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Mononuclear Coordination Complexes of Fullerene C_{60} with Zerovalent Cobalt Having $S = 1/2$ Spin State: $Co(\eta^2\text{-}C_{60})(L)(C_6H_5CN)\cdot(o\text{-}C_6H_4Cl_2)$ (L = 1,2-bis(diphenylphosphino)ethane and 1,1′-bis(diphenylphosphino)ferrocene)

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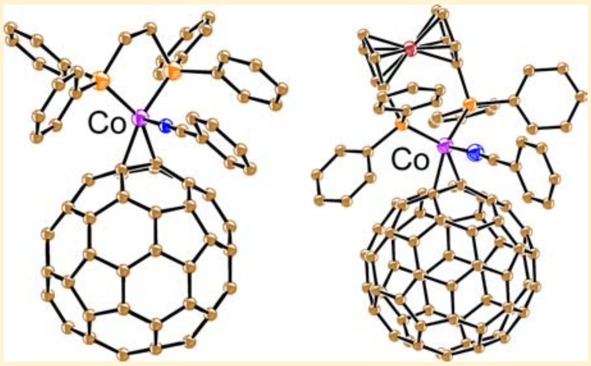
Ⓢ *Supporting Information*

ABSTRACT: Two mononuclear coordination complexes of fullerene C_{60} with cobalt, $Co(\eta^2\text{-}C_{60})(dppe)(C_6H_5CN)\cdot C_6H_4Cl_2$ (**1**) and $Co(\eta^2\text{-}C_{60})(dppf)(C_6H_5CN)\cdot C_6H_4Cl_2$ (**2**) (dppe is 1,2-bis(diphenylphosphino)ethane and dppf is 1,1′-bis(diphenylphosphino)ferrocene) have been obtained by sodium fluorenone reduction of the $Co(dppe)Cl_2$ or $Co(dppf)Br_2$ and C_{60} mixtures. The IR and visible−NIR spectra of **1** and **2** indicate the neutral state of fullerenes. Therefore, cobalt atoms formally have the zerovalent state. Cobalt coordinates to the 6−6 bond of C_{60} by η^2-type coordination with Co−C bond lengths in the 2.008(3)−2.060(3) Å range. Diphosphine and benzonitrile ligands additionally coordinate to cobalt to form a distorted square-pyramidal environment for the cobalt atoms. Complexes **1** and **2** are rare examples of fullerene coordination complexes with paramagnetic metal centers. Both complexes manifest intense asymmetric EPR signals attributed to zerovalent cobalt atoms, which can be fitted by three components with $g = 2.261$−2.124 (**1**) and $g = 2.258$−2.092 (**2**). Effective magnetic moments of **1** and **2** indicate the low-spin ($S = 1/2$) state of Co^0. In accordance with EPR spectra, DFT calculations show that the spin density is localized mainly on the central cobalt atoms and only slightly delocalized into C_{60}, benzonitrile, dppe, or dppf ligands.



■ INTRODUCTION

Fullerene C_{60} forms a variety of coordination complexes with transition metals that exhibit the η^2-type coordination to the 6−6 bonds of C_{60}. Among these metals are iridium, palladium, platinum, ruthenium, rhodium, osmium, manganese, chromium, titanium, and some others.[1] Fullerenes coordinate to transition metals by substituting ligands or occupying available coordination sites in the coordination sphere of metal atoms.[1] We developed a reduction method to prepare nickel−fullerene complexes when starting $Ni(dppp)Cl_2$ and fullerenes C_{60} or C_{70} mixtures are reduced by sodium fluorenone, thus allowing the structural characterization of $\{Ni(dppp)(\eta^2\text{-}C_{60})\}\cdot 0.84C_6H_{14}\cdot 0.16C_6H_4Cl_2$ and $\{Ni(dppp)(\eta^2\text{-}C_{70})\}\cdot 0.5C_6H_4Cl_2$, where dppp is 1,3-bis(diphenylphosphino)propane.[2]

Metal−fullerene complexes can be interesting for the development of magnetic assemblies when the coordinating metal has spin since fullerenes potentially can transfer magnetic interaction between them. To develop this field, the preparation of fullerene complexes with paramagnetic metal atoms is important, for example, with zerovalent cobalt since it has d^9 electron configuration with $S = 1/2$ spin state. Up to now, polycrystalline C_{60} complexes with diamagnetic cobalt(I), $(R\text{-}\eta^5\text{-}C_5H_5)Co(Ph_3P)(\eta^2\text{-}C_{60})$ (R is −H, −COMe, $-CO_2Et$), were reported.[4] Among fullerene complexes with paramagnetic metals, only complex $Cp_2V(II)(\eta^2\text{-}C_{60})$ with vanadium(II) was studied in solution.[3] We made efforts to develop synthesis of coordination complexes starting from $Co(L)Br_2$ salts and fullerenes (L = Ph_3P, 1,2-bis(diphenylphosphino)ethane (dppe), and 1,1′-bis(diphenylphosphino)ferrocene (dppf)) by

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their reduction with sodium fluorenone. Starting from Co-$(Ph_3P)_2Br_2$ and C_{60} mixture, a compound containing binuclear dimeric structure, $\{Co(Ph_3P)(C_6H_5CN)\}_2(\mu_2\text{-}\eta^2,\eta^2\text{-}C_{60})_2$ (**3**), was obtained. It contains two fullerene cages bridged by two zerovalent cobalt atoms. The cobalt atoms with $S = 1/2$ are closely located in the dimers. Moreover, calculations showed that fullerenes can effectively transfer magnetic interaction between the coordinated cobalt atoms. As a result, a strong enough magnetic interaction is realized between spins in **3** with exchange interaction $J/k_B = -28.6$ K.[5] The use of $Co(L)Br_2$ with diphosphine ligands (L) such as dppe and dppf instead of Ph_3P allows the synthesis and the first characterization of mononuclear coordination complexes of fullerene C_{60} with zerovalent cobalt $Co(\eta^2\text{-}C_{60})(dppe)(C_6H_5CN)\cdot C_6H_4Cl_2$ (**1**) and $Co(\eta^2\text{-}C_{60})(dppf)(C_6H_5CN)\cdot C_6H_4Cl_2$ (**2**) whose structural, optical, and magnetic properties are presented and discussed in detail. It should be noted that the compounds with zerovalent cobalt are not well described, and characterizations of their magnetic properties are still very scarce.

■ RESULTS AND DISCUSSION

Synthesis. The reduction of $Co(L)Br_2$ and fullerene C_{60} mixtures by sodium fluorenone in pure *o*-dichlorobenzene generates the $C_{60}^{\bullet-}$ radical anions in solution according to the NIR spectrum. The crystals of ionic compounds like $\{Co^I(dppe)_2{}^+\}(C_{60}{}^{\bullet-})\cdot 2C_6H_4Cl_2$ can be precipitated as a result of slow diffusion of hexane into the obtained solution.[6] Cobalt−fullerene coordination complexes discussed in this paper are formed when the $Co(dppe)Cl_2$ (**1**) or $Co(dppf)Br_2$ (**2**) and fullerene C_{60} mixtures are reduced by sodium fluorenone in the solution containing few drops of benzonitrile. Benzonitrile additionally coordinates to cobalt allowing the formation of cobalt−fullerene coordination complexes, and the crystals of $Co(\eta^2\text{-}C_{60})(dppe)(C_6H_5CN)\cdot C_6H_4Cl_2$ (**1**) and $Co(\eta^2\text{-}C_{60})(dppf)(C_6H_5CN)\cdot C_6H_4Cl_2$ (**2**) were precipitated by the diffusion of hexane. Apparently, in contrast to nickel, which is able to form coordination complexes with fullerenes in nearly square-planar coordination geometry,[2] cobalt does not tend to form coordination complexes with fullerenes in square-planar or tetrahedral geometry. Coordination of benzonitrile molecules to cobalt atoms produces a distorted square-pyramidal coordination environment favorable for the formation of coordination Co−C bonds with fullerenes. The quality and yield of crystals of **1** and **2** can be increased when the reaction mixture is preheated during 10 min with an excess of zinc powder, the solution is cooled to room temperature, and several drops of benzonitrile is added. Two equivalents of sodium fluorenone is added after standing of the solution overnight. We suppose the developed approach allows the preparation of coordination complexes of fullerenes with other transition metals. This work is in progress.

Optical Spectra. The IR spectra of **1**, **2**, and starting $Co(dppe)Cl_2$ or $Co(dppf)Br_2$ are shown in Supporting Information. The spectra can be presented as a superposition of the spectra of C_{60}, CoL, C_6H_5CN, and $C_6H_4Cl_2$. IR active bands of C_{60} at 526, 576, 1182, and 1429 cm^{-1} remain unsplit in the spectra of **1** and **2** or this splitting is not well resolved. Nevertheless, the absorption band of the $F_{1u}(4)$ mode at 1429 cm^{-1}, which is sensitive to charge transfer to the fullerene molecule, is noticeably shifted to 1413 and 1416 cm^{-1} in the spectra of **1** and **2**, respectively. That can be due to the π-back-donation from a metal to a fullerene molecule.[1a] The previously studied nickel−fullerene complexes show essentially stronger splitting of the $F_{1u}(2)$ and $F_{1u}(4)$ C_{60} modes, and the shift of the $F_{1u}(4)$ mode was almost the same (the average position is at 1416 cm^{-1}).[2] The absorption band of the CN stretching mode in C_6H_5CN is shifted from 2235 cm^{-1} (starting C_6H_5CN) to smaller wavenumbers in the spectra of **1** and **2** (2204−2205 cm^{-1}), indicating coordination of benzonitrile to cobalt.

The UV−visible−NIR spectra of **1** and **2** are shown in Figure 1. The absorption bands in the UV range at 259 and 336 nm (**1**) and 255 and 332 nm (**2**) can be attributed to C_{60}. The bands in the visible range at ~450 (shoulder), 690 and 910 nm in the spectrum of **1** and at ~460 (shoulder), 675 and 914 nm in the spectrum of **2** can be ascribed to the cobalt-fullerene complex. Similar bands at 460 and 650−700 nm are observed in the spectra of other metal-fullerene coordination complexes and can be attributed to charge transfer between metal and fullerene units.[1e,h,i,7] The absence of absorption of the $C_{60}^{\bullet-}$ radical anions at 1070−1080 nm[8] in the spectra of **1** and **2** indicates that fullerenes most probably have the neutral state in these complexes. Since diphosphine and benzonitrile ligands are also neutral, cobalt atoms should have formally the zerovalent state though coordination of fullerene and diphosphine to cobalt can essentially redistribute electron density on the cobalt atoms due to the donation from the filled orbitals of C_{60} or diphosphine to a vacant orbital of cobalt and a simultaneous back-donation from the occupied metal *d* orbitals.

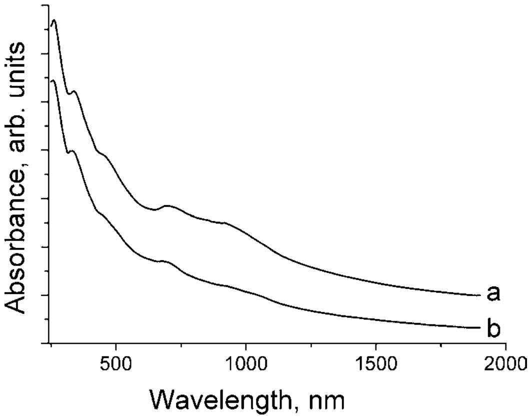

Figure 1. UV−visible−NIR spectra of **1** (a) and **2** (b) in KBr pellets.

Crystal Structures of 1 and 2. Molecular structure of the $Co(\eta^2\text{-}C_{60})(L)(C_6H_5CN)$ units and the environment of cobalt atoms in **1** and **2** are shown in Figure 2. Cobalt coordinates to the 6−6 bond of C_{60} by η^2-type coordination with Co−C(C_{60}) bond lengths of 2.008(2) and 2.023(2) Å in **1** and 2.051(3) and 2.060(3) Å in **2**. That is close to the length of strong Co−C bonds in alkylcobalamines (1.99−2.03 Å)[9a] but noticeably shorter than the length of the coordination Co−C(C_{60}^-) bonds in ionic complexes of fullerenes with cobalt(II) porphyrins (2.26−2.28 Å).[9b−d] The 6−6 bonds involved in the coordination with cobalt are elongated up to 1.492(3) in **1** and 1.486(4) Å in **2** (the average length of other 6−6 bonds in C_{60} is 1.396(5) in **1** and 1.392(5) Å in **2**). This elongation can be attributed to the π-back-donation.[1a] The Co−P bonds of 2.177(1) and 2.195(1) Å length in **1** and 2.241(1) and 2.256(1) Å length in **2** are longer than the Co−C(C_{60}) bonds. The coordination units in **1** and **2** have different bridging units and different P−Co−P angles of 88.51(2)° and 104.94(2)°, respectively. It is seen that this slightly affects the length of the

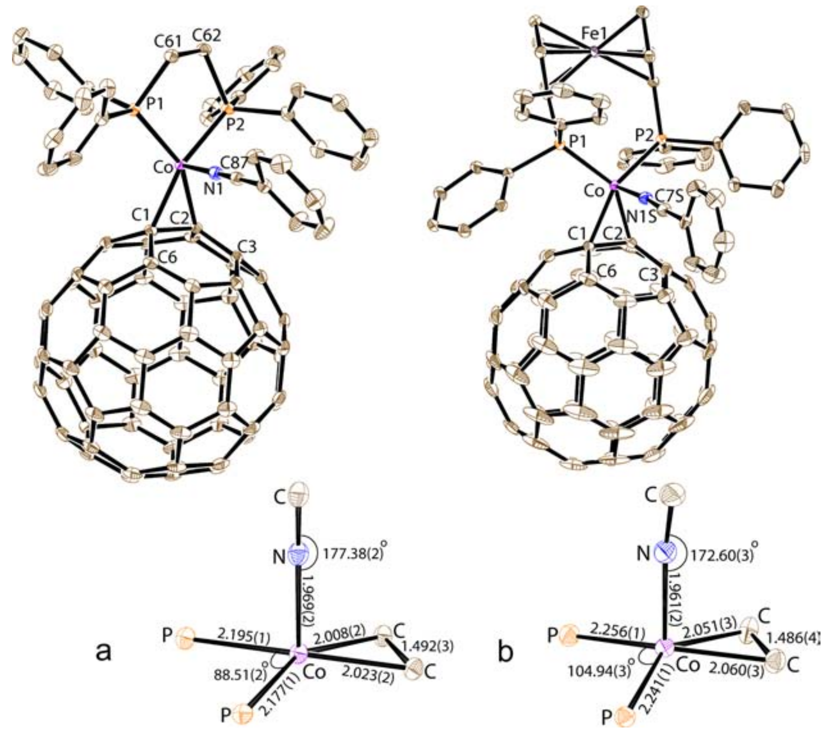

Figure 2. Molecular structure of the Co(η^2-C_{60})(dppe)(C_6H_5CN) (a) and Co(η^2-C_{60})(dppf)(C_6H_5CN) (b) coordination units. Surrounding of the cobalt atoms with the bond lengths (Angstrom) is shown below. Phosphorus is orange, carbon is brown, nitrogen is blue, and cobalt is violet. Only one orientation is shown for the phenyl substituent in Ph_3P and benzonitrile in **2**. Ellipsoid probability is 50%. Atoms are labeled for Tables 1 and 2

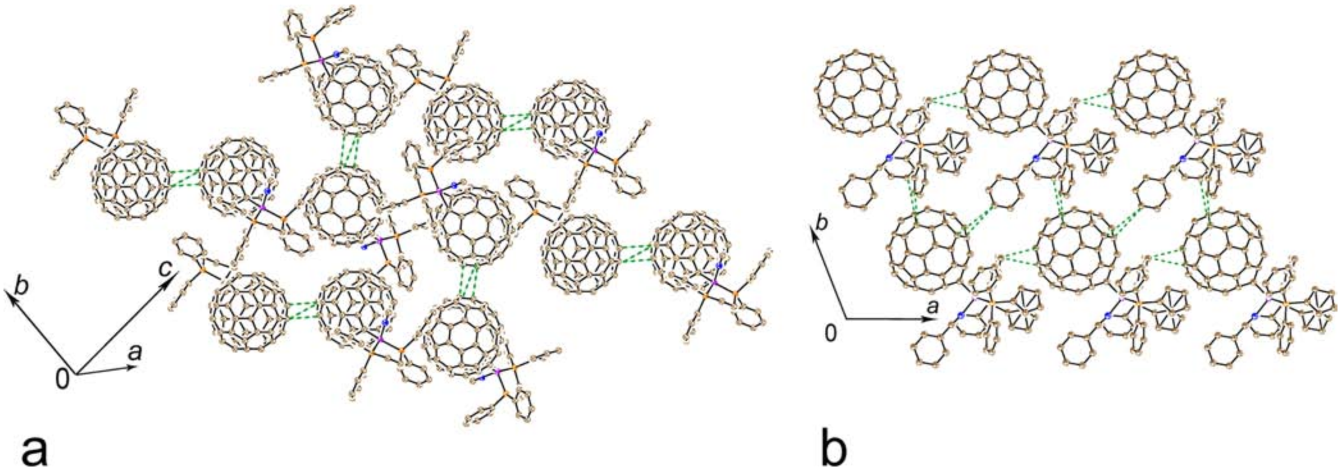

Figure 3. View on the layers formed by fullerene cages in **1** (a) and view of the crystal structure of **2** along the *c* axis (b). van der Waals C···C contacts are shown by green dashed lines. Solvent $C_6H_4Cl_2$ molecules are omitted for clarity.

Co−C(C_{60}) and Co−P bonds since they are longer in **1** by 0.04−0.06 Å than those in **2**. Coordination environment of the cobalt atoms is formed by two carbon atoms of C_{60}, two phosphorus atoms of a diphosphine ligand, and one nitrogen atom of benzonitrile and can be described as a distorted square pyramid (Figure 2, insets). Thus, planarity of the C_2CoP_2 fragment is broken due to the coordination of benzonitrile, and the cobalt atom is shifted from the C_2P_2 plane by 0.240 and 0.343 Å for **1** and **2**, respectively, toward a nitrogen atom of C_6H_5CN. Benzonitrile forms short coordination Co−N bonds of 1.969(2) and 1.961(2) Å length in **1** and **2**, respectively. It is arranged nearly perpendicular to the C_2P_2 plane and the Co−N≡C angle in both complexes is close to 180° (177.38(2)° for **1** and 172.60(2)° for **2**). Since the dppf ligand contains a ferrocene spacer between the phosphorus atoms, a short metal−metal Co−Fe distance (4.27 Å) is realized in **2**. Previously, short M···Fe distances were found in the η^2-C_{60} complexes with Pd(dppf) and Pt(dppf).[1h]

Complex **1** has layered crystal structure (Figure 3a) in which fullerene layers are separated by Co(dppe)·C_6H_5CN and solvent molecules. Each C_{60} is surrounded by six fullerenes. The other three neighbors are located closer to each other with the center-to-center interfullerene distances of 10.222, 10.224, and 10.037 Å. A pair of fullerenes with a shorter center-to-center distance form three van der Waals C···C contacts in the 3.28−3.46 Å range (these contacts are shown by green dashed lines in Figure 3a), whereas two other fullerenes do not form van der Waals contacts with C_{60}. Three fullerene neighbors of

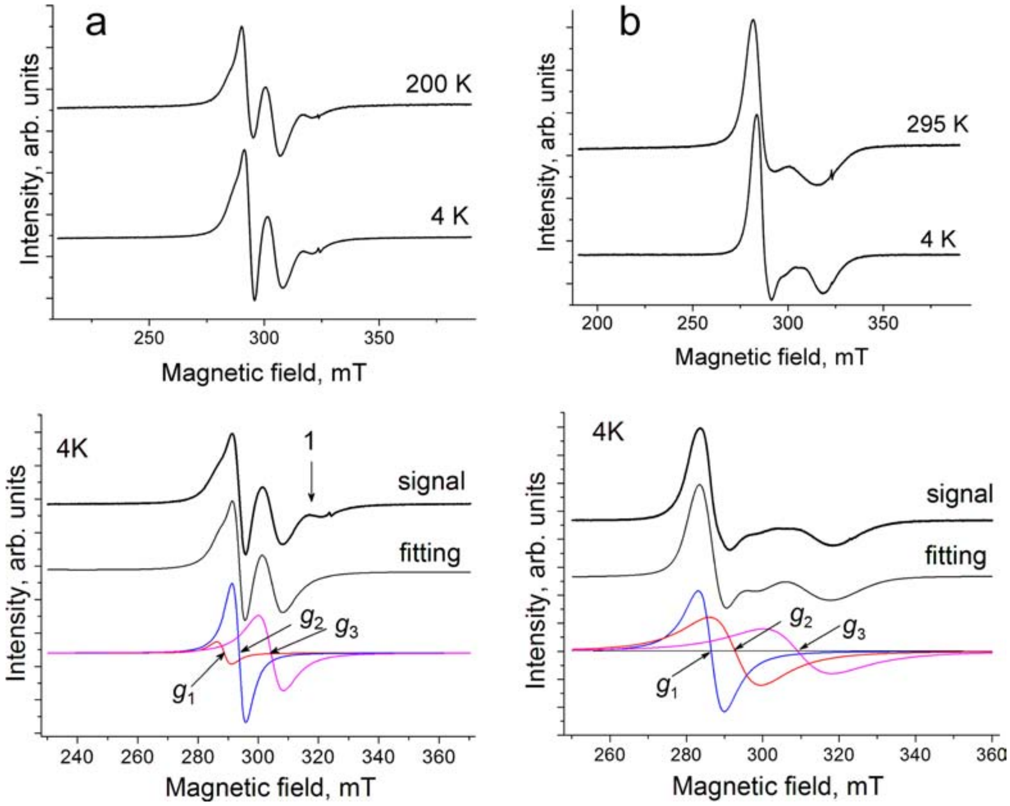

Figure 4. EPR spectra of polycrystalline **1** at 200 and 4 K (a) and **2** at 295 and 4 K (b). The bottom panels show the fitting of the signals at 4 K by three Lorentzian lines. The values of *g*-factors are in the text. Arrow 1 indicates an EPR line attributed to the admixture of Co(dppe)Cl_2.

six are positioned quite far from fullerene and center-to-center interfullerene distances are longer than 12.2 Å. Complex **2** forms isolated fullerene packing with center-to-center interfullerene distances longer than 13.3 Å due to the presence of bulky substituents. The distances between cobalt atoms in both structures exceed 10.3 Å showing that only weak magnetic interaction is possible between spins localized on cobalt atoms in **1** and **2**.

Magnetic Properties of 1 and 2. Magnetic properties of the complexes were studied by SQUID and EPR techniques. Cobalt atoms in the zerovalent state have the d^9 electron configuration and should have $S = 1/2$ spin state. Previously, an isotropic EPR signal with $g = 2.2$ was observed for the $[\{PhB(CH_2P\mathit{i}Pr_2)_3\}Co(\mu\text{-}N_2)]_2[Mg(THF)_4]$ complex containing zerovalent cobalt.[10] The EPR spectra of polycrystalline **1** and **2** measured in anaerobic conditions are shown in Figure 4. Both complexes exhibit strongly asymmetric intense signals observed in the whole studied temperature range (295−4 K). The EPR spectra of **1** at 200 and 4 K can be fitted by three Lorentzian lines with $g_1 = 2.2613$ and line width (ΔH) of 2.4 mT, $g_2 = 2.2085$ and $\Delta H = 5.4$ mT, and $g_3 = 2.1301$ and $\Delta H = 8.3$ mT at 200 K and $g_1 = 2.2388$ and $\Delta H = 4.9$ mT, $g_2 = 2.2016$ and $\Delta H = 4.6$ mT, and $g_3 = 2.1244$ and $\Delta H = 8.3$ mT at 4 K (Figure 4a). The experimental and the calculated spectra are in a good agreement except an additional weak line in the spectrum of **1** at about 318.0 mT ($g = 2.0336$, Figure 4a, bottom panel, arrow 1). Intensity of this line is only several percent of those of the three lines with $g = 2.260−2.130$, and it can be attributed to the impurity of starting Co(dppe)Cl_2, which shows a single line with close *g*-factor of 2.0357.[5] It is seen that all three lines are slightly shifted to larger *g*-factors and two of the three lines are broadened upon temperature decrease. The spectra of **2** can also be fitted well by three lines with $g_1 = 2.2576$ and $\Delta H = 6.7$ mT, $g_2 = 2.2140$ and $\Delta H = 13.5$ mT, and $g_3 = 2.0949$ and $\Delta H = 18.8$ mT at 295 K and $g_1 = 2.2576$ and $\Delta H = 6.8$ mT, $g_2 = 2.2092$ and $\Delta H = 13.4$ mT, and $g_3 = 2.0920$ and $\Delta H = 17.9$ mT at 4 K (Figure 4b). The line attributed to the admixture of Co(dppe)Cl_2 is not observed in the spectrum of **2**. The *g*-factors and linewidths of all three components only weakly depend on the temperature decrease from RT down to 4 K. Generally, the lines observed in the spectrum of **2** are essentially broader than those in the spectrum of **1**, but the *g*-factors have close values ($g = 2.258−2.092$ in the spectrum of **2** and $g = 2.261−2.124$ in the spectrum of **1**). All three components observed in the spectra of **1** and **2** can unambiguously be attributed to zerovalent cobalt since the $C_{60}^{\bullet-}$ radical anions generally show EPR signals with smaller *g*-factors (2.000−1.996), which are also strongly narrowed with the temperature decrease.[8c,11] Very weak narrow signals in the spectra of both complexes at about 323.7 mT (Figure 4) can be attributed to some defects localized on fullerenes, and their intensities are extremely small compared with that of the major signal from Co^0. The absence of EPR signal from $C_{60}^{\bullet-}$ justifies the neutral state of fullerenes in both complexes in accordance with the data of optical spectra. Exposure of crystals of **1** and **2** to air for 24 h resulted in the disappearance of the EPR signal from cobalt most probably due to oxidation of Co^0 to EPR silent diamagnetic Co^I.[4] Thus, both complexes are air-sensitive and should be stored in anaerobic conditions. The EPR spectra observed for mononuclear complexes **1** and **2** are noticeably different from those of previously studied cobalt−fullerene complex **3** with binuclear dimeric structure for which an isotropic signal with $g = 2.3053$ and line width (ΔH) of 10.7 mT at 298 K was found.

Additionally to the isotropic central signal, a half-field signal and triplet wings were also observed at higher and lower magnetic fields. These features are characteristic of triplet species, which appear due to strong magnetic interaction between two closely located magnetic centers.[5] Thus, mono- and binuclear dimeric structures of fullerenes with cobalt can be distinguished by their EPR spectra.

Effective magnetic moments of **1** and **2** are 1.86 and 1.83 μ_B, respectively, at 300 K. That indicates a low-spin ($S = 1/2$) state of Co^0 in both complexes (the calculated values for one noninteracting $S = 1/2$ spin is 1.73 μ_B). Estimated Weiss temperatures in the 20−300 K range for **1** and **2** are +0.3 and +0.6 K, respectively (see Supporting Information, Figures S3 and S4). Thus, only paramagnetic nature exists between the spins localized on the cobalt atoms possibly because of long distances between them (>10 Å) and magnetic isolation of the cobalt atoms by diamagnetic components.

Theoretical Calculations. Theoretical analysis of the electronic structure of $Co(\eta^2\text{-}C_{60})(dppe)(C_6H_5CN)$ and $Co(\eta^2\text{-}C_{60})(dppf)(C_6H_5CN)$ complexes was performed using the crystallographic data for **1** and **2** without *o*-dichlorobenzene.[12] The doublet states were calculated at the UB3LYP/LanL2DZ/6-31G(d,p) level of theory[13,14] and the other methods (Supporting Information, Table S2). Selected and sum of Mulliken atomic spin densities and the spin density distributions are shown in Table 1 and Figure 5. The highest spin density locates on the central cobalt atom in each complex. The coordinated carbon atoms C1 and C2 of C_{60} have the second highest spin density and the negative one. However, the absolute values of spin density are ~6.9% and 8.6% compared with those of the cobalt atom in $Co(\eta^2\text{-}C_{60})(dppe)(C_6H_5CN)$ and $Co(\eta^2\text{-}C_{60})(dppf)(C_6H_5CN)$, respectively. The cyanonitrogen N1 and N1S atoms of benzonitrile have the third highest spin density, and the phosphorus P1 and P2 atoms have the lowest one among the coordinated atoms. Therefore, spin density is localized mainly on the central cobalt atom, and slightly delocalized into C_{60}, benzonitrile, dppe, or dppf ligands; this conclusion is supported by the data of EPR spectroscopy. Selected and sum of Mulliken atomic charges are shown in Table 2. The central cobalt atom and C_{60} molecule have the negative charges, and dppe, dppf, and benzonitrile have the positive charges. Especially, the dppe and dppf have large positive charges, electron density of which flows into the C_{60} molecule through the central cobalt atom. The other methods also indicate a similar tendency of UB3LYP (Table S3 and S4 and Figures S5 and S6, Supporting Information).

Table 1. Selected and Sum[a] of Mulliken Atomic Spin Densities[b]

$CoC_{60}(dppe)(C_6H_5CN)$		$CoC_{60}(dppf)(C_6H_5CN)$	
Co	1.224	Co	1.303
dppe	*0.005*	dppf	*−0.003*
P1	0.010	P1	−0.004
P2	0.000	P2	0.004
C61	−0.005	Fe1	0.001
C62	−0.005		
C_6H_5CN	*0.013*	C_6H_5CN	*0.004*
N1	0.039	N1S	0.037
C87	−0.022	C7S	−0.027
C_{60}	*−0.241*	C_{60}	*−0.304*
C1	−0.085	C1	−0.112
C2	−0.083	C2	−0.106
C3	0.025	C3	0.028
C6	0.025	C6	0.027

[a] Sum of Mulliken atomic spin densities is italic. [b] Atoms are numbered according to Figure 2a,b.

CONCLUSION

In summary, we obtained for the first time the mononuclear coordination complexes of fullerenes with cobalt, $Co(\eta^2\text{-}C_{60})(dppe)(C_6H_5CN)\cdot C_6H_4Cl_2$ (**1**) and $Co(\eta^2\text{-}C_{60})(dppf)(C_6H_5CN)\cdot C_6H_4Cl_2$ (**2**). An important role of benzonitrile in the formation of these complexes has been shown. Benzonitrile together with diphosphine forms a square-pyramidal environment for the cobalt atoms, and this geometry allows the coordination of cobalt to fullerene. Like all transition metals, cobalt coordinates to the 6−6 bond of C_{60} by the η^2-type. Fullerenes are neutral in the complexes. That allows one to suppose a zerovalent state of cobalt atoms, which have d^9 electron configuration and $S = 1/2$ spin state. Theoretical calculations also show doublet states for zerovalent cobalt atoms and the localization of spin density on the central cobalt atom, whereas spin density is only slightly delocalized into C_{60}, benzonitrile, dppe, or dppf ligands. Thus, **1** and **2** are rare examples of fullerene complexes with paramagnetic metal. Spins localized on cobalt atoms are magnetically diluted in **1** and **2** due to long distances between them. However, the reported approach can be useful in the design of magnetic metal−fullerene assemblies when several paramagnetic metal centers coordinate to one fullerene molecule or multinuclear metal−fullerene structures with several fullerenes are formed. The use of other paramagnetic metals in the synthesis of new metal−fullerene coordination complexes is also possible when using this approach.

EXPERIMENTAL SECTION

Materials. $Co(dppe)Cl_2$ and 1,1′-bis(diphenylphosphino)ferrocene (dppf) were purchased from Aldrich. $Co(dppf)Br_2$ was obtained by dissolving stoichiometric amounts of $CoBr_2$ and dppf in acetonitrile and stirring of the obtained solution at 60 °C during 4 h. The solution was cooled to room temperature and dark blue polycrystalline powder of $Co(dppf)Br_2$ precipited, which was then filtered off and dried under vacuum (yield is 90%). C_{60} of 99.98% was purchased from MTR Ltd. All manipulations for the synthesis of **1** and **2** were carried out in a MBraun 150B-G glovebox with controlled inert atmosphere and the content of H_2O and O_2 less than 1 ppm. Sodium fluorenone was obtained as previously desribed.[2a] Solvents were purified in argon atmosphere. *o*-Dichlorobenzene ($C_6H_4Cl_2$) was distilled over CaH_2 under reduced pressure, benzonitrile (C_6H_5CN) was distilled over sodium under reduced pressure, and hexane was distilled over Na/benzophenone. The crystals of **1** and **2** were stored in the glovebox. KBr pellets for the measurements of IR and UV−visible−NIR spectra were also prepared in the glovebox. EPR and SQUID magnetic measurements were performed on polycrystalline samples of **1** and **2** sealed in 2 mm quarz tubes under 10^{-5} Torr.

Synthesis. $Co(\eta^2\text{-}C_{60})(dppe)(C_6H_5CN)\cdot C_6H_4Cl_2$ (**1**) and $Co(\eta^2\text{-}C_{60})(dppf)(C_6H_5CN)\cdot C_6H_4Cl_2$ (**2**) were obtained by the reduction of a stoichiometric mixture of $Co(dppe)Cl_2$ (22 mg, 0.042 mmol for **1**) or $Co(dppf)Br_2$ (32.5 mg, 0.042 mmol for **2**) and C_{60} (30 mg, 0.042 mmol) with sodium fluorenone (22 mg, 0.108 mmol) in 14 mL of *o*-dichlorobenzene in the presence of three drops of benzonitrile at 120 °C during 20 min. The color of the solutions turned green. Cooled solution was filtered in a 50 mL glass tube of 1.8 cm in diameter with a ground glass plug, and 30 mL of hexane was layered over the solution. The crystals of the complexes were precipitated during 1 month as black blocks for both **1** and **2**. The solvent was decanted from the crystals, and they were washed with hexane. Crystals with the size up

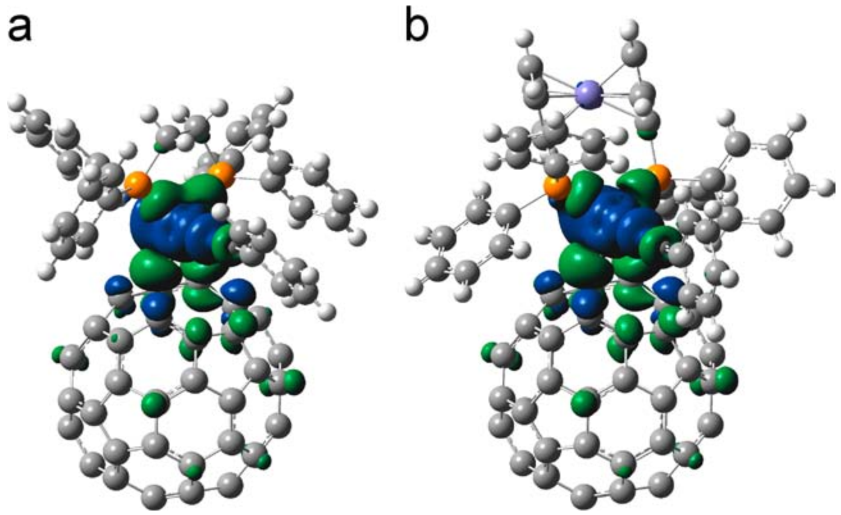

Figure 5. The isosurface plots for spin density distribution of (a) $CoC_{60}(dppe)(C_6H_5CN)$ and (b) $CoC_{60}(dppf)(C_6H_5CN)$ at the UB3LYP/LanL2DZ/6-31G(d,p) level of theory. The isosurface value is 0.0009 electron/au^3. The isosurfaces in blue and green denote the positive and negative spin density, respectively.

Table 2. Selected and Sum[a] of Mulliken Atomic Charges[b]

$CoC_{60}(dppe)(C_6H_5CN)$			$CoC_{60}(dppf)(C_6H_5CN)$		
Co		−0.287	Co		−0.391
dppe		*0.746*	dppf		*0.791*
	P1	0.582		P1	0.677
	P2	0.613		P2	0.720
	C61	−0.387		Fe	−0.196
	C62	−0.393			
C_6H_5CN		*0.118*	C_6H_5CN		*0.086*
	N1	−0.219		N1S	−0.232
	C87	0.086		C7S	0.071
C_{60}		*−0.577*	C_{60}		*−0.486*
	C1	−0.099		C1	−0.086
	C2	−0.119		C2	−0.093
	C3	0.056		C3	0.025
	C6	0.058		C6	0.038

[a] Sum of Mulliken atomic charges is italic. [b] Atoms are numbered according to Figure 2a,b.

to 0.4 × 0.4 × 0.6 mm^3 were obtained with 40−50% yield. The yield and quality of crystals can be increased when starting $Co(L)Cl_2(Br_2)$, and C_{60} mixture is preheated with an excess of zinc powder (180 mg) during 10 min at 160 °C. Cooling of the solution, addition of three drops of benzonitrile and standing overnight produce slightly green solution. The addition of sodium fluorenone (22 mg, 0.108 mmol) and stirring of the solution at 80 °C during 20 min provides deep green solution, which was cooled, filtered, and layered with hexane. Crystals were obtained during 1 month and isolated similarly (yield 50−60%).

The composition of **1** and **2** was determined from X-ray diffraction on single crystals. Several crystals tested from the synthesis had the same unit cell parameters indicating that only one crystal phase formed.

General. UV−visible−NIR spectra were measured in KBr pellets on a PerkinElmer Lambda 1050 spectrometer in the 250−2500 nm range. FT-IR spectra were obtained in KBr pellets with a PerkinElmer Spectrum 400 spectrometer (400−7800 cm^{-1}). EPR spectra were recorded for a polycrystalline sample of **1** and **2** from 4 to 295 K with a JEOL JES-TE 200 X-band ESR spectrometer equipped with a JEOL ES-CT470 cryostat. A Quantum Design MPMS-XL SQUID magnetometer was used to measure static magnetic susceptibility at 100 mT magnetic field in cooling and heating conditions in the 300−1.9 K range. A sample holder contribution and core temperature independent diamagnetic susceptibility (χ_d) were subtracted from the experimental values. The χ_d values for **1** and **2** were obtained by the extrapolation of the data (20−300 K) in the high-temperature range and fitting the data with the following expression: $\chi_M = C/(T - \Theta) + \chi_d$, where C is Curie constant and Θ is Weiss temperature. Effective magnetic moments (μ_{eff}) were calculated with formula: $\mu_{eff} = (8\chi_M T)^{1/2}$.

X-ray Crystallographic Study. Crystal data for **1** at 100(2) K: $C_{99}H_{30}Cl_2CoNP_2$, M_r = 1425.01, black block, monoclinic, $P2_1/n$, a = 15.7351(6), b = 16.0529(3), c = 25.5120(10) Å, β = 106.433(5)°, V = 6180.9(4) Å^3, Z = 4, d_{calc} = 1.531 g·cm^{-3}, μ = 0.779 mm^{-1}, $F(000)$ = 2888, $2\theta_{max}$ = 69.50°, reflections measured 96335, unique reflections 13618, reflections with $I > 2\sigma(I)$ = 12752, parameters refined 946, R_1 = 0.0483, wR_2 = 0.1283, GOF = 1.014. CCDC 945307.

Crystal data for **2** at 120(1) K: $C_{107}H_{37}Cl_2CoFeNP_2$, M_r = 1584.00, black block, triclinic, $P\bar{1}$, a = 13.3142(15), b = 14.8668(15), c = 20.051(2) Å, α = 94.646(10)°, β = 106.285(10)°, γ = 116.348(10)°, V = 3315.1(6) Å^3, Z = 2, d_{calc} = 1.587 g·cm^{-3}, μ = 0.661 mm^{-1}, $F(000)$ = 1606, $2\theta_{max}$ = 56.56°, reflections measured 30676, unique reflections 15794, reflections with $I > 2\sigma(I)$ = 11852, parameters refined 1137, restraints 297, R_1 = 0.0504, wR_2 = 0.1477, G.O.F. = 1.042. CCDC 943487.

Data collection for the crystal of **1** was carried out with a MAR225 CCD detector at 100(2) K using synchrotron radiation at the BESSY storage ring, BL 14.2 (λ = 0.9050 Å), PSF of the Free University of Berlin, Germany. X-ray diffraction data for **2** were collected at 150(2) K on a Bruker Smart Apex II CCD diffractometer with graphite monochromated Mo Kα radiation using a Japan Thermal Engineering Co. cooling system DX-CS190LD. Raw data reduction to F^2 was carried out using Bruker SAINT.[15] The structures were solved by direct method and refined by the full-matrix least-squares method against F^2 using SHELX-97.[16] Non-hydrogen atoms were refined in the anisotropic approximation. Positions of hydrogen atoms were included into refinement in a riding model. One of four phenyl substituents in **2** is disordered between two orientations with the 0.81(3)/0.19(3) occupancies. Coordinated benzonitrile molecules in **2** are disordered between two orientations with the 0.52(3)/0.48(3) occupancies. Two $C_6H_4Cl_2$ molecules in **2** having 0.5 occupancies are located on the inversion centers. As a result, they are statistically disordered between two orientations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

IR spectra, magnetic susceptibility, computational details, total energies and values of $\langle S^2 \rangle$, selected and sum of Mulliken atomic spin densitiesand atomic charges, isosurface plots for spin density distribution at several levels of the theory, and crystallographic information in CIF format. 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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■ REFERENCES

(1) (a) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Acc. Chem. Res.* **1992**, *25*, 134. (b) Bashilov, V. V.; Petrovskii, P. V.; Sokolov, V. I.; Lindeman, S. V.; Guzey, I. A.; Struchkov, Yu. T. *Organometallics* **1993**, *12*, 991. (c) Balch, A. L.; Catalano, V. J.; Lee, J. W.; Olmstead, M. M.; Parkin, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 8953. (d) Balch, A. L.; Catalano, V. J.; Lee, J. W. *Inorg. Chem.* **1991**, *30*, 3980. (e) Shevelev, Y. A.; Markin, G. V.; Konarev, D. V.; Fukin, G. K.; Lopatin, M. A.; Shavyrin, A. S.; Baranov, E. V.; Lyubovskaya, R. N.; Domrachev, G. A. *Dokl. Chem.* **2007**, *412*, 18. (f) Usatov, A. V.; Martynova, E. V.; Neretin, I. S.; Slovokhotov, Y. L.; Peregudov, A. S.; Novikov, Y. N. *Eur. J. Inorg. Chem.* **2003**, 2041. (g) Thompson, D. M.; Bengough, M.; Baird, M. C. *Organometallics* **2002**, *21*, 4762. (h) Song, L.-C.; Wang, G.-F.; Liu, P.-C.; Hu, Q.-M. *Organometallics* **2003**, *22*, 4593. (i) Balch, A. L.; Olmstead, M. M. *Chem. Rev.* **1998**, *98*, 2123.

(2) (a) Konarev, D. V.; Khasanov, S. S.; Yudanova, E. I.; Lyubovskaya, R. N. *Eur. J. Inorg. Chem.* **2011**, 816. (b) Konarev, D. V.; Simonov, S. V.; Khasanov, S. S.; Lyubovskaya, R. N. *Dalton Trans* **2011**, *40*, 9176.

(3) Cherkasov, V. K.; Rad'kov, Y. F.; Lopatin, M. A.; Bochkarev, M. N. *Russ. Chem. Bull.* **1994**, *43*, 1834.

(4) Song, L.-C.; Liu, P.-C.; Hu, Q.-M.; Lu, G.-L.; Wang, G.-F. *J. Organomet. Chem.* **2003**, *681*, 264.

(5) Konarev, D. V.; Kuzmin, A. V.; Simonov, S. V.; Khasanov, S. S.; Yudanova, E. I.; Lyubovskaya, R. N. *Dalton Trans.* **2011**, *40*, 4453.

(6) Konarev, D. V.; Troyanov, S. I.; Nakano, Y.; Ustimenko, K. A.; Otsuka, A.; Yamochi, H.; Saito, G.; Lyubovskaya, R. N. *Organometallics* **2013**, *32*, 4038.

(7) (a) Denisov, N. N.; Lobach, A. S.; Nadtochenko, V. A. *Russ. Chem. Bull.* **1996**, *45*, 1103. (b) Goldshleger, N. F.; Denisov, N. N.; Nadtochenko, V. A.; Kaplunov, M. G.; Kulikov, A. V. *Russ. Chem. Bull.* **1997**, *46*, 2032.

(8) (a) Semkin, N. V.; Spitsina, N. G.; Krol, S.; Graja, A. *Chem. Phys. Lett.* **1996**, *256*, 616. (b) Konarev, D. V.; Khasanov, S. S.; Saito, G.; Otsuka, A.; Yoshida, Y.; Lyubovskaya, R. N. *J. Am. Chem. Soc.* **2003**, *125*, 10074. (c) Konarev, D. V.; Lyubovskaya, R. N. *Russ. Chem. Rev.* **2012**, *81*, 336.

(9) (a) Rossi, M.; Glusker, J. P.; Randaccio, L.; Summers, M. F.; Toscano, P. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1985**, *107*, 1729. (b) Konarev, D. V.; Khasanov, S. S.; Otsuka, A.; Yoshida, Y.; Lyubovskaya, R. N.; Saito, G. *Chem.—Eur. J.* **2003**, *9*, 3837. (c) Konarev, D. V.; Khasanov, S. S.; Otsuka, A.; Saito, G.; Lyubovskaya, R. N. *Dalton Trans.* **2009**, 6416. (d) Konarev, D. V.; Khasanov, S. S.; Otsuka, A.; Saito, G.; Lyubovskaya, R. N. *Chem.—Eur. J.* **2006**, *12*, 5225.

(10) Betley, T. E. Coordination chemistry from trigonally coordinated iron platforms: chemistry relevant to dinitrogen reduction. Dissertation (Ph.D.), California Institute of Technology, 2005. http://resolver.caltech.edu/CaltechETD:etd-05272005-103515.

(11) (a) Konarev, D. V.; Lyubovskaya, R. N. *Russ. Chem. Rev.* **1999**, *68*, 19. (b) Reed, C. A.; Bolskar, R. D. *Chem. Rev.* **2000**, *100*, 1075.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.

(13) Ragavachari, K. *Theor. Chem. Acc.* **2000**, *103*, 361 and references cited therein..

(14) For Co(η^2-C_{60})(dppe)(PhCN), $E = -4443.2691$ hartree and $\langle S^2 \rangle = 0.852$. For Co($\eta^2$- C_{60})(dppf)(PhCN), $E = -4873.8483$ hartree and $\langle S^2 \rangle = 0.905$.

(15) *Saint*, Bruker Analytical X-ray Systems, Madison, Wisconsin, U.S.A, 1999.

(16) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.