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Cobalt-Catalyzed Hydroalkylation of [60]Fullerene with Active Alkyl Bromides: Selective Synthesis of Monoalkylated Fullerenes

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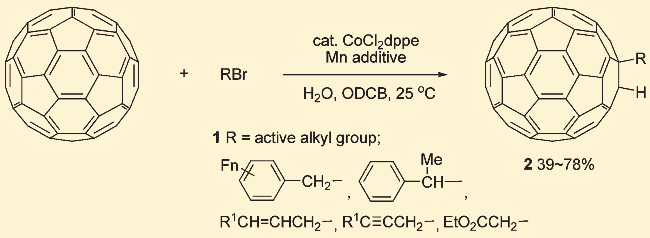
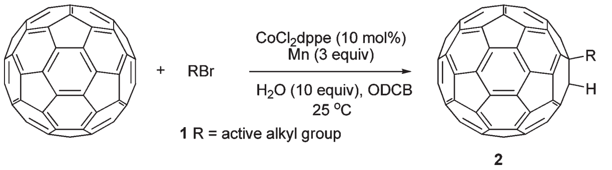
S *Supporting Information*

ABSTRACT: The Co-catalyzed hydroalkylation of C_{60} with reactive alkyl bromides **1** (RBr) in the presence of Mn reductant and H_2O at ambient temperature gave the monoalkylated C_{60} (**2**) in good to high yields. The use of CoLn/Mn/H_2O under Ar atmosphere is crucial for the success of the present transformation. The reaction most probably proceeds through the Co(0 or I) complex-promoted generation of a radical ($R^\bullet$) followed by addition to C_{60}. This hydroalkylation method was applied to the synthesis of zinc porphyrin attached C_{60} (**2l**), dendrimer attached C_{60} (**2m**), and fullerene dimer (**2n**), which were not easily available through the previously known methods.



INTRODUCTION

Chemical functionalization of fullerenes provides a variety of potentially useful molecular materials for biological and electronic devices.[1] Numerous efforts for chemical modification of fullerenes have been made during the last few decades, involving various cycloadditions,[1] addition of free radicals,[2,3] and multiaddition of organocoppers.[1f] The nuclophilic addition of organolithiums or Grignard reagents is one of the classical methods for monofunctionalization of fullerene,[4] but this method is accompanied by the following drawbacks: low chemical yields, low selectivity of monoalkylation, high loading of organometallic reagents, and low compatibility with a wide range of functional groups. Transition-metal-catalyzed functionalization of fullerenes[5] has been proved to be a useful method to overcome those disadvantages; for example, Itami and co-workers reported that Rh or Pd catalyst can promote the selective monoarylation of fullerene efficiently by using organoboron compounds.[5h,i] The addition of nucleophiles through radical intermediates proceeds rapidly, but it is difficult to control its selectivity and reactivity; often polysubstituted fullerenes are obtained.[2] It occurred to us that the combination between a transition-metal-catalyzed method and radical chemistry may lead to an efficient alkylation procedure for fullerene.[5e,o] Herein, we report a novel cobalt-catalyzed highly selective hydroalkylation of C_{60} with active alkyl bromides **1** that affords the monoalkyl-functionalized fullerenes **2** in good to high yields under mild reaction conditions (eq 1). Moreover, we have successfully applied this method to the synthesis of monosubstituted fullerenes bearing Zn-porphyrin, G3-dendrimer, and fullerene dimer in good yields. Porphyrin- or dendrimer-bound fullerenes and fullerene dimer, which were previously prepared through the cycloaddition reactions, have been already proved to be promising materials for the optoelectronic materials, although an efficient synthetic method of porphyrin- or dendrimer-bound monoadducts of C_{60} derivatives and monosubstituted fullerene dimers has never been reported.[1d,g,6−8]



(1)

The combination of transition-metal catalysis and free radical reaction has emerged as a novel strategy for new efficient synthetic methodologies.[9,10] Recently, Oshima and co-workers developed an efficient cobalt-catalyzed radical transformation of alkenes with alkyl halides in the presence of Grignard reagents.[10a−e] However, this methodology was not applicable for the funtionalization of C_{60} because of the drawback of Grignard reagents toward the alkylation of C_{60}, as mentioned above.[4] We envisioned that, due to its facile radical accepting characteristics, the selective monofunctionalization of C_{60} would become feasible by the proper choice of transition-metal catalysts, alkyl halides, and additives.

RESULTS AND DISCUSSION

Screening of the Reaction Conditions. Screening of various transition-metal catalysts (10 mol %) and additives (3 equiv) in wet 1,2-dichlorobenzene (ODCB) at room temperature for 50 h under Ar atmosphere (Table 1) was carried out using C_{60} and benzyl bromide (**1a**, 3 equiv). The reaction did not proceed

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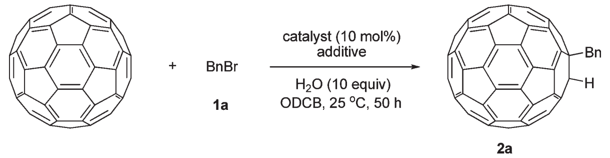
Table 1. Optimization of the Reaction Conditions[a]



entry	catalyst	additive (3.0 equiv)	yield of **2a** (%)[b]	recovery of C_{60} (%)[c]
1	$CoCl_2$dppe	none	0	96
2	None	Mn	0	94
3	$CoCl_2$	Mn	4	88
4	$CoCl_2$dppe	Mn	88 (76)[d]	(8)[d]
5	$CoCl_2$dppe	Fe	80[e]	12
6	$CoCl_2$dppe	Zn	56	25
7	$CoCl_2$dppe	Cu	0	97
8	$CoBr_2$dppe	Mn	40	39
9	CoI_2dppe	Mn	45	24
10	$CoCl_2$dppm	Mn	71	17
11	$CoCl_2$dppf	Mn	73	14
12	$CoI_2(PPh_3)_2$	Mn	0	85
13	$PdCl_2$dppe	Mn	0	88
14	$PdCl_2[P(OPh)_3]_2$	Mn	0	93
15	$Pd(PPh_3)_4$	Mn	5	84
16	$RhCl(PPh_3)_3$	Mn	29	58
17	$[Rh(COD)Cl]_2$	Mn	2	89
18	$NiCl_2$dppf	Mn	20	68
19	$NiCl_2(PPh_3)_2$	Mn	24	60

[a] Reaction conditions: A 1,2-dichlorobenzene (ODCB, 4 mL) solution of catalyst (10 mol %) and additive (3 equiv) under Ar atmosphere was stirred for 1 h at 25 °C. Next, C_{60} (21.6 mg), H_2O (10 equiv), and benzyl bromide (3 equiv) were added, and the resulting mixture was stirred for 50 h at 25 °C. [b] ^1H NMR yield determined using 2,4,6-trimethylpyridine as an internal standard. [c] HPLC yield determined using C_{70} as an internal standard. [d] Isolated yield. [e] The reaction time is 5 days.

without Co catalyst or Mn reductant (entries 1 and 2). Combination of a phosphine-free $CoCl_2$ catalyst with Mn additive gave a low conversion, producing **2a** in a very low yield (entry 3). To our delight, $CoCl_2$dppe catalyst [dppe = bis(diphenylphosphino)ethane] combined with Mn additive[11] showed a high reactivity, affording **2a** in 76% isolated yield (entry 4). HPLC analysis and ^1H and ^{13}C NMR spectra showed a high selectivity for the monoaddition product **2a**. As byproduct, a very small amount of the inseparable multiadducts was produced together with recovered C_{60} (8%) (see the Supporting Information).[12] The high selectivity of the monoadduct should be attributed to the mild reaction conditions. The metal additives other than Mn were also tested. Fe additive gave an appreciable conversion, although a prolonged reaction time (5 days) was needed (entry 5). It should be noticed that under additional prolonged reaction times (5 days plus 1 day), the reaction with Fe additive did not increase the amount of multiadducts, although with Mn additive the amount of multiadducts was slightly increased under a prolonged reaction time (50 h plus 24 h) and the yield of **2a** was decreased. Zn powder was also active, although the yield was lower than that of Mn and Fe, while copper additive was completely inactive (entries 6 and 7). The diverse activity of metal additives may be due to the difference of their standard reduction potentials; the reduction potentials (E^0/V, $M^{x+} + xe \rightleftharpoons M^0$)[13] of Mn (−1.185), Zn (−0.7618), and Fe (−0.447) have abilities enough to reduce Co^{2+} to $Co^{0 \text{ or } I}$ (−0.28), while Cu (0.521) additive cannot reduce Co^{2+}. These results indicate that the present catalytic hydroalkylation proceeds via a mechanism involving Co(0 or I).

Other cobalt catalysts having different counteranions and ligands were also examined. In the presence of Mn additive, the reaction gave poorer product conversions when $CoCl_2$dppe catalyst was replaced with $CoBr_2$dppe or CoI_2dppe catalyst (entries 8 and 9). The reaction with other cobalt catalysts having bidentate ligands, such as $CoCl_2$dppm [dppm = bis(diphenylphosphino)methane] and $CoCl_2$dppf [dppf = bis(diphenylphosphino)ferrocene], were also active, affording **2a** in 71% and 73% yields, respectively (entries 10 and 11). In contrast to the case for cobalt catalysts bearing bidentate ligands, the cobalt catalyst having monodentate ligand, such as $CoI_2(PPh_3)_2$, was inactive (entry 12).

In addition to cobalt catalysts, we also tested several other transition metal catalysts, such as Pd, Rh, and Ni with Mn additive. Pd catalysts having bidentate ligand (dppe) or monodentate ligands ($P(OPh)_3$ and PPh_3) were not effective to produce **2a** (entries 13−15). In sharp contrast, the reaction proceeded with Rh- and Ni-catalysts bearing phosphine ligands. For example, $RhClPPh_3$ catalyst gave 29% yield of **2a**, while the phosphine-free $[Rh(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) catalyst was inactive (entries 16 and 17). $NiCl_2$dppf and $NiCl_2(PPh_3)_2$ catalysts showed lower product conversions, producing **2a** in 20% and 24% yields, respectively (entries 18 and 19). These results suggest that the high efficiency of present reaction not only depends on the transition metal species, but also highly depends on the attached phosphine ligands.

Overall, the hydroalkylation of C_{60} with $CoCl_2$dppe catalyst and Mn additive has been proved to be the most efficient condition. It should be noted that without H_2O the reaction did not proceed at all. Moreover, in the presence of oxygen, the reaction results in a very low conversion of C_{60}. Therefore, all of the handlings were conducted in the glovebox under argon gas.

Co-Catalyzed Synthesis of Various Monoalkylated Fullerenes. Under optimized conditions, the scope of Co-catalyzed hydroalkylation of C_{60} with various active alkyl bromides was examined (Table 2). All of the reactions were monitored by TLC and HPLC analysis, and the corresponding products **2** were isolated by using silica gel column chromatography; it was not necessary to use HPLC for purification of the products. In each case, a very small amount of the inseparable multiadducts was observed as side-products,[12] but they were separated by the silica gel column chromatography. A variety of functional groups, such as ester, cyano, methoxy, and α-methyl groups on benzyl moiety, were tolerated, affording the monoalkylated products **2b**−**f** in good yields with excellent monoalkylation-selectivity (entries 1−5). It should be noted that the products **2b**−**f** showed a high solubility in toluene or *o*-dichlorobenzene. Moreover, the reaction of C_{60} with benzyl bromides having an ester (**1b** and **1c**) or a cyano group (**1d**) afforded a small amount of the single bonded fullerene dimers as byproducts (Figure 1).[12] Allyl bromide, cinnamyl bromide, propargyl bromide, and 1-bromo-2-butyne were also active alkyl sources, producing the corresponding products **2g**−**j** in good to high yields (entries 6−9). Ethyl 2-bromoacetate **1k** showed a lower reactivity, giving **2k** in 36% yield even under longer reaction times (96 h) (entry 10). It should be noted that although the reaction of C_{60} with benzyl

Table 2. Co-Catalyzed Hydroalkylation of C_{60} with Various Active Alkyl Bromides[a]

entry	R−Br	1	amount of **1** (equiv)	time (h)	2	yield of **2** (%)[b]	recovery of C_{60} (%)[b]
1	3-$CO_2Me-C_6H_4CH_2Br$	**1b**	1.5	48	**2b**	58	30
2	4-$CO_2Me-C_6H_4CH_2Br$	**1c**	1.5	48	**2c**	66	15
3	2-$NC-C_6H_4CH_2Br$	**1d**	1.5	40	**2d**	51	39
4	4-$MeO-C_6H_4CH_2Br$	**1e**	2.0	48	**2e**	66	21
5	$C_6H_5CH(Me)Br$	**1f**	3.0	50	**2f**	48	24
6	$CH_2{=}CHCH_2Br$	**1g**	4.0	86	**2g**	74	15
7	(*E*)-$C_6H_5CH{=}CHCH_2Br$	**1h**	1.5	34	**2h**	78	13
8	$CH{\equiv}CCH_2Br$	**1i**	3.0	86	**2i**	75	12
9	$MeC{\equiv}CCH_2Br$	**1j**	3.0	60	**2j**	42	41
10	EtO_2CCH_2Br	**1k**	3.0	96	**2k**	36	38

[a] Reaction conditions: A 1,2-dichlorobenzene (ODCB, 4 mL) solution of $CoCl_2$dppe (10 mol %) and Mn (3 equiv) under Ar atmosphere was stirred for 1 h at 25 °C. Next, C_{60} (21.6 mg), H_2O (10 equiv), and RBr (1.5−4.0 equiv) were added, and the resulting mixture was stirred for 34−96 h at 25 °C. [b] Isolated yields.

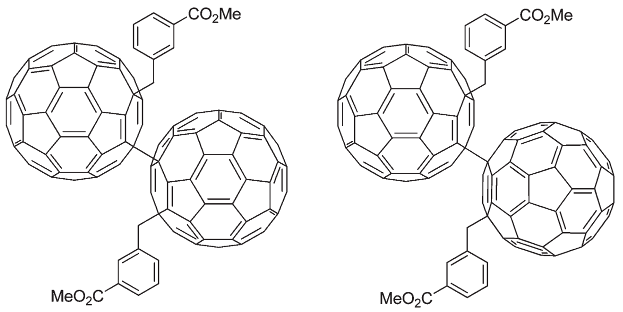
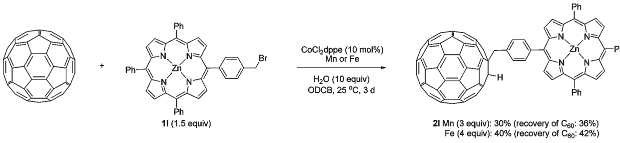


Figure 1. Two isomers of single bonded fullerene dimer **3b**.

bromides having an electron-withdrawing substituent on benzene ring, such as **1b**, **1c**, and **1d**, produced a small amount of the single bonded fullerene dimers **3** in ~3% yields (for the representative structure **3b**, see Figure 1), the corresponding dimers were unable to identify in the other cases due to their extremely small amounts. In contrast to these active alkyl bromides, inactive alkyl bromides, such as butyl bromide or bromomethylcyclopropane, did not undergo the present catalytic hydroalkylation at elevated temperatures.

Co-Catalyzed Synthesis of Zn-Porphrin- and Dendrimer-Bound Hydrofullerenes, and Fullerene Dimer. The present cobalt catalysis was successfully applied to the construction of fullerene-bound macromolecules, which may be useful for versatile electronic materials.[1d,6,7] For example, under the standard conditions, C_{60} reacted with benzyl bromide derivative **1l** having a zinc porphyrin (ZnP) moiety at *para*-position, affording the ZnP-C_{60} product **2l** in 30% yield, while in the presence of Fe additive instead of Mn it gave **2l** in 40% yield (eq 2).[1d,10] Similarly, the reaction of C_{60} with single benzylic bromide group at the focal point of the third-generation dendrimer [G-3]-Br **1m** gave the fullerene-bound dendrimer **2m** in 48% yield (eq 3).[1d,11] This dendritic macromolecule dramatically improved the solubility of fullerene in various organic solvents. This method also provides an interesting opportunity for synthesis of the potentially useful fullerene dimer containing two fullerene units bridged through electroactive spacer.[5h,8] The reaction of 1,5-bis(bromomethyl)-1,4-bis(3′,7′-dimethyloctyloxy)benzene **1n** and 2 mol equiv of C_{60} under standard reaction conditions produced fullerene dimer **2n** in 39% yield, which showed a good solubility in toluene and ODCB (eq 4).[5h,12] It was also noted that the single bonded fullerene dimers produced in the reactions of C_{60} with **2l**, **2m**, and **2n** were unable to identify.



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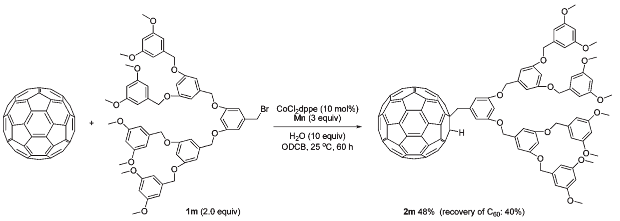

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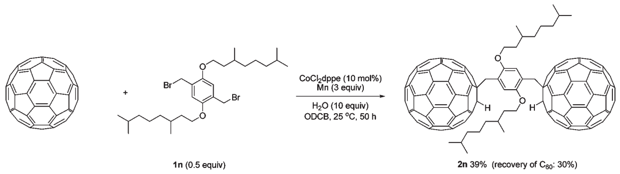

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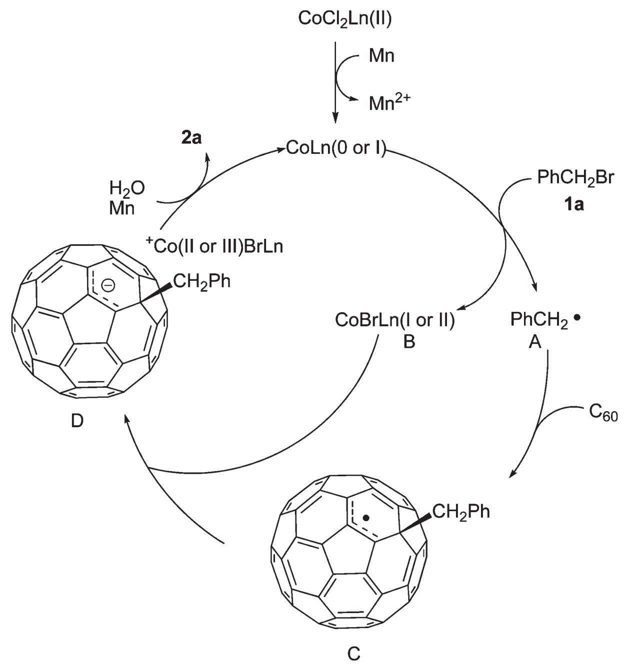
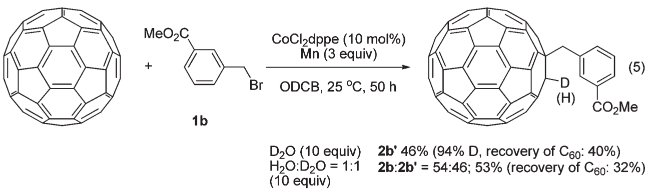
Reaction Mechanism. A plausible mechanism for the present transformation is shown in Scheme 1. Initially, the Co(II) complex is reduced to the electron-rich Co(0) species by Mn reductant.[11] A single electron transfer from the Co(0) complex to benzyl bromide **1a** generates benzyl radical **A** along with Co(I) complex **B**. Addition of the radical **A** to C_{60} forms the delocalized fullerenyl-radical intermediate **C**. Intermediate **C** would be trapped by the Co(I) complex **B** to afford the delocalized fullerenyl−cobalt(II) complex **D**. Protonolysis of intermediate **D** produces the corresponding product **2a** along with the Co(0) catalyst upon treatment with Mn reductant. Of course, the reduction of the Co(II) to Co(I) may occur at the beginning, instead of the reduction to Co(0), and the catalytic cycle may proceed through Co(I) species.

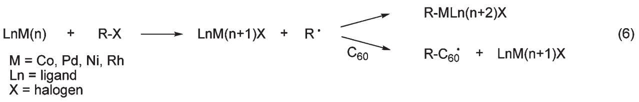
Several experimental observations support the proposed mechanism. When C_{60} was treated with **1a** under standard conditions by using *n*-Bu_3SnH, instead of H_2O, **2a** was obtained in good yield.[4b] Furthermore, as mentioned in Table 2 (entry 1), the reaction of C_{60} with **1b** gave the single bonded fullerene dimer $RC_{60}-C_{60}R$ **3b** as a side-product in 3% yield (Figure 1).

Scheme 1. Proposed Reaction Mechanism



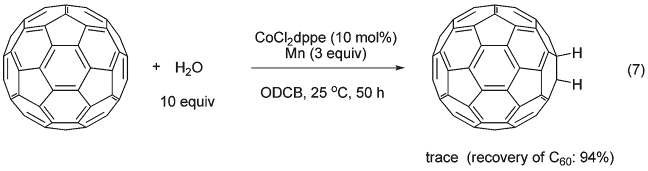
^{1}H NMR spectra showed that this dimer consists of a 1:1 mixture of two isomers.[12] Many experimental and theoretical studies on those dimers demonstrated that they are generally formed by coupling of $RC_{60}^{\bullet}$ radicals.[14] These observations suggest that the present reaction must proceed through the formation of the fullerenyl radical intermediate **C**. Formation of a very small amount of dimer also indicates the conversion of fullerenyl-radical **C** to fullerenyl−cobalt(II or III) complex **D** is a rapid step. Moreover, the reaction of C_{60} and **1b** in the presence of D_2O instead of H_2O under otherwise the standard conditions gave the corresponding product **2b′** in 46% yield with 94% deuterium incorporation, implying that a proton in product **2a** was derived from the added water (eq 6). A similar reaction was conducted with a 1:1 mixture of H_2O and D_2O, yielding the protonated and deuterated products **2b** and **2b′** in a 54:46 ratio (eq 5). The yield difference between H_2O and D_2O is due to the isotope effect of O−D and O−H bond,[15] which reflects the hydrolysis step of the intermediate **D**.





A reason for the yield difference of **2a** depending on transition metals (Co, Pd, Ni, and Rh: Table 1, entries 4, 13−15, 16, and 18,19) is perhaps due to the reactivity difference of the LnM-(n + 1)X (Ln = ligand; X = halogen) complex, which is similar to the intermediate **B** in Scheme 1, toward $R^{\bullet}$ (eq 6). To obtain a high product yield, the alkyl radical ($R^{\bullet}$) must react with C_{60} before its reaction with the MLn(n + 1)X species, which may lead to the formation of the oxidative addition complex R−MLn(n + 2)X. The diverse reactivity of the transition metals suggests that the combination of different metals and ligands highly affects the reactivity of LnM(n + 1)X.[9] It is also known that a certain transition-metal catalyst undergoes facile formation of a transition-metal−C_{60} complex.[16,17] It has been reported that Pd complexes having phosphine ligands react readily with C_{60} under ambient temperature, forming LnPd−C_{60} complexes in high yields.[15] Indeed, in the reaction with $Pd(PPh_3)_4$ catalyst (Table 1, entry 15), a very small amount of the corresponding Pd-$(PPh_3)_2$−C_{60} complex was detected, which was confirmed by HPLC analysis and ^{1}H NMR spectra as compared to an authentic sample prepared from the reported method.[16d] Ni, Rh, and Co complexes have also been reported to react with C_{60}, although the use of a higher reaction temperature or special ligands was needed.[17]

An alternative reaction pathway, such as the initial generation of C_{60} radical anion through the reduction of C_{60} with metal reductant followed by reaction with benzyl bromide,[3a] is unlikely because the reaction of C_{60} and H_2O in the absence of alkyl bromides under otherwise the standard conditions gave a trace amount of dihydrofullerene ($C_{60}H_2$) as shown in eq 7. This result is completely different from the reported zinc-mediated monoalkylation of C_{60}, in which Meier and co-workers reported that the reaction of C_{60} with H_2O in the presence of excess amounts of zinc dust gave $C_{60}H_2$ in 50% yield.[3a]



CONCLUSION

We have found a new and efficient Co-catalyzed selective monoalkylation of C_{60} with active alkyl bromides. A wide range of functional groups are tolerated in the present catalytic hydroalkylation. In contrast to the classical organometallic addition methods, the present catalytic reaction is carried out under very mild reaction conditions with remarkably higher yields. Monosubstituted zincporphyrin−fullerene, fullerene-bound dendrimer, and fullerene dimer have thus been synthesized in good yields for the first time, which are otherwise difficult to obtain. The present hydroalkylation of C_{60} seems to proceed through a Co-catalyzed generation of an active alkyl radical followed by addition to C_{60}. Cobalt catalyst combined with Mn reductant in the presence of H_2O under argon is crucial for the efficient and selective formation of the fullerene monoadducts. Investigation on further catalytic functionalization of fullerenes and application to materials science are in progress.

EXPERIMENTAL PROCEDURES

Materials. Anhydrous 1,2-dichlorobenzene (Aldrich), toluene, carbon disulfide, hexane, (WAKO), transition metal catalysts, reductants (Aldrich), n-Bu_3SnH (Aldrich), and alkyl bromides (**1**) (Aldrich) were purchased and used as received. CoX_2(ligand)[18] and zinc porphyrin (ZnP) benzyl bromide **1l**[19] were prepared following the reported literature. The structures of products were determined by using ^{1}H NMR, ^{13}C NMR, HMRS, and by comparison of representative products **2a**,[3a,19] **2f**,[3d] **2g**,[3a,5j,20] **2i**,[21] and **2k**[3a] with reported literature.

Representative Procedures of Co-Catalyzed Hydroalkylation of C_{60} and Benzyl Bromide. A suspension of $CoCl_2$dppe (1.6 mg, 0.003 mmol) and Mn (5 mg, 0.09 mmol) in 1,2-dichlorobenzene (ODCB, 4 mL) was stirred for 1 h under Ar atmosphere at 25 °C. To the suspension were added C_{60} (21.6 mg, 0.03 mmol), benzyl bromide (11 μL, 0.09 mmol), and H_2O (5.4 μL, 0.3 mmol) subsequently in a glovebox. The reaction mixture was stirred at 25 °C for 50 h and monitored by TLC and HPLC analysis (elution with toluene at 0.6 mL/min flow rate, detection at 320 nm, 4 °C). The mixture was filtered through a short florisil pad using 1,2-dichlorobenzene as an eluent. After concentration, the residue was purified with silica gel chromatography (toluene/hexane = 1/4) to afford **2a** in 76% yield (18.5 mg).

Methyl 3-[([60]Fulleren-1(2*H*)-yl)methyl]benzoate (2b). Dark brown solid; soluble solvents: $CHCl_3$, toluene, ODCB; ^{1}H NMR (500 MHz) δ 3.99 (3H, s), 4.81 (2H, s), 6.61 (1H, s), 7.62 (1H, t, J = 8.0 Hz), 8.02 (1H, d, J = 8.0 Hz), 8.13 (1H, d, J = 8.0 Hz), 8.52 (1H, s); ^{13}C NMR (125 MHz) δ 52.35, 52.65, 59.12, 65.64, 128.84, 129.05, 130.62, 132.44, 135.85, 136.18, 136.27, 136.33, 139.97, 140.23, 141.61, 141.68, 141.90, 141.99, 142.08, 142.23, 142.58, 142.61, 143.25, 144.57, 144.76, 145.43, 145.46, 145.56, 145.82, 146.18, 146.23, 146.29, 146.44, 146.46, 146.93, 147.37, 147.54, 153.64, 154.83, 166.98; UV−vis λ_{max}/nm ($CHCl_3$) 256, 307, 327, 433; HRMS (ESI, positive) calcd for $C_{69}H_{10}O_2Na$ $[M + Na]^+$, 893.0573; found, 893.0567.

Methyl 3-[([60]Fulleren-1(2*D*)-yl)methyl]benzoate (2b′). Dark brown solid; soluble solvents: $CHCl_3$, toluene, ODCB; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$ = 1/4) δ 3.96 (3H, s), 4.82 (2H, s), 7.60 (1H, t, J = 7.6 Hz), 8.00 (1H, d, J = 7.6 Hz), 8.12 (1H, d, J = 7.6 Hz), 8.48 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$ = 1/4) δ 51.72, 52.41, 58.47 (C−D, t, J = 21.5 Hz), 65.11, 128.42, 128.72, 130.33, 132.02, 135.18, 135.76, 135.78, 135.90, 139.61, 139.84, 141.18, 141.24, 141.43, 141.63, 141.72, 142.15, 142.80, 144.10, 144.28, 144.95, 144.97, 145.06, 145.14, 145.31, 145.63, 145.75, 145.81, 145.96, 145.99, 146.46, 146.86, 147.02, 152.94, 153.01, 154.13, 165.55; UV−vis λ_{max}/nm ($CHCl_3$) 255, 307, 326, 433; HRMS (ESI, positive) calcd for $C_{69}H_9DO_2Na$ $[M + Na]^+$, 894.0636; found, 894.0633.

Methyl 4-[([60]Fulleren-1(2*H*)-yl)methyl)benzoate (2c). Dark brown solid; soluble solvents: $CHCl_3$, toluene, ODCB; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$ = 1/4) 3.94 (3H, s), 4.85 (2H, s), 6.61 (1H, s), 7.87 (2H, d, J = 8.4 Hz), 8.16 (2H, d, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$ = 1/4) 51.62, 52.85, 59.09, 65.18, 129.40, 129.68, 131.00, 135.72, 135.86, 139.58, 139.91,140.41, 141.20, 141.30, 141.44, 141.58, 141.66, 141.76,142.20, 142.21, 142.86, 144.13, 144.31, 144.98, 145.02, 145.08, 145.17, 145.33, 145.65, 145.79, 145.86, 146.01, 146.03, 146.40, 146.90, 147.06, 152.94, 154.03, 165.47; UV−vis λ_{max}/nm ($CHCl_3$) 256, 308, 326, 433; HRMS (ESI, negative) calcd for $C_{69}H_9O_2$ $[M - H]^-$, 869.0608; found, 869.0610.

2-[([60]Fulleren-1(2*H*)-yl)methyl]benzonirile (2d). Dark brown solid; soluble solvents: toluene, ODCB, low in $CHCl_3$; ^{1}H NMR (500 MHz, $CDCl_3/CS_2$ = 1/4) δ 5.05 (2H, s), 6.65 (1H, s), 7.54 (1H, t, J = 7.5 Hz), 7.72 (1H, t, J = 7.5 Hz), 7.82 (1H, d, J = 7.5 Hz), 7.94 (1H, d, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$ = 1/4) δ 50.56, 59.77, 65.21, 115.06, 117.53, 128.00, 132.12, 132.20, 132.95, 136.01, 136.17, 139.29, 139.46, 140.08, 141.28, 141.46, 141.68, 141.83, 141.86, 142.29, 142.35, 142.96, 144.19, 144.46, 145.09, 145.15, 145.23, 145.34, 145.48, 145.72, 145.91, 145.97, 146.15, 146.47, 147.01, 147.21, 152.78, 153.08; UV−vis λ_{max}/nm ($CHCl_3$) 255, 309, 325, 432; HRMS (ESI, positive) calcd for $C_{68}H_7NNa$ $[M + Na]^+$, 860.0471; found, 860.0469.

2-(4-Methoxybenzyl)-1,2-dihydro[60]fullerene (2e). Dark brown solid; soluble solvents: $CHCl_3$, toluene, ODCB; ^{1}H NMR (500 MHz, $CDCl_3/CS_2$ = 1/4) δ 3.88 (3H, s), 4.71 (2H, s), 6.62 (1H, s), 7.04 (1H, d, J = 8.5 Hz), 7.72 (1H, d, J = 8.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$ = 1/4) δ 52.24, 54.96, 58.98, 66.08, 114.03, 127.57, 132.28, 135.90, 136.23, 139.84, 140.05, 141.45, 141.51, 141.79, 141.84, 141.90, 142.07, 142.42, 143.09, 144.44, 144.57, 145.24, 145.29, 145.33, 145.65, 146.03, 146.10, 146.23, 146.25, 146.27, 146.83, 147.16, 147.30, 153.75, 155.30, 159.00; UV−vis λ_{max}/nm ($CHCl_3$) 256, 308, 326, 433; HRMS (ESI, positive) calcd for $C_{68}H_{10}ONa$ $[M + Na]^+$, 865.0624; found, 865.0621.

2-((*E*)-Cinnamyl)-1,2-dihydro[60]fullerene (2h). Dark brown solid; soluble solvents: $CHCl_3$, toluene, ODCB; ^{1}H NMR (500 MHz, $CDCl_3/CS_2$ = 1/4) δ 4.35 (2H, d, J = 7.0 Hz), 6.61 (1H, s), 7.18−7.35 (3H, m), 7.44 (2H, t, J = 7.5 Hz), 7.64 (2H, d, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$ = 1/4) δ 50.31, 58.68, 64.71, 124.37, 126.66, 127.98, 128.72, 136.00, 136.21, 136.57, 136.74, 140.13, 140.21, 141.54, 141.56, 141.86, 141.94, 142.16, 142.46, 143.15, 144.47, 144.61, 145.28, 145.30, 145.33, 145.44, 145.70, 146.06, 146.08, 146.13, 146.30, 147.19, 147.34, 153.68, 155.31; UV−vis λ_{max}/nm ($CHCl_3$) 257, 326, 433; HRMS (ESI, negative) calcd for $C_{69}H_{10}$−H $[M - H]^-$, 837.0710; found, 837.0712.

2-(But-2-ynyl)-1,2-dihydro[60]fullerene (2j). Dark brown solid; soluble solvents: toluene, ODCB, low in $CHCl_3$; ^{1}H NMR (500 MHz, $CDCl_3/CS_2$ = 1/4) δ 2.16 (3H, t, J = 2.5 Hz), 4.27 (2H, q, J = 2.5 Hz), 6.70 (1H, S); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$ = 1/4) δ 3.96, 37.42, 59.24, 63.92, 74.89, 81.29, 140.02, 140.06, 141.48, 141.60, 141.81, 141.86, 142.18, 142.37, 142.39, 142.87, 143.02, 144.38, 144.52, 145.15, 145.22, 145.25, 145.42, 145.58, 145.88, 145.97, 146.02, 146.21, 146.78, 147.08, 147.26, 153.54, 154.35; UV−vis λ_{max}/nm ($CHCl_3$) 256, 326, 433; HRMS (ESI, negative) calcd for $C_{64}H_6$−H $[M - H]^-$, 773.0397; found, 773.0395.

2-(4-(ZnP)-benzyl)-1,2-dihydro[60]fullerene (2l). Dark purple red solid; soluble solvents: ODCB, low in $CHCl_3$ and toluene; ^{1}H NMR (500 MHz, $CDCl_3/CS_2$ = 1/4) δ 5.06 (2H, s), 6.80 (1H, s) 7.71−7.76 (9H, m), 8.16−8.18 (8H, m), 8.35 (2H, d, J = 8.5 Hz), 8.87−8.90 (8H, m); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$ = 1/4) δ 53.06, 59.18, 65.85, 120.94,126.37, 127.24, 129.38, 131.60, 131.92, 131.99, 134.21, 134.45, 135.83, 136.02, 139.68, 139.97, 141.35, 141.38, 141.65, 141.74, 141.92, 142.30, 142.41, 142.77, 142.92, 144.30, 144.40, 145.10, 145.17, 145.30, 145.46, 145.90, 145.96, 146.05, 146.12, 146.59, 149.72, 149.89, 149.97, 153.42, 154.80; UV−vis λ_{max}/nm ($CHCl_3$) 291, 299, 425, 550; HRMS (ESI, positive) calcd for $C_{105}H_{30}N_4ZnNa$ $[M + Na]^+$, 1433.1654; found, 1433.1650.

2-(3,5-Bis(3,5-bis(3,5-dimethoxybenzyloxy)benzyloxy)-benzyl)-1,2-dihydro[60]fullerene (2m). Dark brown solid; soluble solvents: THF, $CHCl_3$, toluene, ODCB; ^{1}H NMR (500 MHz, $CDCl_3/CS_2$ = 1/4) δ 3.77 (24H, s), 4.62 (2H, s), 4.92 (8H, s), 5.10 (4H, s), 6.39 (4H, t, J = 2.5 Hz), 6.51−6.54 (11H, m), 6.70 (4H, d, J = 2.5 Hz), 6.72 (1H, t, J = 2.5 Hz), 7.01 (2H, d, J = 2.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$ = 1/4) δ 53.04, 55.36, 58.69, 65.63, 70.01, 70.07, 100.01, 101.60, 101.89, 105.23, 105.36, 106.08, 110.69, 135.84, 136.21, 138.11, 139.00, 139.48, 139.85, 140.06, 141.52, 141.58, 141.79, 141.95, 142.01, 142.19, 142.49, 142.53, 143.09, 144.48, 144.65, 145.29, 145.35, 145.38, 145.80, 146.17, 146.22, 146.31, 146.38, 147.03, 147.30, 147.47, 153.90, 155.40, 159.90, 160.16, 160.96; UV−vis λ_{max}/nm ($CHCl_3$) 256, 308, 326, 434; HRMS (ESI, positive) calcd for $C_{117}H_{60}O_{14}Na$ $[M + Na]^+$, 1711.3875; found, 1711.3868.

(2,5-Bis(2,6-dimethylheptyloxy)-1,4-phenylene)bis(methylene)difullerene (2n). Dark brownish red solid; soluble solvents: $CHCl_3$, toluene, ODCB; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$ = 1/4) δ 0.84 (6H, d, J = 2.8 Hz), 0.85 (6H, d, J = 3.2 Hz), 1.00 (6H, d, J = 6.8 Hz), 1.14−1.51 (18H, m), 1.66−1.70 (2H, m), 1.79−1.85 (2H, m), 1.92−1.99 (2H, m), 4.12 (2H, d, J = 6.8 Hz), 4.13 (2H, d, J = 6.8 Hz), 4.80−4.90 (4H, m), 6.66 (2H, s), 7.37 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$ = 1/4) δ 19.68, 22.71, 22.79, 25.04, 28.14, 30.15. 36.50, 37.58, 39.37, 46.06, 58.89, 65.75, 66.97, 116.73, 124.51, 135.17, 135.25, 135.86, 135.87, 139.37, 139.81, 141.03, 141.20, 141.34, 141.45, 141.56, 141.80, 142.12, 142.83, 144.12, 144.25, 144.90, 144.95, 145.28, 145.70, 145.77, 145.90, 146.53, 146.80, 147.01, 150.75, 153.57, 155.22, 155.30; UV−vis λ_{max}/nm ($CHCl_3$) 255, 326, 435; HRMS (ESI, negative) calcd for $C_{148}H_{49}O_2$ $[M - H]^-$, 1857.3732; found, 1857.3733.

Single Bonded Fullerene Dimer (3b). A 1:1 mixture of two isomers; dark brown solid; soluble solvents: ODCB, low in $CHCl_3$ and toluene; ^1H NMR (500 MHz, $CDCl_3/CS_2$ = 1/4) δ 3.87 (6H, s), 4.52 (1H, d, J = 5.5 Hz), 4.55 (1H, d, J = 5.5 Hz), 4.75 (2H, d, J = 13.0 Hz), 7.44 (2H, t, J = 8.0 Hz), 7.78−7.79 (2H, m), 7.98−8.00 (2H, m), 8.30 (1H, s), 8.32 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$ = 1/4) δ 48.78, 49.08, 51.77, 60.30,128.13, 128.66, 128.68, 130.20, 131.78, 134.88, 135.58, 138.00, 138.96, 139.00, 139.41, 139.44, 140.97, 141.05, 141.89, 141.93, 142.01, 142.16, 142.38, 142.57, 142.59, 142.61, 142.62, 142.65, 142.95, 142.98, 143.01, 143.04, 143.17, 143.19, 143.23, 143.29, 143.35, 143.70, 143.79, 143.86, 144.09, 144.09, 144.10, 144.14, 144.16, 144.21, 144.23, 144.26, 144.30, 144.32, 144.37, 144.39, 144.52, 144.55, 144.58, 144.77, 144.97, 145.08, 145.54, 145.57, 145.58, 145.61, 145.64, 146.59, 146.79, 146.84, 146.86, 146.93, 147.12, 147.22, 147.24, 147.48, 148.30, 148.42, 148.50, 148.52, 148.59, 148.71, 148.73, 148.96, 149.32, 152.54, 152.83, 153.62, 153.79, 156.12, 165.82; UV−vis λ_{max}/nm ($CHCl_3$) 257, 331, 445; HRMS (ESI, positive) calcd for $C_{138}H_{18}O_4Na$ $[M + Na]^+$, 1761.1097; found, 1761.1102.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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