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Formation of $\{Co(dppe)\}_2\{\mu_2\text{-}\eta^2{:}\eta^2\text{-}\eta^2{:}\eta^2\text{-}[(C_{60})_2]\}$ Dimers Bonded by Single C−C Bonds and Bridging η^2-Coordinated Cobalt Atoms

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Ⓢ *Supporting Information*

ABSTRACT: Coordination of two bridging cobalt atoms to fullerenes by the η^2 type in $\{Co(dppe)\}_2\{\mu_2\text{-}\eta^2{:}\eta^2\text{-}\eta^2{:}\eta^2\text{-}[(C_{60})_2]\}\cdot 3C_6H_4Cl_2$ [**1**; dppe = 1,2-bis(diphenylphosphino)ethane] triggers fullerene dimerization with the formation of two intercage C−C bonds of 1.571(4) Å length. Coordination-induced fullerene dimerization opens a path to the design of fullerene structures bonded by both covalent C−C bonds and η^2-coordination-bridged metal atoms.

Fullerenes form a variety of σ-bonded neutral and negatively charged dimers and polymers, some of which show promising magnetic and conducting properties.[1,2] Neutral σ-bonded species are generally obtained by treating fullerenes at high temperature and under high pressure,[1a,2a] whereas fullerene anions dimerize and polymerize at milder conditions.[1b,c,2b,c] The coordination chemistry of fullerenes has been developing rapidly, allowing one to obtain fullerene complexes with transition metals such as palladium, nickel, ruthenium, and others.[3] Besides monomeric complexes, transition metals can bridge fullerenes into dimeric and polymeric species.[4] In some of them, the decrease of interfullerene center-to-center (ctc) distances is observed. For example, they are only 9.69−9.72 Å in the $\{Co(Ph_3P)(C_6H_5CN)\}_2(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_{60})_2$ (**2**) and $\{Ni(Ph_3P)\}_2(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_{60})_2$ dimers as well as in the $[\{Ni(Me_3P)_2\}(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_{60})]_\infty$ polymer.[4b−d] These distances are shorter than those in closely packed molecular and ionic solids with monomeric fullerenes (9.9−10.0 Å).[5] A closer approach of fullerenes in the metal-bridged structures implies the dimerization or polymerization of fullerenes. The design of dimers and polymers bonded by both C−C bonds and metal bridges is a very challenging task in the development of functional fullerene compounds in which effective magnetic coupling can be realized between coordinated paramagnetic metals, and charge transfer from metal to fullerene can provide high conductivity. However, such compounds are still unknown.

In this work, we show that the coordination of two bridging Co(dppe) units [dppe = 1,2-bis(diphenylphosphino)ethane] to fullerene C_{60} provides the formation of $\{Co(dppe)\}_2\{\mu_2\text{-}\eta^2{:}\eta^2\text{-}\eta^2{:}\eta^2\text{-}[(C_{60})_2]\}$ dimers (**1**) bonded by both two single C−C bonds and two bridging η^2-coordinated cobalt atoms. That is the first $[(C_{60})_2]$ dimer obtained via coordination-induced fullerene dimerization. It is shown that the $[(C_{60})_2]$ dimers perform as an effective spin coupler for paramagnetic cobalt atoms. We discuss the molecular structure and optical properties of the dimer and present theoretical investigations of a possible formation mechanism and its electronic structure.

In the previously studied dimeric unit of another type **2**, C_{60} moieties bridged by two $Co(Ph_3P)(C_6H_5CN)$ units were not bonded directly with each other. The synthesis of **2** was carried out in *o*-dichlorobenzene ($C_6H_4Cl_2$) from $Co(Ph_3P)_2Br_2$ and C_{60} under reduction with zinc dust in the presence of C_6H_5CN.[4b] To understand the effect of the diphosphine ligand on the structure of cobalt fullerene complexes, we carried out synthesis with $Co(dppe)Cl_2$ and C_{60} under reduction with zinc dust. The reaction in $C_6H_4Cl_2$ provided air-sensitive crystals of $\{Co(dppe)\}_2\{\mu_2\text{-}\eta^2{:}\eta^2\text{-}\eta^2{:}\eta^2\text{-}[(C_{60})_2]\}\cdot 3C_6H_4Cl_2$ (**1**) in poor yield (<5%). The structure of directly bonded $[(C_{60})_2]$ dimers coordinated by bridged Co(dppe) units in **1** was determined with R_1 = 0.0787. The reaction in the presence of *N*,*N*-dimethylformamide (DMF) as the coordinating solvent resulted in essentially higher yield (56%) of platelike crystals of $\{Co(dppe)\}_2\{\mu_2\text{-}\eta^2{:}\eta^2\text{-}\eta^2{:}\eta^2\text{-}[(C_{60})_2]\}\cdot x$DMF (**3**), which also contain these dimers. However, the crystal structure could not be refined with reasonable accuracy ($R_1 \sim 0.25$) because of a disorder of DMF molecules and their release from the crystals.

The crystal structure of **1**[6] contains two $\{Co(dppe)\}_2\{\mu_2\text{-}\eta^2{:}\eta^2\text{-}\eta^2{:}\eta^2\text{-}[(C_{60})_2]\}$ units, one of which is disordered over two positions. The molecular structure of the ordered unit is shown in Figure 1a. Each of two cobalt atoms in **1** is coordinated by two fullerene molecules via two η^2-type bonds of 2.080(3)−2.096(4) Å length. Coordination is realized to the 6−6 C−C bonds of C_{60}, which are elongated to 1.432(4)−1.447(5) Å in comparison with the average length of the other 6−6 C−C bonds in C_{60} (1.39 Å). This elongation is explained by the metal-to-C_{60} π-back-donation.[3a] Each cobalt atom is additionally coordinated by a bidentate dppe ligand with a Co−P(dppe) bond length of 2.274(1)−2.290(1) Å. The coordination environment of the cobalt atoms is a distorted tetrahedral one formed by two pairs of carbon atoms and two phosphorus atoms (Figure 1b). The coordination of two bridging cobalt atoms assists the approach of

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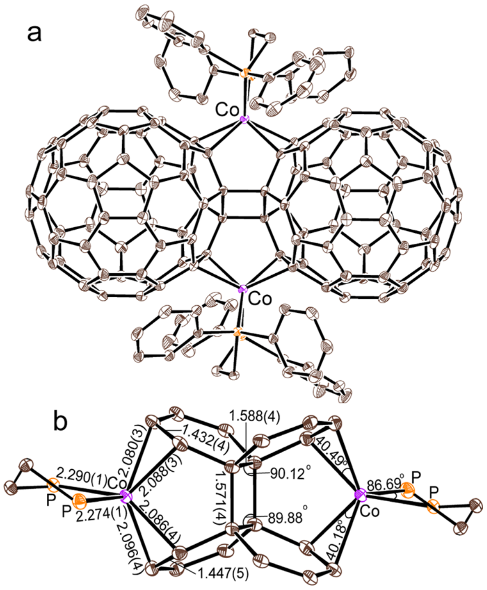

Figure 1. (a) View on the $\{Co(dppe)\}_2\{\mu_2\text{-}\eta^2:\eta^2\text{-}\eta^2:\eta^2\text{-}[(C_{60})_2]\}$ dimer in **1**. (b) Selected bond lengths and angles in the coordination environment of cobalt atoms in **1**. Cobalt, carbon, and phosphorus atoms are in violet, brown, and orange color, respectively. The ellipsoid probability is 30%. Phenyl substituents of dppe are omitted in part b.

fullerene cages close to each other, their dimerization, and the formation of two single interfullerene C−C bonds of 1.571(4) Å length under the formation of a cyclobutane ring (Figure 1). As a result, the ctc distance between the fullerene spheroids in **1** is only 9.07 Å. These parameters for the major orientation of the disordered dimer are 1.581(7) and 9.06 Å, respectively. The ctc distance and length of the interfullerene C−C bonds in **1** are almost the same as those in the doubly bonded neutral $[(C_{60})_2]$ dimer [9.05 and 1.575(7) Å][7] as well as in the doubly bonded negatively charged $[(C_{60}^-)_2]$ dimer [9.07 and 1.581(3) Å].[1c] Dimerization of fullerenes in **1** is induced by the coordination of bridged cobalt atoms with the dppe ligand to the 6−6 bonds of two adjacent C_{60} hexagons, fixing two fullerene molecules at a short distance and in the orientation suitable for dimerization (Figure 1b). In contrast to **1**, the mutual arrangement of C_{60} is not suitable to form the interfullerene C−C bonds, and the fullerene spheres remain located far from each other in previously studied nickel- and cobalt-bridged dimers.[4b,c] Cobalt atoms are separated by a distance of 6.450(5) Å in **1**, which is longer than that of 5.308(3) Å in **2**.[4b] The dimers are packed in **1** in such a way that fullerene spheres form closely packed zigzag chains along the *b* axis (Figure S3 in the Supporting Information, SI).

The spectra of **1** in the IR and UV−visible−near-IR (NIR) range are shown in the SI (Table S1 and Figures S1 and S2). The band of the $F_{1u}(4)$ vibrational mode in C_{60}, which is sensitive to its charge state,[5] is observed at 1435 cm^{-1}, overlapping with an intense band of Co(dppe) at 1434 cm^{-1}. The $F_{1u}(4)$ band remains nearly unshifted compared with that of the neutral $[(C_{60})_2]$ dimer (1427 cm^{-1}).[7] In addition to the bands of C_{60} and Co(dppe), we also found many weak bands that can appear at symmetry breaking in C_{60} because of dimerization (so-called "silent modes" are manifested).[7] The UV−visible−NIR spectrum of **1** shows a band of C_{60} at 329 nm and broad absorption at about 700 nm attributed to charge transfer from metal to fullerene.[3,4] The absorption bands of $C_{60}^{\bullet-}$ at 930−950 and 1060−1080 nm[5] are not observed in the spectrum of **1**. Therefore, complex **1** contains neutral $[(C_{60})_2]$ dimers, and the coordinated cobalt atoms should also have zero oxidation state with a d^9 electron configuration of the $S = {}^1/_2$ spin state. A similar electronic state of cobalt was found in other cobalt fullerene complexes.[4b,8]

Neutral $[(C_{60})_2]$ dimers form in solution in the presence of $FeCl_3$ as the oxidizer.[9] Under reduction conditions, dimerization of $C_{60}^{\bullet-}$ is observed, but the $(C_{60}^-)_2$ dimers are unstable at room temperature and dissociate.[1b] The dimerization of C_{60} in **1** is realized most probably in the coordination sphere of the cobalt atoms. This idea is supported indirectly by the experimental facts that the $[(C_{60})_2]$ dimers do not form in similar conditions with $Co(Ph_3P)_2Br_2$ and complex **2** forms with monomeric C_{60}.[4b] The sterical volumes of Ph_3P and C_6H_5CN in **2** and dppe in **1** are close. To clarify the reasons for the formation of covalently linked $[(C_{60})_2]$ dimers in **1**, quantum-chemical modeling of virtual complexes **4**−**7** was carried out. These complexes can be intermediates at the formation of **1**. Their molecular structures were optimized based on the PBE density functional method using the basis of cc-pVTZ quality with the *PRIRODA* program package.[10] This approach allows one to reproduce well the geometry of **1** and **2** (Figures S4 and S5 in the SI).

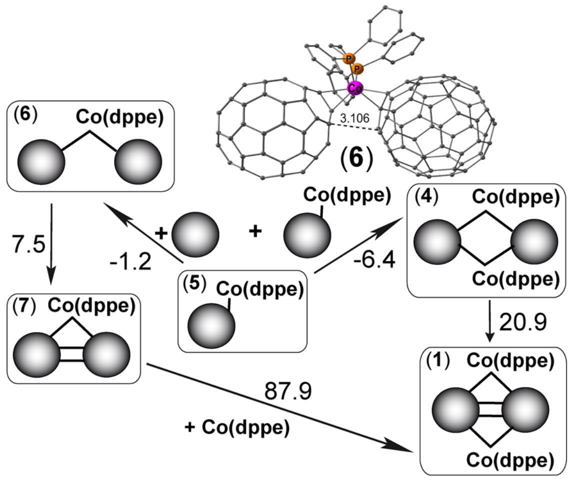

Figure 2. Reaction heat for conversion of virtual intermediates (**4**−**7**; Figure S5 in the SI) and **1** (positive value for the exothermic case are in kcal mol^{-1}). Inset: structure of **6**.

The symmetric complex $\{Co(dppe)\}_2(\mu_2\text{-}\eta^2:\eta^2\text{-}C_{60})_2$ (**4**) without C−C bonds between fullerenes, whose structure is similar to that of **2**, is higher in energy by 20.9 kcal mol^{-1} than isomeric complex **1** (Figure 2). Hence, dimerization of C_{60} must be the driving force to form **1**. For C−C bond formation between C_{60} ligands, flexibility of C_{60} binding with the metal center is desirable. $Co(dppe)(\eta^2\text{-}C_{60})_2$ (**6**; Figure 2, inset) is an appropriate candidate for this purpose. Its formation from **5** and C_{60} is a weakly endothermic reaction with an energy increase by 1.2 kcal mol^{-1}. The transformation of **6** into $Co(dppe)\{\eta^2:\eta^2\text{-}[(C_{60})_2]\}$ (**7**) dimers with two C−C bonds between fullerenes leads to an energy release of 7.5 kcal mol^{-1}. However, the 2 + 2 cycloaddition is a symmetry-forbidden reaction, and such a process has a high activation barrier. Most probably, the electron transfer catalyzes this process. It can be electron transfer to **6** or the interaction of **5** with $C_{60}^{\bullet-}$. In these cases, radical addition of $C_{60}^{\bullet-}$ to C_{60} in the coordination sphere of the cobalt atom leads to formation of the $[(C_{60})_2]^-$ ligand. Indeed, the calculated electron affinity of **6** is higher than those of C_{60} and **7** by 4 and 1 kcal mol^{-1}, respectively. This ratio provides the recovery of the charged state of **6** after the formation of **7** with excess electrons. Complex **7** formed in this reaction has only one position suitable for binding the second Co(dppe) unit to yield **1** with 87.9 kcal mol^{-1} exothermic reaction heat. Thus, the most stable state consisting of two Co(dppe) and two C_{60} is complex **1** in which C−C bonds are formed between two neutral C_{60} moieties.

Theoretical analysis of the electronic structure of the $\{Co(dppe)\}_2\{\mu_2\text{-}\eta^2{:}\eta^2\text{-}\eta^2{:}\eta^2\text{-}[(C_{60})_2]\}$ dimer was performed on the basis of the crystal structure.[11] The broken-symmetry singlet and triplet states were calculated at the UB3LYP and UM11/cc-pVTZ/cc-pVDZ levels of theory, and the total energies (E_S and E_T), $\langle S^2 \rangle$ values, and energy differences (ΔE_{ST}) are shown in the SI (Table S2). UB3LYP and UM11 functionals qualitatively afforded similar results. However, the wave functions of UM11 were more heavily contaminated by the higher spin states than those of UB3LYP. On the basis of UB3LYP and UM11 methods, the singlet states were estimated to be more stable energetically than the triplet ones by 28.7 and 118.8 K. These values are close to those calculated for the dimers in **2**, in which the singlet state is more stable by 113.6 K than the triplet one and the experimentally determined magnetic exchange interaction from SQUID data is $J/k_B = -28.6$ K.[4b] Therefore, moderate magnetic coupling between the spins localized on Co^0 is realized in both dimers. The $[(C_{60})_2]$ dimer in **1** is the effective spin coupler between cobalt $^1/_2$ spins, in which the π-electronic system of $[(C_{60})_2]$ is spin-polarized to mediate the magnetic interaction. The energy diagrams for frontier Kohn−Sham orbitals of the singlet state in dimer **1** are shown in Figure 3. The 597th α and β orbitals are singly occupied molecular orbitals (SOMOs). These SOMOs do not localize only on the cobalt atom but are spread over the $[(C_{60})_2]$ dimer, in which the d orbital of cobalt and the π orbital of the $[(C_{60})_2]$ dimer are dominant. Calculated charge and spin densities of cobalt, dppe, and C_{60} are summarized in Table S3 and Figure S7 in the SI. Natural population analysis (NPA) shows that the charge on cobalt is close to zero. The Mulliken spin densities are nearly the same as those of NPA, and the spin density is mainly distributed on the cobalt atoms along with small portions on fullerenes (Table S3 in the SI).

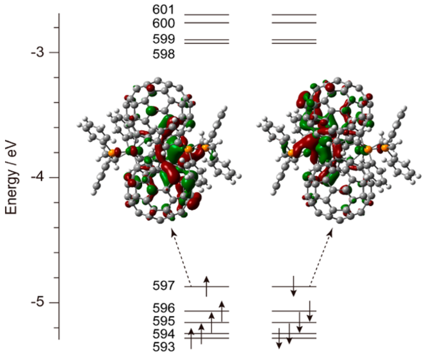

Figure 3. Energy diagram for frontier Kohn−Sham orbitals calculated at the UB3LYP/cc-pVTZ/cc-pVDZ level of theory.

In this work, we showed that the coordination of cobalt atoms as bridges between two fullerene molecules triggers the formation of new types of fullerene dimers bonded by both interfullerene C−C bonds and η^2-coordinated metal atoms. According to the calculations, paramagnetic cobalt in zero oxidation state shows moderate magnetic coupling between spins in the dimers because fullerenes mediate the magnetic coupling through the spin-polarized π-electronic system. It can be supposed that the Co(dppe) units can also bridge fullerenes in one-dimensional polymers, allowing coordination-induced polymerization of fullerenes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, IR and UV−visible−NIR spectra of **1** and starting compounds, synthesis of **1**, materials, X-ray crystal structure determination for **1**, and details of theoretical calculations. 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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(6) Crystal data: Synchrotron X-ray data were collected on the BL14.2 at the BESSY storage ring (λ = 0.81036 Å; Berlin, Germany). $\{Co(dppe)\}_2[(C_{60})_2]\cdot 3C_6H_4Cl_2$, $C_{190}H_{60}Cl_6Co_2P_4$, triclinic, $P\bar{1}$, a = 17.145(1) Å, b = 17.552(1) Å, c = 19.776(1) Å, α = 99.756(5)°, β = 93.345(9)°, γ = 102.701(8)°, V = 5693.2(5) $Å^3$, Z = 2, T = 100 K, 27263 reflections, 2307 parameters, 72 restraints, R1(F) = 0.0787 for 24261 reflections with $I > 2\sigma(I)$, wR2 (all F^2) = 0.1950, CCDC 1052993.

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