Organic LETTERS

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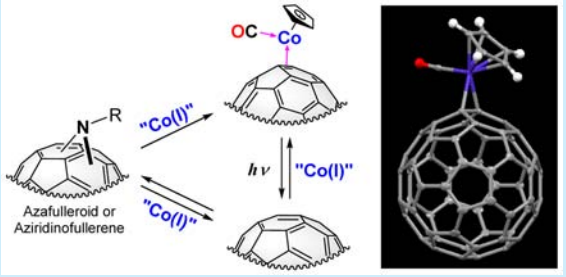
Co(I)-Mediated Removal of Addends on the C_{60} Cage and Formation of the Monovalent Cobalt Complex CpCo(CO)(η^2-C_{60})

Yoshifumi Hashikawa, Michihisa Murata, Atsushi Wakamiya, and Yasujiro Murata*

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Supporting Information

ABSTRACT: The removal of addends on the fullerene C_{60} cage plays an important role in the final stage for synthesizing endohedral fullerenes by the molecular surgery method. We developed a cobalt-mediated reaction to regenerate C_{60} from *N*-substituted C_{60} derivatives (aziridinofullerene and azafulleroid). In these reactions, we found the formation of a green monovalent-cobalt complex of C_{60}, and its structure was unambiguously determined by X-ray analysis. The characteristic electronic structure of this cobalt complex was studied by IR and UV−vis absorption spectroscopy and electrochemical analyses.



The functionalization and skeletal modification of fullerenes C_{60} and C_{70} have been investigated in order to elucidate their intrinsic properties such as electron-accepting abilities and shielding environments inside the cage.[1] These methods have great potential to create an opening on the cage that can accept small atom(s) and/or molecule(s).[2] In contrast to these chemical modifications of the σ-skeleton, retro-reactions for removing organic addends from fullerene cages were limited. The retro-Bingel[3] and retro-Diels−Alder (retro-DA)[4] reactions are known as conventional methods for removal of addends on the fullerene cage (Figure 1a,b). Some reports have appeared on metal-catalyzed,[5] base-assisted,[6] and acid-promoted[7] retro-reactions (Figure 1c). Our research group has been developing retro-reactions for synthesizing endohedral (hetero)fullerenes,[8] such as photochemical elimination of an S═O unit, carbonyl coupling (using $TiCl_4$/Zn, phosphite, or phosphine), and retro-DA reactions. Recently, Whitby and co-workers developed an improved method for removal of addends on the open-cage C_{60} derivative (Figure 1b).[4f,g] Here, we report a novel approach for removal of addends from *N*-substituted C_{60} derivatives (azafulleroid and aziridinofullerene) by using a Co(I) complex as well as the X-ray structure of a green monovalent-cobalt complex having an η^2-C_{60} ligand (CpCo(CO)(η^2-C_{60})), which was also formed in these reactions.

Cyclopentadienylcobalt dicarbonyl $CpCo(CO)_2$ has been used for the [2 + 2 + 2] cycloaddition, intra/intermolecular cyclization, and ring-opening reactions, which have been applied to the total synthesis of natural products as key steps.[9] The typical reaction mechanism is explained as follows: CO ligand(s) of $CpCo(CO)_2$ are replaced by other ligand(s) or reaction substrate(s), followed by oxidative coupling for formation of the cobaltacycle of Co(III) and finally reductive elimination to afford target compounds and Co(I) species. As reaction substrates, we focused on *N*-substituted C_{60} derivatives **2**−**4** since a nitrogen atom bearing naked lone pair electrons is expected to act as a directing group or a possible ligand in the cobalt-mediated reaction.

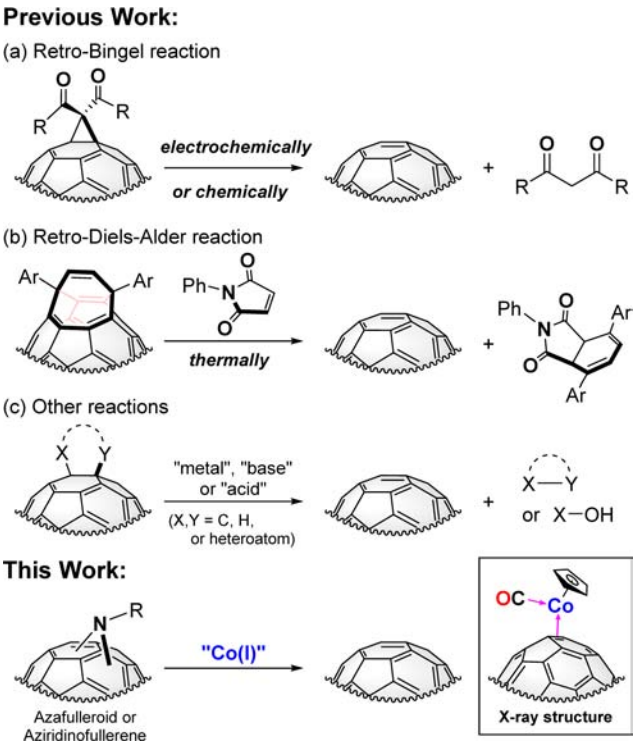


Figure 1. Conventional methods for removal of addends on the C_{60} cage (previous work) and a new method (this work).

We performed the reaction of *N*-substituted C_{60} derivatives **2**−**4** with $CpCo(CO)_2$ as well as their heteroatom analogues **5**−

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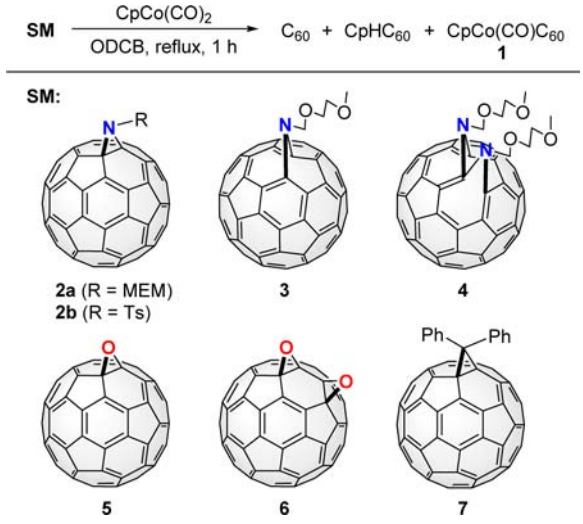
7.[10] The results were summarized in Table 1. By the reaction of **2a** with equimolar $CpCo(CO)_2$, C_{60} was obtained in 42% yield

Table 1. Removal of Addends from Substituted C_{60} Derivatives by $CpCo(CO)_2$



entry	SM	$CpCo(CO)_2$ (equiv)	C_{60}[a] (%)	$CpHC_{60}$[a] (%)	**1**[a] (%)
1	**2a**	1	42	25	4
2	**2a**	2	45	16	27
3[b]	**2a**	2	34	11	15
4[c]	**2a**	2	0	0	0
5	**2b**	2	26	11	<1
6	**3**	2	32	9	16
7	**4**	4	<1	2	3
8[d]	**5**	2	6	10	18
9	**6**	4	2	6	2
10[e]	7	2	0	0	0

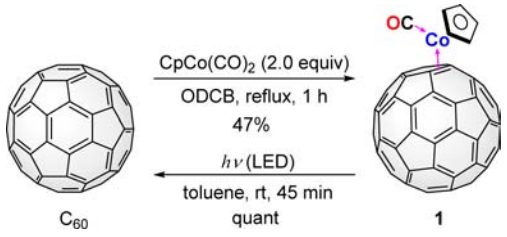
[a]Isolated yields. [b]Conducted at 150 °C. [c]Conducted at 120 °C. [d]Multiadducts $[CpCo(CO)]_nC_{60}$ were also formed. [e]Converted into multicobalt adducts of **7** with recovered **7** in 9% yield.

with DA-adduct $CpHC_{60}$ (25%) and a trace amount of green compound **1** (entry 1). This newly formed compound **1** has an ^{1}H NMR signal at 5.56 ppm ($CDCl_3/CS_2$ (1:1)) for the Cp ring, IR (infrared ray) carbonyl stretching at 2012 cm^{-1}, and a molecular ion peak at m/z 871.9645 ($[C_{66}H_5OCo]^{\bullet-}$) detected by the ESI (electrospray ionization) method, indicating the structure is a $CpCo(CO)$ unit on the C_{60} cage via π-coordination with a molecular formula of $CpCo(CO)C_{60}$.

When the amount of $CpCo(CO)_2$ was increased up to 2 equiv, cobalt complex **1** was formed from **2a** in an improved yield (27%), whereas the yield of C_{60} was maintained (45%) (entry 2). The reaction of **2a** with $CpCo(CO)_2$ at lower temperatures (150 and 120 °C) decreased the conversion into C_{60} (entries 3 and 4). Likewise, aziridinofullerene **2b** having a tosyl group was mainly converted into C_{60} and $CpHC_{60}$ in 26 and 11% yields, respectively (entry 5). This reaction can be applied to [5,6]-isomer **3**, resulting in the formation of C_{60} (32%), $CpHC_{60}$ (9%), and **1** (16%) (entry 6). The conversion of bis-[5,6]-bridged iminofullerene **4** was quite low, probably due to the sterically protected reaction site or trapping of $CpCo(CO)_2$ by two 2-methoxyethoxymethyl (MEM) groups (entry 7). 1,2-Epoxy[60]-fullerene **5** is accessible for other varieties in the fused-C_{60} systems[11] and readily undergoes thermal deoxygenation to furnish C_{60} under MS (mass spectroscopy) conditions or the presence of phosphine.[12] In the presence of 2-fold $CpCo(CO)_2$, **5** was completely consumed to give C_{60} (6%), $CpHC_{60}$ (10%), **1** (18%), and multiadducts $[CpCo(CO)]_nC_{60}$ (entry 8), whereas **5** was decomposed into insoluble solids and recovered only in 11% yield after being refluxed in *o*-dichlorobenzene (ODCB) for 1 h in the absence of $CoCp(CO)_2$. For 1,2;3,4-diepoxy[60]fullerene **6**, the decomposition into insoluble solids was dominant rather than conversion into C_{60} (entry 9). In contrast to compounds **2**–**6**, the reaction of **7** with $CpCo(CO)_2$ gave multicobalt adducts of **7** ($[CpCo(CO)]_n$**7**) with a small amount of **7** (9%) instead of the formation of C_{60} (entry 10).

The reaction of **2**–**6** with $CpCo(CO)_2$ always afforded $CpCo(CO)C_{60}$ (**1**) as a side product by overreaction of regenerated C_{60} with a second $CpCo(CO)_2$ (Table 1). We conducted a reaction of pristine C_{60} with $CpCo(CO)_2$. The color of the reaction mixture gradually changed from purple to dark green, and **1** was obtained in 47% yield (Scheme 1). Unlike the

Scheme 1. Synthesis of $CpCo(CO)C_{60}$ (1)



iridium complex (η^5-indenyl)$Ir(CO)C_{60}$,[13] this cobalt complex exhibited remarkable stability in air and even under CO atmosphere (no ligand exchange). Additionally, it is possible to purify **1** using a silica gel column or by HPLC equipped with a Buckyprep column. However, upon photoirradiation of the toluene solution of **1**, the $CpCo(CO)$ moiety was quantitatively lost to regeneration of C_{60} within 45 min (Scheme 1), indicating that **1** is a potential synthon of C_{60} as is the case for $CpHC_{60}$.[4c] Thus, the net conversion of **2a** into C_{60} equevalents reaches 88% in total (Table 1, entry 2).

We also found that 1 equiv of Brønsted or Lewis acid also worked for the conversion of **2a** into C_{60}: *p*-TsOH·H_2O (12%), TfOH (38%), and $Sc(OTf)_3$ (36%).[7a] This elimination reaction was accompanied by partial deprotection of the MEM group on the N atom. In these reactions, the protonation by Brønsted acids or coordination of Lewis acids onto the N atom should assist the elimination of the N–R group from **2**. Similarly, $CpCo(CO)_2$ is considered to be attracted by the directing effect of the N atom to cause removal of the N–R group. However, we cannot exclude the alternative possibility that oxidative addition of the C–N bond to the cobalt(I) center leads to the regeneration of C_{60} even though a such complex was not observed.

The single crystals of **1** suitable for X-ray analysis were obtained from the toluene solution, and the structure was unambiguously determined (Figure 2). This is the first example of a monovalent cobalt complex having an η^2-C_{60} ligand.[14,15] Complex **1** has a structure where one of the carbonyl ligands in $CpCo(CO)_2$ is replaced by C_{60} in an η^2-fashion through the [6,6]-bond. The bond length of C1–O1 (1.129(4) Å) is comparable with that for $(\eta^5$-$C_5R_5)Co^I(CO)_2$ (1.13–1.18 Å), while the coordination bond Co1–C1 is slightly longer (1.772(3) vs 1.64–1.73 Å).[16] The coordination bonds, Co1–C2 (2.015(3) Å) and Co1–C3 (2.031(3) Å), are close to the Co–C(C_{60}) bonds (2.01–2.06 Å) in zerovalent cobalt

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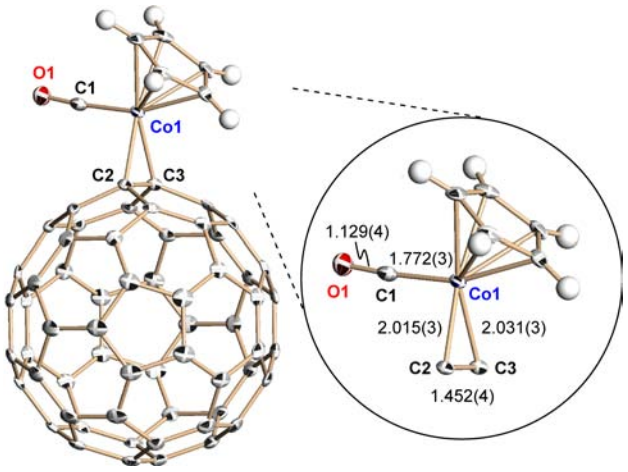

Figure 2. Single-crystal X-ray structure of $CpCo(CO)C_{60}$ (**1**) with 50% probability of thermal ellipsoids. The inset shows an enlarged view surrounding the monovalent cobalt-center with selected bond lengths (units in Å).

complexes $Co^0(PR_3)_2(PhCN)(\eta^2\text{-}C_{60})$[17] but shorter than the σ-type coordination Co−C(C_{60}^-) bonds (2.28−2.32 Å) in ionic complexes $[A^+][(Co^{II}\ porphyrin)(C_{60}^-)]$ (A^+: countercation).[18] This may be attributed to the noticeable chemical stability of **1**. Compared to typical [6,6]-bonds in C_{60} (1.38 Å),[1c] the C2−C3 bond is significantly elongated (1.452(4) Å), presumably due to $d-\pi^*$ type back-donation from the cobalt-center to C_{60}.[17] This can be also proved by IR carbonyl stretching[19] as an indicator of electron density on the metal-center: 2012 cm^{-1} for $CpCo(CO)(\eta^2\text{-}C_{60})$ shifted to higher energy than 1978 cm^{-1} for $CpCo(CO)(\eta^2\text{-}C_2H_4)$,[20] reflecting the electron-withdrawing character of C_{60}.

The cyclic and differential pulse voltammetries were conducted for C_{60} and **1** (Figure 3). Complex **1** has two quasi-reversible reduction waves at −1.21 and −1.57 V, respectively, suggesting the formation of electrochemically stable radical anion $\mathbf{1}^{\bullet-}$ and dianion $\mathbf{1}^{2-}$. These reduction potentials are cathodically shifted by 0.12 and 0.09 V, respectively, compared to C_{60}. This results are consistent with DFT calculations: a higher-lying LUMO level for **1** (−5.43 eV) vs C_{60} (−5.99 eV) (B3LYP/6-31G(d) for C, H, and O and LanL2DZ for Co).[21]

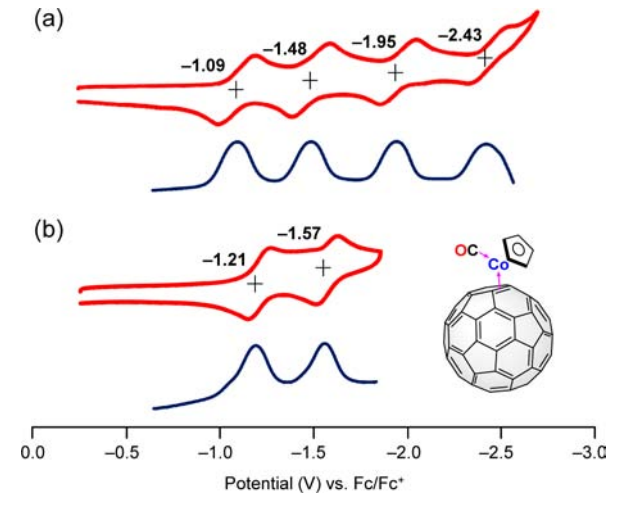

Figure 3. Cyclic and differential pulse voltammograms (indicated by red and blue, respectively) of (a) C_{60} and (b) $CpCo(CO)C_{60}$ (**1**) using 0.50 mM samples with 0.10 M $n\text{-}Bu_4N{\cdot}BF_4$ in ODCB at a scan rate of 100 mV s^{-1}.

The UV−vis absorption spectra of C_{60} and **1** were shown in Figure 4. Except for the absorption at 338 nm, the maximum

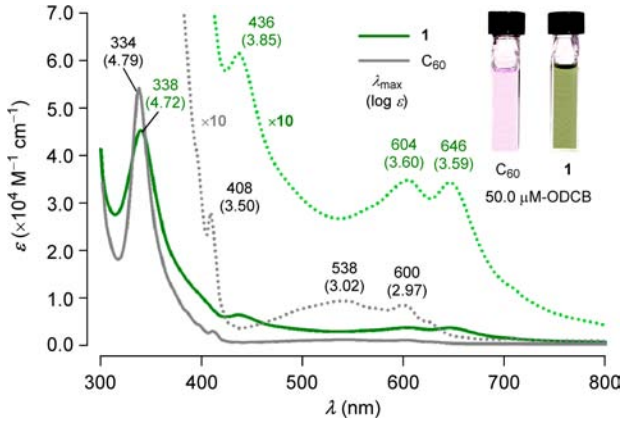

Figure 4. UV−vis absorption spectra of C_{60} (gray) and $CpCo(CO)C_{60}$ (**1**) (green) for 50.0 μM solutions in ODCB. The enlarged spectra (10-fold) were plotted by dotted lines. The maximum absorption wavelengths λ_{max} (nm) were shown with log ε in parentheses.

absorption wavelengths λ_{max} of **1** were bathochromically shifted by up to 66 nm with increased absorption coefficients ε, originated from the extended π-conjugation including the CpCo moiety (HOMO and LUMO were shown in Figure S8).

In summary, we developed a method for removal of addends on the C_{60} cage using a stoichiometric amount of $CpCo(CO)_2$. The substituents were successfully removed for *N*-substituted C_{60} derivatives. This method has a potential usage for applying the final stages in syntheses of endohedral fullerenes and/or heterofullerenes. Furthermore, it may be extended to regioselective functionalization of fullerene derivatives as a key reaction during the protection/deprotection process for synthesizing multifunctionalized C_{60} derivatives. We also found the formation of green compound **1** as a side product, and the solid-state structure was clearly determined by X-ray analysis. This cobalt complex **1** was effectively synthesized by the reaction of C_{60} with $CpCo(CO)_2$ and exhibited a remarkable stability under CO atmosphere.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03238.

Supplementary figures and tables, detailed experimental procedures, characterization data, and computational results (PDF)

Crystallographic data for **1** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: yasujiro@scl.kyoto-u.ac.jp.

ORCID

Yasujiro Murata: 0000-0003-0287-0299

Notes

The authors declare no competing financial interest.

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