−C(13)−C(18) 127.0(3), Co−C(19)−C(20) 126.7(3), Co−C(19)−C(24) 118.1(3), average $C^{ortho}{-}C^{ipso}{-}C^{ortho\prime}$ 114.8(4).

low CShM value obtained for that geometry: *S*(*SP*-4) = 0.57 and 0.24 for compounds **3** and **4**, respectively.[30] As far as we know, these are the first organocobalt(III) compounds for which an *SP*-4 geometry has been unambiguously established. This is quite an unexpected result, especially for the perchlorophenyl compound **4**, given that its heavier-metal homologous species $[Rh^{III}(C_6Cl_5)_4]^-$ is known to exhibit a distorted pseudo-(*OC*-6) geometry.[45] A similar situation in which two of the C_6Cl_5 groups act as small-bite chelating ligands, C_6Cl_5-*κC*,*κCl*^{2}, toward the metal center was also found for the neutral isoelectronic d^6 species $[Pt^{IV}(C_6Cl_5)_4]$.[46] Conversely, every C_6Cl_5 group acts in compound **4** as a terminal (yet considerably swung) monodentate ligand, C_6Cl_5-*κC*, with no evidence for any Co···Cl^{ortho} secondary bonding interaction. Thus, the structure of the $[Co^{III}(C_6Cl_5)_4]^-$ (d^6) anion bears more similarity to those found for the isoleptic derivatives of its neighboring elements $[Fe^{III}(C_6Cl_5)_4]^-$ (d^5)[47] and $[Ni^{III}(C_6Cl_5)_4]^-$ (d^7)[26] in spite of their different electronic configurations. The whole $[Co^{III}(C_6Cl_5)_4]^-$ anion is chiral because of the helicoidal arrangement of the C_6Cl_5 rings around the Co center (tilt angle: 60−65° with respect to the best metal coordination plane). The C_6Cl_5 rings adopt a mutually *trans* staggered disposition probably to avoid energetically unaffordable Cl···Cl nonbonding interactions between neighboring *ortho*-Cl atoms.[48] In compound **3**, however, the less sterically demanding C_6F_5 rings are mutually *trans* eclipsed and exactly perpendicular to the coordination plane; hence, the $[Co^{III}(C_6F_5)_4]^-$ anion is not chiral (centrosymmetric space group). Acute $C^{ortho}{-}C^{ipso}{-}C^{ortho\prime}$ angles are also found in both kinds of C_6X_5 rings.[31]

All four Co−C distances in compound **3** are identical by crystal symmetry (S_4 axis). The slight elongation of the Co−C_6Cl_5 bonds in **4** (204.2(4) pm average value) with respect to the Co−C_6F_5 one in **3** (198.50(15) pm) might arise from the aforementioned way of minimizing interligand Cl···Cl nonbonding interactions. Both of these $Co^{III}{-}C(sp^2)$ bond lengths

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are significantly longer than the Co^{III}−C(sp) distances found in the homoleptic *OC*-6 anions $[Co^{III}(C{\equiv}E)_6]^{3-}$ (average Co−C = 190.8(3) and 190.4(4) pm for E = $CSiMe_3$[5] and N,[49] respectively), probably because of the different hybridization in each case —although the effect of π interaction between the alkynyl or cyano ligands and the Co^{III} center in the latter compounds cannot be excluded. The slightly shorter Co−C(sp^2) distances observed in the *OC*-6 hexacarbene cations bis[hydrotris(3-methyl-imidazoline-2-yliden-1-yl)borate]cobalt(III) (194.3(4)−195.9(5) pm) and hexakis(oxazolidin-2-ylidene)cobalt(III) (193.7(4) pm) can be attributed to the cationic nature of these complexes.[6a]

Magnetic Properties of the Organocobalt(III) Derivatives. No signals were observed in the ^{19}F NMR spectrum of **3** between −100 and −200 ppm, and the ^{13}C NMR spectrum of **4** in the standard region contains only resonances corresponding to the $[NBu_4]^+$ cation but no signals that could be assigned to the C_6Cl_5 groups. The failure to obtain well-defined NMR spectra would, in principle, point to a paramagnetic behavior of the anion. However, neither X- nor Q-band EPR spectra could be observed for polycrystalline powder samples of compounds **3** and **4** between 4.2 and 298 K. In contrast to all this inconclusive evidence, magnetic susceptibility measurements on bulk samples of both compounds unequivocally showed that they are indeed paramagnetic. The thermal dependence of the $T\chi(T)$ product for compound **3** (Figure 8) tends to a constant

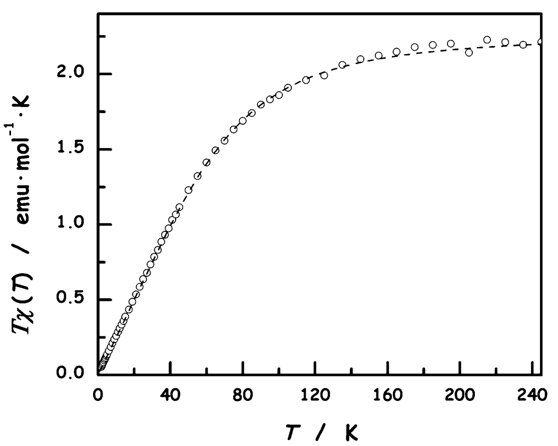

Figure 8. Experimental thermal dependence of the $T\chi$ product for a polycrystalline powder sample of **3** (○). The dashed line corresponds to the calculated dependence using the expression given by eq 8 with the parameters given in Table 3.

value at comparatively higher temperatures, while at lower temperatures it displays a linear dependence, since $\chi(T)$ tends to a finite value as the temperature approaches zero. Similar trends are observed for compound **4** (Supporting Information, Figure S4). From the high-temperature asymptotic value of $T\chi(T)$, the magnetic moment per formula, μ_∞, can be derived. The μ_∞ values obtained (Table 3) indicate that the electronic configuration of the Co^{III} center is a spin triplet.

Given the paramagnetic nature of compounds **3** and **4**, and with the energy-level scheme depicted in Figure 4, the ground state of **3** and **4** should be the spin triplet $^3B_2$ associated with the $(e)^4(a_1)^1(b_2)^1$ configuration.[50] The EPR-silent nature of compounds **3** and **4** prevents the unambiguous establishment of their precise electronic symmetry. Compound **3**, however, has been shown to exhibit crystallographically imposed axial symmetry (S_4). It is also reasonable to assume an axial local

Table 3. Magnetic Parameters Obtained from Experimental $T\chi(T)$ Data Measured in Polycrystalline Powder Samples of 3 and 4[a]

compound	3	4
μ_∞ (μ_B)[b]	4.1(1)	3.4(1)
$g_\perp$	3.20(4)	2.62(8)
D/k_B [K]	208(6)	134(9)

[a] See text for details. [b] Calculated magnetic moment for a triplet spin system (S = 1) with spin-only contribution: μ_{eff} = 2.83 μ_B.

symmetry for the Co^{III} center (d^6) in compound **4**, as it is actually found for the Co^{II} center (d^7) in the precursor species **2** (see above). Under an axial crystal field, the S = 1 triplet splits into a singlet and a doublet, with D denoting the energy separation between them, that is, zero-field splitting (ZFS). The magnetic behavior of an intermediate-spin d^6 entity under an axial symmetry can be described by the following spin-Hamiltonian:

$$\mathcal{H} = \mu_B H_0\{(g_\perp \sin\theta)S_x + (g_\parallel \cos\theta)S_z\} + D\left\{S_z^2 - \frac{1}{3}S(S+1)\right\} \quad (7)$$

The thermal dependence of the $T\chi(T)$ product is consequently given by eq 8:[51]

$$T\chi(T) = \frac{2N\mu_B^2}{3k_B}\frac{g_\parallel^2 e^{-D/k_BT} + g_\perp^2(2k_BT/D)(1 - e^{-D/k_BT})}{1 + 2e^{-D/k_BT}} \quad (8)$$

Moreover, when the $a_1(z^2)$ and $b_2(xy)$ levels (Figure 4) are sufficiently close together, a simple calculation of the single-electron levels in D_4 symmetry indicates that their corresponding energy separation with respect to the lower $e(xz, yz)$ level is much smaller than that with respect to the upper $b_1(x^2{-}y^2)$ empty orbital. In such a case, we can disregard the effect of the higher-energy level and just consider the $e(xz, yz)$, $a_1(z^2)$, and $b_2(xy)$ single-electron states to describe our system. Consequently, by making use of the hole formalism, the problem is reduced to one involving just two particles (holes). Moreover, only the excited spin-triplets $^3E(a_1e)$, $^3E(b_2e)$, and $^3B_2(e^2)$ will have to be considered in addition to the ground state $^3B_2(b_2a_1)$.

Under D_4 symmetry, the angular momentum components L_z and (L_x, L_y) transform as A_2 and E, respectively. Since $A_2 \otimes B_2 = B_1$ and $E \otimes B_2 = E$, the following expressions are obtained:

$$g_\parallel = g_e,\ g_\perp = g_e + 2\zeta\Lambda,\ \text{and}\ D = \frac{1}{3}\zeta^2\Lambda \quad (9)$$

where ζ is the spin−orbit coupling constant for one electron and Λ accounts for the mixing of wave functions coming from the ^3E excited states to the $^3B_2$ ground state.[52] Following our model, $g_\parallel$ does not significantly depart from the free-electron g value ($g_\parallel = g_e$), and the $g_\perp$ and D values can be estimated by fitting eq 8 to the experimental data. For compound **3**, an excellent fit is obtained for the $T\chi(T)$ evolution along the whole temperature range (Figure 8) using the values given in Table 3. The same procedure was applied to compound **4** (Table 3). In this case, however, only data above 20 K were considered in the calculation, due to an additional peak occurring at ~6 K (Supporting Information, Figure S4, inset). The batch dependence of its relative intensity suggests, as in compound **2** (see above), that the extra contribution is due to an impurity that despite all efforts could not be completely removed.

As already noted by other authors dealing with related nonorganometallic systems,[53] the fitting process leading to estimates of $g_{\perp}$ and D parameters for compounds **3** and **4** lacks the desired robustness, since several sets of $g_{\perp}$ and D values can actually be obtained. In selecting the particular set of parameters given in Table 3, we relied upon the evidence of a significant ZFS contribution indicated by the shape of the experimental thermal evolution of $T\chi(T)$ (Figure 8 and Supporting Information, Figure S4). Further indication is given by the high μ_{∞} values obtained (Table 3), well above that expected for an $S = 1$ system with spin-only contribution: $\mu_{\infty} \approx 2.83\ \mu_B$. The required orbital contribution to the magnetic moment is associated with the aforementioned mixing of excited states into the $^3B_2$ ground state via spin−orbit coupling, which is also responsible for the ZFS contribution quantified by the D parameter. Finally, it is interesting to note that the estimated D values are much higher than our experimentally available microwave-frequency, which provides a reasonable explanation for the EPR-silent nature of our organocobalt(III) compounds.

There are just a few precedents for nonorganometallic Co^{III} coordination compounds with *SP*-4 geometry and $S = 1$ configuration, where the metal is surrounded by four sulfur atoms, $Co(S)_4$,[53,54] four nitrogen atoms, $Co(N)_4$,[55] or two nitrogen and two oxygen atoms, $Co(N)_2(O)_2$.[56] In all these cases, the values of the high-temperature limit of the magnetic moment per unit formula, μ_{∞}, are also higher than the spin-only value ($\mu_{\infty} \approx 2.83\ \mu_B$), ranging from 3.0 to 3.5 μ_B. Moreover, in the following $Co(S)_4$ cases, the analysis of the thermal evolution of the magnetic susceptibility was carried out assuming an axial symmetry and using eq 8, which enabled estimates of the ZFS parameter as indicated: bis(biuretato)-cobaltate(III) ($D/k_B \approx 59$ K),[55c] bis(benzene-1,2-dithiolato)-cobaltate(III) ($D/k_B \approx 54$ K) and bis(toluene-3,4-dithiolato)-cobaltate(III) ($D/k_B \approx 57$ K).[53] The comparatively higher D and μ_{∞} values obtained for our homoleptic $Co(C)_4$ organocobalt(III) compounds **3** and **4** (Table 3), denote a substantially higher orbital contribution in their ground-state electronic structure.

■ CONCLUDING REMARKS

The homoleptic organocobalt(III) compounds $[NBu_4][Co^{III}(C_6X_5)_4]$ [X = F (**3**), Cl (**4**)] have been obtained in good yields by oxidation of the corresponding $[NBu_4]_2[Co^{II}(C_6X_5)_4]$ precursors [X = F (**1**), Cl (**2**)] with Br_2 (eq 6). The corresponding $[Co^{III}(C_6X_5)_4]^-/[Co^{II}(C_6X_5)_4]^{2-}$ couples are electrochemically related by quasi-reversible one-electron exchange processes at moderate potentials (Figure 5).

Compounds **3** and **4** exhibit *SP*-4 structures, as established by X-ray diffraction methods (Figures 6 and 7). The structure of the $[Co^{III}(C_6X_5)_4]^-$ anions is unperturbed by any covalent interaction with the cation and should therefore truly reflect the stereochemical preference of these homoleptic species. To the best of our knowledge, these are first examples of *SP*-4 geometry in organocobalt(III) chemistry. The observed structure with no axial ligands or interactions is, in fact, quite unusual for d^6 metal ions. The structure is especially unexpected in the case of the perchlorophenyl derivative $[Co^{III}(C_6Cl_5)_4]^-$ since it is in sharp contrast with that found for the heavier-metal isoleptic species $[Rh^{III}(C_6Cl_5)_4]^-$ reported by M. P. García and her co-workers.[45] In the latter, as well as in the neutral isoelectronic (d^6) compound $[Pt^{IV}(C_6Cl_5)_4]$,[46] the metal centers achieve heavily distorted octahedral environments as the result of additional M···Cl secondary bonding interactions established with two *ortho*-Cl atoms.

In contrast to the diamagnetic nature of those pseudo-octahedral Rh^{III} and Pt^{IV} compounds, the magnetic properties of compounds **3** and **4** involve an intermediate-spin system ($S = 1$) with substantial spin−orbit contribution. This particular behavior arises from the absence of any axial interaction, which entails significant stabilization of the d_{z^2} orbital (Figure 4).

The organocobalt(II) precursors **1** and **2** both exhibit *SP*-4 geometry and low-spin behavior ($S = 1/2$). Attending to their stereochemical and magnetic properties, they bear much similarity with their heavier-metal homologues $[Rh^{II}(C_6Cl_5)_4]^{2-}$ and $[Ir^{II}(C_6Cl_5)_4]^{2-}$, which were also prepared by M. P. García and her co-workers,[45,57] as well as with the d^7 related derivatives $[Ni^{III}(C_6X_5)_4]^-$ and $[Pt^{III}(C_6Cl_5)_4]^-$.[26,58] Thanks to the high symmetry of the metal local environment in the homoleptic (*SP*-4)-$[Co^{II}(C_6X_5)_4]^{2-}$ species and making use of the same energy-level diagram as before (Figure 4), it has been possible to derive a thorough analysis of their EPR spectra by assuming some degree of d−s mixing in the ground-state configuration. This can be considered a fairly safe approach, since it relies on a minimum of independent variables not exceeding the number of experimental parameters available.

All the organocobalt compounds presented here nicely exemplify the close relationship between molecular geometry and magnetic properties. They complete the family of homoleptic perhaloaryl compounds of first-row transition metals: $[M(C_6X_5)_x]^{q-}$ (M = Ti, V, Cr, Mn, Fe, Co, Ni).[59]

■ EXPERIMENTAL SECTION

All the manipulations and operations were carried out under purified argon using Schlenk techniques. Solvents were dried using an MBraun SPS-800 System. Published methods were used to prepare the mixed halo complex $[NBu_4]_2[CoCl_2Br_2]$[60] as well as Et_2O solutions of the organolithium derivatives LiC_6X_5 (X = F,[61] Cl[62]). The procedures given here in detail to prepare compounds **1** and **2** are optimizations of those briefly outlined in a previous communication.[14] Bromine solutions were prepared by diluting a measured volume of $Br_2(l)$ in the appropriate amount of CCl_4 and were titrated by standard procedures before use. Elemental analyses were carried out with a PerkinElmer 2400-Series II microanalyzer. IR spectra of KBr discs were recorded on a PerkinElmer Spectrum One (4000−350 cm^{-1}) spectrophotometer. Mass spectra were registered by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) techniques on Bruker MicroFlex or AutoFlex spectrometers. Unless otherwise stated, the spectroscopic measurements were carried out at room temperature.

Synthesis of $[NBu_4]_2[Co^{II}(C_6F_5)_4]$ (1). To an Et_2O solution (70 cm^3) of LiC_6F_5 (15.5 mmol) at −78 °C was added solid $[NBu_4]_2[CoCl_2Br_2]$ (2.0 g, 2.58 mmol); the mixture was stirred for 14 h, while it reached room temperature. Then the green solid was filtered, washed with Et_2O (3 × 5 cm^3), and extracted in CH_2Cl_2 (70 cm^3). The CH_2Cl_2 extract was concentrated to ca. 5 cm^3. The subsequent addition of ^{i}PrOH (20 cm^3) caused the precipitation of a yellowish-green solid, which was filtered, washed with ^{i}PrOH (3 × 5 cm^3) and Et_2O (3 × 5 cm^3), and dried (**1**: 2.63 g, 2.17 mmol; 84% yield). Anal. Found: C 55.2, H 5.9, N 2.2; $C_{56}H_{72}F_{20}N_2Co$ requires C 55.5, H 6.0, N 2.3%. IR (KBr): $\tilde{\nu}_{max}$ = 2970 (m), 2877 (w), 1483 (s), 1440 (vs), 1381 (w), 1291 (w), 1171 (w), 1050 (sh), 1032 (m), 945 (vs; C−F), 882 (w; $[NBu_4]^+$), 754 (m; C_6F_5: X-sensitive vibration),[27] 739 (w; $[NBu_4]^+$), 574 cm^{-1} (w). MS (MALDI−, *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB)): *m/z*: 560 $[Co(C_6F_5)_3]^-$, 412 $[Co(C_6F_5)_2F]^-$, and 393 $[Co(C_6F_5)_2]^-$.

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Table 4. Crystal Data and Structure Refinement for $1 \cdot 0.3CH_2Cl_2$, 3, and $4 \cdot 2.5CH_2Cl_2$

	$1 \cdot 0.3CH_2Cl_2$	3	$4 \cdot 2.5CH_2Cl_2$
formula	$C_{56.3}H_{66.6}Cl_{0.6}CoF_{20}N_2$	$C_{40}H_{36}CoF_{20}N$	$C_{42.5}H_{41}Cl_{25}CoN$
M_t (g mol^{-1})	1231.52	969.63	1510.94
T (K)	100(2)	100(2)	100(2)
λ (pm)	71.073	71.073	71.073
crystal system	monoclinic	tetragonal	triclinic
space group	$P2_1/n$	$I4_1/a$	$P\bar{1}$
a (pm)	1172.01(11)	1804.82(13)	1331.92(3)
b (pm)	2599.3(2)	1804.82(13)	1536.15(4)
c (pm)	1951.14(15)	1224.39(9)	1634.79(6)
α (deg)	90.00	90.00	117.445(3)
β (deg)	93.031(2)	90.00	92.385(3)
γ (deg)	90.00	90.00	95.370(2)
V (nm^3)	5.9355(9)	3.9883(5)	2.941 72(15)
Z	4	4	2
ρ (g cm^{-3})	1.378	1.615	1.706
μ (mm^{-1})	0.416	0.556	1.461
F(000)	2542	1960	1510
θ range (deg)	1.57−20.79	2.26−24.98	3.87−25.00
final R indices $[I > 2\sigma(I)]^a$			
R_1	0.0803	0.0272	0.0576
wR_2	0.2028	0.0675	0.1410
R indices (all data)			
R_1	0.1431	0.0328	0.0618
wR_2	0.2421	0.0693	0.1441
goodness-of-fit on F^2 ^{b}	1.037	1.030	1.062

$^aR_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. ^{b}Goodness-of-fit $= [\sum w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

Single crystals suitable for X-ray diffraction purposes with formula $[NBu_4]_2[Co(C_6F_5)_4]\cdot 0.3CH_2Cl_2$ were obtained by slow diffusion of an n-hexane (12 cm^3) layer into a solution of 10 mg of **1** in 3 cm^3 of CH_2Cl_2 at −30 °C.

Synthesis of $[NBu_4]_2[Co^{II}(C_6Cl_5)_4]$ (2). To an Et_2O solution (80 cm^3) of LiC_6Cl_5 (15.5 mmol) at −78 °C was added solid $[NBu_4]_2[CoCl_2Br_2]$ (2.0 g, 2.58 mmol). The temperature of the bath was allowed to reach 0 °C, and then the mixture was stirred in an ice bath for a further 12 h. The suspended orange solid was filtered, washed at 0 °C with Et_2O (3 × 5 cm^3) and MeOH (3 × 15 cm^3), and vacuum-dried (**2**: 3.32 g, 2.15 mmol; 83% yield). Anal. Found: C 43.2, H 4.5, N 1.7; $C_{56}H_{72}Cl_{20}N_2Co$ requires C 43.6, H 4.7, N 1.8%. IR (KBr): $\tilde{\nu}_{max}$ = 2963 (m), 2875 (w), 1469 (m), 1380 (w), 1311 (s), 1280 (vs), 1213 (s), 1167 (w), 1044 (w), 880 (w; $[NBu_4]^+$), 810 (m; C_6Cl_5: X-sensitive vibration),[27] 737 (w; $[NBu_4]^+$), 708 (w), 665 (vs), 595 (w), 579 cm^{-1} [m; ν(M−C)]. MS (MALDI−, DCTB): m/z: 800 $[Co(C_6Cl_5)_3]^-$, 588 $[Co(C_6Cl_5)_2Cl]^-$, and 376 $[Co(C_6Cl_5)Cl_2]^-$.

Synthesis of $[NBu_4][Co^{III}(C_6F_5)_4]$ (3). Bromine dissolved in CCl_4 (0.27 mmol) was added dropwise to a room-temperature suspension of **1** (0.31 g, 0.25 mmol) in $CHCl_3$ (20 cm^3). After 1 h of stirring, the deep blue solid formed was separated by filtration, washed with $CHCl_3$ (3 × 3 cm^3), and vacuum-dried (**3**: 0.22 g, 0.23 mmol, 92% yield). Anal. Found: C 49.1, H 4.0, N 1.2; $C_{40}H_{36}CoF_{20}N$ requires C 49.5, H 3.7, N 1.4%. IR (KBr): $\tilde{\nu}_{max}$ = 2970 (m), 2877 (w), 1634 (w), 1501 (s), 1465 (s), 1341 (m), 1254 (w), 1066 (m), 1045 (sh), 956 (s; C−F), 884 (w; $[NBu_4]^+$), 782 (w; C_6F_5: X-sensitive vibration),[27] 739 (w; $[NBu_4]^+$), 489 cm^{-1} (w). MS (MALDI−, DCTB): m/z: 560 $[Co(C_6F_5)_3]^-$, 412 $[Co(C_6F_5)_2F]^-$, and 393 $[Co(C_6F_5)_2]^-$. Single crystals suitable for X-ray diffraction purposes were obtained by slow diffusion of an n-hexane (15 cm^3) layer into a solution of 6 mg of **3** in 4 cm^3 of Me_2CO at −30 °C.

Synthesis of $[NBu_4][Co^{III}(C_6Cl_5)_4]$ (4). Bromine dissolved in CCl_4 (0.37 mmol) was added dropwise to a suspension of **2** (0.39 g, 0.25 mmol) in $CHCl_3$ (20 cm^3) cooled in an ice bath. By following the same procedure as that described for isolating compound **3**, complex **4** was obtained as a deep blue solid (0.22 g, 0.17 mmol, 68% yield). Anal. Found: C 36.4, H 2.6, N 0.9; $C_{40}H_{36}Cl_{20}CoN$ requires C 37.0, H 2.8, N 1.1%. IR (KBr): $\tilde{\nu}_{max}$ = 2965 (m), 2875 (w), 1478 (w), 1378 (w), 1323 (s), 1313 (s), 1286 (vs), 1216 (w), 1135 (w), 1059 (w), 877 (w; $[NBu_4]^+$), 827 (m; C_6Cl_5: X-sensitive vibration),[27] 757 (w), 739 (w; $[NBu_4]^+$), 704 (w), 675 (s), 601 cm^{-1} [w; ν(M−C)]. MS (MALDI−, DCTB): m/z: 800 $[Co(C_6Cl_5)_3]^-$, 588 $[Co(C_6Cl_5)_2Cl]^-$, and 376 $[Co(C_6Cl_5)Cl_2]^-$. Single crystals suitable for X-ray diffraction purposes with formula $[NBu_4][Co(C_6Cl_5)_4]\cdot 2.5CH_2Cl_2$ were obtained by slow diffusion of an ^{i}PrOH (20 cm^3) layer into a solution of 15 mg of **4** in 4 cm^3 of CH_2Cl_2 at −30 °C.

X-ray Structure Determinations. Crystal data and other details of the structure analyses are presented in Table 4. Crystals suitable for X-ray diffraction studies were obtained as indicated in each synthetic procedure. Crystals were mounted at the end of a quartz fiber. The radiation used in all cases was graphite monochromated Mo Kα (λ = 71.073 pm). For $\mathbf{1}\cdot 0.3CH_2Cl_2$ and **3**, X-ray intensity data were collected on a Bruker Smart Apex diffractometer, and the diffraction frames were integrated using the SAINT program.[63] For $\mathbf{4}\cdot 2.5CH_2Cl_2$, X-ray intensity data were collected on an Oxford Diffraction Xcalibur diffractometer, and the diffraction frames were integrated using the CrysAlis RED program.[64] The sets of data were corrected for absorption with SADABS.[65] The structures were solved by Patterson and Fourier methods, and refined by full-matrix least-squares on F^2 with SHELXL-97.[66] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints except as noted below. All hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters equal to 1.2 times the U_{iso} values of their attached parent atoms (1.5 times for the methyl hydrogen atoms). In the structure of $\mathbf{1}\cdot 0.3CH_2Cl_2$, some of the C atoms of the $[NBu_4]^+$ cations were found to be disordered over two sets of positions, which were refined with partial occupancy of 0.5. For some of these disordered C atoms, constraints in the interatomic distances were applied, and no H atoms were added on. Furthermore, a very diffuse CH_2Cl_2 molecule was found in the final stages of the refinement. The occupancy of its atoms was fixed to 0.3, and constraints in its geometry were applied. In the structure of $\mathbf{4}\cdot 2.5CH_2Cl_2$, some solvent molecules were found during the refinement. These molecules were extremely diffuse, and thus constraints were applied. The model finally retained consisted of five CH_2Cl_2 molecules, with partial occupancy 0.6, 0.6, 0.5, 0.4, and 0.4, whose C−Cl distances were constrained to acceptable values. Common sets of anisotropic thermal parameters were used for all the Cl atoms and all the C atoms. Full-matrix least-squares refinement of these models against F^2 converged to the final residual indices given in Table 4.

EPR Measurements. EPR data were recorded using a Bruker Elexsys E580 spectrometer operating in X-band or in Q-band. The magnetic field was determined with a Bruker ER035 M gaussmeter. An HP53152A frequency counter was used to measure frequency in the Q-band experiment. The polycrystalline powder samples were introduced in fused quartz tubes and sealed under an Ar atmosphere. An Oxford CF900 continuous-flow cryostat refrigerated with He(l) or N_2(l) where appropriate was used in X-band measurements below room temperature. For low-temperature Q-band measurements the cavity with the sample was immersed in an Oxford CF935 continuous-flow cryostat.

Magnetic Measurements. Magnetic measurements of polycrystalline powder samples were carried out using a Quantum Design SQUID-based MPMS-XL5 magnetometer. The magnetometer was calibrated using standard palladium and dysprosium oxide reference samples supplied by QuantumDesign. The accuracy of the measurements was better than 1%. Polycrystalline powder samples were mounted using gelatin capsule containers. The preparation was made in an inert atmosphere to avoid any possible sample degradation. Special care was taken during the preparation and installation in the sample holder to avoid any magnetic contamination. During measurements the sample was kept in a helium atmosphere. Isothermal direct-current magnetization curves, $M(\mu_0H)$, at T = 1.8, 5, and 78 K were taken in the magnetic field range of $0 < \mu_0H < 5$ T. Magnetic alternating current susceptibility measurements were performed from 1.8 to 265 K at 10 Hz and 4.0 Oe amplitude.

Electrochemistry. Electrochemical studies were carried out using an EG&G model 273 potentiostat in conjunction with a three-electrode cell, in which the working electrode was a platinum disc, the auxiliary electrode was a platinum wire, and the reference was an aqueous SCE separated from the test solution by a fine-porosity frit and an agar bridge saturated with KCl. Where possible, solutions were 5×10^{-4} mol dm^{-3} in the test compound and 0.1 mol dm^{-3} in $[NBu_4][PF_6]$ as the supporting electrolyte. At the end of each voltammetric experiment, $[Fe(\eta^5\text{-}C_5H_5)_2]$ was added to the solution as an internal standard for potential measurements. Under the conditions used, the $E°$ value for the couple $[Fe(\eta^5\text{-}C_5H_5)_2]^+$−$[Fe(\eta^5\text{-}C_5H_5)_2]$ was 0.47 V.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystal data for compounds **1**·$0.3CH_2Cl_2$ (CCDC-1011064), **3** (CCDC-1011065), and **4**·$2.5CH_2Cl_2$ (CCDC-1011066) in CIF format; additional Figures concerning magnetic characterization; technical details of the EPR simulation procedure; full details of the model to describe the magnetic properties of tetragonal low-spin d^7 systems as well as the protocol for analyzing their EPR-derived parameters; EPR-data analysis in some selected low-spin Co(II) systems with axial symmetry reported in the literature. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: menjon@unizar.es. (B.M.)

*E-mail: alonso@unizar.es. (P.J.A.)

Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to the lasting Memory of Prof. Dr. María P. García.

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