ChemComm



View Article Online

COMMUNICATION



Cite this: DOI: 10.1039/c5cc01534k

Ni-Catalyzed direct 1,4-difunctionalization of [60]fullerene with benzyl bromides†

Weili Si,^a Xuan Zhang,^a Naoki Asao,^a Yoshinori Yamamoto^{ab} and Tienan Jin*^a

Received 19th February 2015, Accepted 5th March 2015

DOI: 10.1039/c5cc01534k

www.rsc.org/chemcomm

A new Ni-catalyzed direct 1,4-difunctionalization of [60]fullerene with various benzyl bromides has been developed. The use of a DMSO additive combined with a nickel catalyst is indispensable for the formation of 1,4-dibenzyl fullerenes with a variety of functional groups. The reaction proceeds through the formation of a fullerene monoradical species.

1,4-Difunctional fullerenes possessing two functional groups in the 1,4-position of the fullerene core are one of the important classes of electron-accepting materials for high performance organic photovoltaics (OPVs).11,4-Bisadducts are known to show a higher LUMO energy level compared to the 1,2-adducts,^{1b} which is beneficial for obtaining a higher open circuit voltage in OPVs.² In addition, among the 1,4-adducts, the 1,4-dialkyl adducts such as 1,4-dibenzyl and disilylmethyl fullerenes exhibit a better solubility and higher LUMO levels than the 1,4-diaryl adducts.^{1b} In this context, a number of synthetic methods for fullerene 1,4-bisadducts have been reported,^{3,4} such as the reaction of fullerene anions with alkyl halides, addition of nucleophiles to fullerene cations, and free radical addition. However, a direct and efficient 1,4-difunctionalization of the pristine [60]fullerene has been rarely developed,^{3c} particularly by using a transitionmetal-catalyzed method which has become one of the most efficient fullerene functionalization methods.⁵ Only one example of transition-metal-catalyzed 1,4-diallylation has been reported by Itami *et al.* during the regioselective tetraallylation of C_{60} using a Pd catalyst.5c

Recently, we have been interested in developing new fullerene functionalization methods by using cobalt or copper catalysts through the formation of a fullerene monoradical species (Scheme 1).⁶ For example, we reported that the low-valent cobalt catalyst is capable of



 $\label{eq:scheme1} \begin{array}{l} \mbox{Transition-metal-catalyzed functionalization of C_{60}: our previous and current studies.} \end{array}$

forming an active alkyl radical species that reacts with C_{60} selectively to afford the mono-substituted hydrofullerenes in the presence of water.^{6a} Furthermore, we have disclosed an uncommon polar solvent effect on the generation and stabilization of a fullerene monoradical species in the Cu-catalyzed dimerization^{6c} and C–H amination of hydrofullerenes.^{6d} Inspired by our previous observations, we focused on the transition-metal-catalyzed direct 1,4-difunctionalization of C_{60} with active bromides to achieve 1,4-bisadducts selectively. Herein, we report a novel Ni-catalyzed direct 1,4-difunctionalization of C_{60} with various functional benzyl bromides to afford 1,4-dibenzyl fullerenes in good to high yields. The reaction proceeds through the formation of a fullerene monoradical intermediate and the use of DMSO co-solvent is significant for the implementation of the present 1,4-difunctionalization sufficiently under mild conditions.

On the basis of our previous Co-catalyzed hydrobenzylation of C_{60} ,^{6a} we examined the selective 1,4-dibenzylation through the optimization of transition metal catalysts and polar cosolvents at room temperature under an argon atmosphere (Table 1). The yields were determined by HPLC analysis using C_{70} as an internal standard. The reaction of C_{60} with benzyl bromide **1a** in the presence of the CoCl₂dppe catalyst and the Mn reductant in 1,2-dichlorobenzene (ODCB) without using any cosolvent and water did not give any products (entry 1). However, we were pleased to find that the reaction proceeded upon adding a small amount of DMSO to the ODCB solution, giving the 1,4-dibenzylation product **2a** in 40% yield along

^a WPI-Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, Sendai 980-8577, Japan. E-mail: tjin@m.tohoku.ac.jp

^b State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116023, China

[†] Electronic supplementary information (ESI) available: Experimental procedures and characterization data. See DOI: 10.1039/c5cc01534k

Communication



| 2 | CoCi ₂ uppe | DMSO | 40 | 0 | 5 | 0 |
|----------------|------------------------|--------------------|--------|----|----|----|
| 3 | CoCl ₂ dppe | DMF | 0 | 18 | 0 | 85 |
| 4 | CoCl ₂ dppe | CH ₃ CN | 0 | 0 | 0 | 99 |
| 5 | CoCl ₂ dppe | THF | 0 | 0 | 0 | 99 |
| 6 | CoCl ₂ dppe | MeOH | 0 | 53 | 0 | 21 |
| 7 | CoCl ₂ dppf | DMSO | 0 | 0 | 0 | 99 |
| 8 | CoCl ₂ bpy | DMSO | 22 | 0 | 5 | 36 |
| 9 ^c | NiCl ₂ dppe | DMSO | 60(58) | 5 | 5 | 18 |
| 10 | NiCl ₂ dppp | DMSO | 43 | 17 | 13 | 0 |
| 11 | NiCl ₂ dppf | DMSO | 39 | 13 | 18 | 0 |
| 12^d | $NiCl_2(PPh_3)_2$ | DMSO | 36 | 3 | 0 | 48 |
| 13 | PdCl ₂ dppe | DMSO | 0 | 0 | 0 | 95 |

^{*a*} Reaction conditions: C_{60} (0.03 mmol), **1a** (3 equiv.), ODCB (4 mL), DMSO (0.15 mL), metal catalyst (10 mol%), Mn (3 equiv.), rt, 12 h, argon atmosphere. ^{*b*} HPLC yields determined using C_{70} as an internal standard. Isolated yields are provided in parentheses. ^{*c*} NiCl₂dppe (5 mol%) and Mn (1.5 equiv.) were used for 24 h. ^{*d*} Reaction time is 5 days.

with dimer 4a in 5% yield (entry 2). It was found that the other polar cosolvents such as DMF, CH₃CN, and THF were inactive in the formation of 2a (entries 3-5) and the use of a protic solvent MeOH produced the hydrobenzylation product 3a preferentially similar to our previous water-incorporated hydrobenzylation reaction (entry 6).^{6a} By using DMSO as a cosolvent, we further examined other cobalt catalysts such as CoCl₂dppf and CoCl₂bpy, which were totally inactive or dramatically decreased the yield of 2a (entries 7 and 8). Among the other transition metal catalysts such as NiCl₂dppe, NiCl₂dppp, and NiCl₂dppf having a bidentate phosphine ligand tested, the use of NiCl₂dppe obviously increased the yield of 2a (58%) and the product selectivity even when using a decreased catalytic loading of 5 mol% (entries 9-11). The reaction with NiCl₂(PPh₃)₂ having a monodentate phosphine ligand exhibited a lower activity, resulting in 2a in 36% yield together with the recovered C₆₀ in 48% yield at longer reaction times (5 days) (entry 12). Other transition metal catalysts such as PdCl₂dppe were tested to be inactive in the present reaction (entry 13). It is noted that, in the absence of transition metal catalysts or without Mn reductant under otherwise identical conditions, almost no products were formed and the use of anhydrous DMSO is crucial for improving the selectivity of 2a.

Under the optimized conditions, the scope of the Ni-catalyzed 1,4-difunctionalization of [60]fullerene with active alkyl bromides was investigated (Table 2). All of the reactions were monitored by TLC and HPLC analysis, and the corresponding 1,4-dialkylfullerenes 2 were isolated by using silica gel column chromatography. In some

Table 2 Ni-catalyzed 1,4-dibenzylation of C_{60} with various functional benzyl bromides $1^{a,b}$



 a Reaction conditions: C₆₀ (0.03 mmol), NiCl₂dppe (5 mol%), Mn (1.5 equiv.), active bromide (3.0 equiv.), ODCB (4 mL), DMSO (0.15 mL), rt, argon atmosphere. b Isolated yields are shown.

cases, a small amount of 1,2-hydroalkylfullerene 3, fullerene dimer 4 or multiadducts were produced. The benzyl bromides 1b and 1c bearing a bromo-substituent at the ortho- or the para-position of the phenyl ring afforded the corresponding 1,4-bisadducts 2b and 2c in 70% and 61% yields, respectively, which can be used as important intermediates in various cross-coupling reactions to construct more complex molecules. The reactions with benzyl bromides 1d-f having methyl, methoxy, and ester functional groups on the phenyl ring produced the corresponding 1,4-bisadducts 2d-f in 70-85% yields regardless of the substitution positions. However, the simple nonsubstituted benzyl bromide 1g resulted in a relatively lower yield of 2g (55%) owing to the increase in the formation of multiadducts. Likewise, 4'-(bromomethyl)-[1,1'-biphenyl]-2-carbonitrile (1h) was also a good benzylic substrate to give the corresponding 1,4-bisadduct 2h in good yield. The naphthyl-incorporated substrate 1i having a bromine substituent at the *α*-position of the naphthalene moiety was also compatible with the present conditions to afford the 1,4-bisadduct 2i in 65% yield, in which the α-bromo-substituent remained intact. It was noted that other active dibromides such as allyl bromide and cinnamyl bromide showed low yields and selectivities, and aromatic dibromides such as bromobenzene and 2-bromonaphthalene were totally inactive.

In order to understand the reaction pathways, we examined the reactions using the fullerene dimer **4a** and **1**,2-hydrobenzylated fullerene **3a**, respectively. The reaction of **4a** with benzyl bromide **1a**



Scheme 2 Control experiments: (a) reaction of dimer **4a** with bromide **1a**, (b) reaction of hydrofullerene **3a** with bromide **1a**. The HPLC yields are shown, which were determined using C_{60} as an internal standard.

under the standard Ni-catalyzed conditions gave the corresponding 1,4-bisadduct **2a** in 51% yield together with **3a** in 27% yield (Scheme 2a). In addition, the reaction of **3a** with **1a** produced **3a** in a low yield of 23% along with **4a** due to some decomposition of **3a** (Scheme 2b). These results indicated that the present 1,4-dibenzylation may proceed predominantly through the formation of a fullerene monoradical species, because it is well known that the single-bonded fullerene dimers such as **4a** dissociate to the stable monoradicals readily in solution.^{6c}

Although the concrete mechanism should be further investigated, on the basis of the present results, we propose that the reaction may involve the formation of radical species (ESI,† Scheme S1). Similar to our previous cobalt catalyst-Mn systems,^{6a} the reduction of Ni(II) by the Mn reductant followed by the reaction of the resulting Ni(0) complex with benzyl bromide forms the benzyl radical species and the Ni(I) complex.⁷ The addition of the resulting benzyl radical to C60 forms the fullerene monoradical (Scheme 1), which might be reversible with the $(ArCH_2)C_{60}$ -Ni(II) complex or with the fullerene dimer 4. Subsequently, the coupling of the fullerene monoradical with the benzyl radical forms the 1,4-bisadduct 2 and the reduction of the Ni(1) complex by Mn regenerates the active Ni(0) complex. We assume that the hydrofullerene 3 is formed by the hydrolysis of the $(ArCH_2)C_{60}$ -Ni(II) complex with a small amount of H₂O in the reaction system, which is proposed to be reversible. Although the unique role of the DMSO polar solvent remains unclear at this stage, we assume that DMSO may facilitate the single electron transfer process and stabilize both fullerene and benzyl radicals.

In conclusion, we have described a new and efficient Ni-catalyzed direct 1,4-difunctionalization of C_{60} with benzyl bromides. A variety of functional groups were tolerated, affording the fullerene 1,4-bisadducts in good to high yields. The use of DMSO as a cosolvent combined with the NiCl₂dppe catalyst enables the reaction to proceed under mild conditions using a catalytic process through the formation of a fullerene monoradical.

This work was supported by a Scientific Research (B) award from the Japan Society for Promotion of Science (JSPS) (No. 25288043) and a World Premier International Research Center Initiative (WPI), MEXT, Japan. W.S. acknowledges the support of the China Scholarship Council (CSC).

Notes and references

- 1 (a) C.-Z. Li, H.-L. Yip and A. K.-Y. Jen, *J. Mater. Chem.*, 2012, 22, 4161; (b) Y. Matsuo, *Chem. Lett.*, 2012, 41, 754.
- 2 C. J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispens, L. Sanchez and J. C. Hummelen, *Adv. Funct. Mater.*, 2001, **11**, 374.
- 3 (a) S. Fukuzumi, T. Suenobu, T. Hirasaka, R. Arakawa and K. M. Kadish, *J. Am. Chem. Soc.*, 1998, **120**, 9220; (b) Y. Matsuo, A. Iwashita, Y. Abe, C. Z. Li, K. Matsuo, M. Hashiguchi and E. Nakamura, *J. Am. Chem. Soc.*, 2008, **130**, 15429; (c) T.-H. Zhang, P. Lu, F. Wang and G.-W. Wang, *Org. Biomol. Chem.*, 2003, **1**, 4403; (d) Y. Matsuo, Y. Zhang, I. Soga, Y. Sato and E. Nakamura, *Tetrahedron Lett.*, 2011, **52**, 2240.
- 4 (a) Y. Tajima, T. Hara, T. Honma, S. Matsumoto and K. Takeuchi, Org. Lett., 2006, 8, 3203; (b) M. Nambo, Y. Segawa and K. Itami, J. Am. Chem. Soc., 2011, 133, 2402; (c) G.-W. Wang, Y.-M. Lu and Z.-X. Chen, Org. Lett., 2009, 11, 1507; (d) Z.-X. Chen and G.-W. Wang, J. Org. Chem., 2005, 70, 2380; (e) W. Si, S. Lu, N. Asao, M. Bao, Y. Yamamoto and T. Jin, Chem. Commun., 2014, 50, 15730.
- 5 For selected examples, see: (a) L. Becker, T. P. Evans and J. L. Bada, J. Org. Chem., 1993, 58, 7630; (b) M. Nambo, R. Noyori and K. Itami, J. Am. Chem. Soc., 2007, 129, 8080; (c) M. Nambo, A. Wakamiya, S. Yamaguchi and K. Itami, J. Am. Chem. Soc., 2009, 131, 15112; (d) B. Zhu and G.-W. Wang, J. Org. Chem., 2009, 74, 4426; (e) B. Zhu and G.-W. Wang, Org. Lett., 2009, 11, 4334; (f) S. Filippone, E. E. Maroto, A. Martín-Domenech, M. Suarez and N. Martín, Nat. Chem. Soc., 2010, 132, 12234; (h) S. Lu, W. Si, M. Bao, Y. Yamamoto and T. Jin, Org. Lett., 2013, 15, 4030; (i) J. Marco-Martínez, S. Reboredo, M. Izquierdo, V. Marcos, J. L. López, S. Filippone and N. Martín, J. Am. Chem. Soc., 2014, 136, 2897; (j) E. E. Maroto, M. Izquierdo, S. Reboredo, J. Marco-Martínez, S. Filippone and N. Martín, Ac. Chem. Res., 2014, 47, 2660.
- 6 (a) S. Lu, T. Jin, M. Bao and Y. Yamamoto, J. Am. Chem. Soc., 2011, 133, 12842; (b) S. Lu, W. Si, M. Bao, Y. Yamamoto and T. Jin, Org. Lett., 2013, 15, 4030; (c) S. Lu, T. Jin, E. Kwon, M. Bao and Y. Yamamoto, Angew. Chem., Int. Ed., 2012, 51, 802; (d) W. Si, S. Lu, M. Bao, N. Asao, Y. Yamamoto and T. Jin, Org. Lett., 2014, 16, 620.
- 7 L. Ford and U. Jahn, Angew. Chem., Int. Ed., 2009, 48, 6386.