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Synthesis of Imino[60]fullerenes Using Nitriles and Trimethylsilylmethyl Triflate

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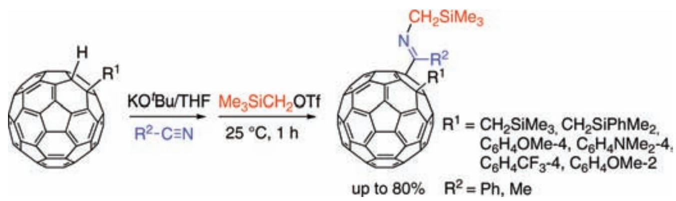
ABSTRACT



The synthesis of a new class of fullerene derivatives, 1-imino-4-silylmethyl[60]fullerene derivatives, is described. The anion ($C_{60}R^{1-}$) of an alkyl- or aryl-adduct of [60]fullerene, $C_{60}R^1H$ (R^1 = CH_2SiMe_3, CH_2SiMe_2Ph, C_6H_4−OMe-4, C_6H_4−NMe_2-4, C_6H_4−CF_3-4 and C_6H_4−OMe-2), was allowed to react with a nitrilium salt [$R^2CNCH_2SiMe_3$][OTf] (Tf = SO_2CF_3) that was generated in situ by the reaction of Me_3SiCH_2OTf and a nitrile solvent R^1CN (R^2 = Ph and Me). The desired imino[60]fullerene derivative $C_{60}(R^1)$ [C(=NCH_2SiMe_3)R^2] was produced in a yield up to 80%. The structure of the product with R^1 = C_6H_4−OMe-4 and R^2 = Ph was determined by single-crystal X-ray analysis.

An imine group is a useful functionality that may serve as a surrogate of the corresponding carbonyl compound,[1] as a precursor of nitrogen compounds, and as a ligand for metal-assisted directed functionalization of nearby carbon atoms.[2] Despite such utilities, imines are rarely found in the repertoire of functionalized fullerene[3] probably because of the hydrolytic instability of the imine group and the paucity of synthetic approaches.[4] We report here the synthesis of new imino-fullerenes **3** by the reaction of a fullerene anion and an in situ generated nitrilium ion. The new reaction was discovered during our effort to find approaches to organofullerene bearing two addends in a 1,4-relative position such as a bis(trimethylsilylmethyl)[60]fullerene **2** (Scheme 1).[5] While the synthesis of **2** can be achieved in 93% yield, as previously reported, by the reaction of an anion derived from the monosilylmethyl compound **1** with Me_3SiCH_2I in benzonitrile, we obtained the imine **3a** when we used Me_3SiCH_2OTf in place of the iodide.

A typical procedure is given: we first synthesized the monoadduct **1** in 93% yield by addition of Me_3SiCH_2MgCl (3 equiv) in THF to a solution of [60]fullerene in a mixture of *o*-dichlorobenzene and DMF (30 equiv).[5] The monoadduct **1** was deprotonated with KO^{t}Bu (1.2 equiv) in PhCN at 25 °C and then treated with Me_3SiCH_2OTf (2.0 equiv) at the same temperature for 1 h to obtain the imino[60]fullerene **3a** in 63% yield. The bistrimethylsilyl compound **2** (9%) and the starting material **1** account largely for the remainder. The imine product **3a** was hydrolytically rather unstable and was quickly purified on triethylamine-impregnated silica gel

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(1) Barton, D.; Oliis, W. D. *Comprehensive Organic Chemistry*; Pergamon Press, 1979.
(2) (a) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174–238. (b) Ackermann, L. *Topics in Organometallic Chemistry*; Chatani, N., Ed.; Springer-Verlag: Berlin, 2007; Vol. 24, pp 35−60. (c) Yoshikai, N.; Matsumoto, A.; Norinder, J.; Nakamura, E *Angew. Chem., Int. Ed.* **2009**, *48*, 2925–2928.
(3) (a) Wudl, F. *J. Mater. Chem.* **2002**, *12*, 1959–1963. (b) Martin, N. *Chem. Commun.* **2006**, 2093–2104. (c) Hirsch, A.; Brettreich, M. *Fullerenes, Chemistry and Reactions*; Wiley-VCH: Weinheim, Germany, 2005. (d) Thilgen, C.; Diederich, F. *Chem. Rev.* **2006**, *106*, 5049–5135. (e) Bonifazi, D.; Enger, O.; Diederich, F. *Chem. Soc. Rev.* **2007**, *36*, 390–414. (f) Matsuo, Y.; Nakamura, E. *Chem. Rev.* **2008**, *108*, 3016–3028.
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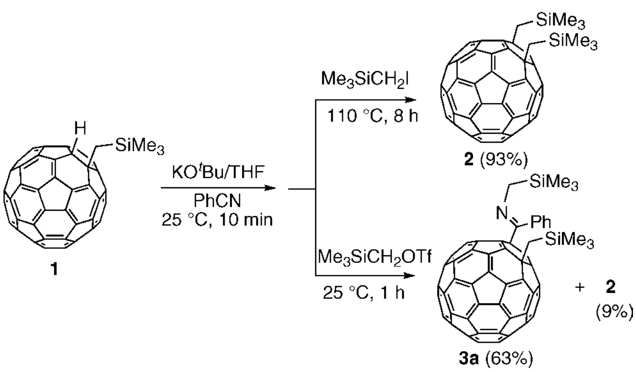
column chromatography or by precipitation by addition of methanol. Some attempts to remove the imine group under acidic conditions resulted in partial scission of the C-acyl bond[6] and did not afford the expected ketone.[7]

We noted that the imine formation takes place under much milder conditions (25 °C) than the formation of bis(silylmethyl) adduct **2** (80−110 °C). The reaction with MeOTf[8] in place of Me_3SiCH_2OTf did not produce the iminofullerene at all but gave a methylated fullerene $C_{60}(CH_2SiMe_3)Me$ (32% HPLC area ratio as a mixture of presumably 1,2- and 1,4-positional isomers; 22% recovery of **1**). The reaction with phenyl triflate (PhOTf) resulted in 100% recovery of **1** after protonation workup.[9] Trimethylsilyl triflate and halides (e.g., Me_3SiOTf, Me_3SiCl) gave back the starting monoalkyl fullerene. The use of a stoichiometric amount of PhCN (and other nitriles in toluene or *o*-dichlorobenzene, instead of the use as a solvent) did not afford the imine product.

Scheme 1. Synthesis of the 1-Imino-4-silylmethyl[60]fullerene and 1,4-Bis(silylmethyl)[60]fullerene



In Table 1, we illustrate the scope of the reaction for some mono(organo)[60]fullerenes and nitriles. $C_{60}(CH_2SiMe_2Ph)H$ showed a reactivity comparable to **1** and gave the corresponding imino[60]fullerene **3b** in 80% yield (entry 2). $C_{60}(C_6H_4-OMe\text{-}4)H$, $C_{60}(C_6H_4-NMe_2\text{-}4)H$, and $C_{60}(C_6H_4-CF_3\text{-}4)H$ differ in the electronic properties of the R groups but showed essentially the same reactivity to give the desired products in similar yields (75−78%). The reaction of $C_{60}(C_6H_4-OMe\text{-}2)H$ that bears an *o*-methoxy group reacted as smoothly as the less hindered compound $C_{60}(C_6H_4-OMe\text{-}4)H$ (entry 6). We could also synthesize a methylimino[60]fullerene **3g** in 32% yield with 60% recovery of **1** (entry 7).

All products (**3a**−**3g**) were characterized by ^1H and ^{13}C NMR, IR, and MS. All imino[60]fullerenes are C_1 symmetric compounds and consist of a racemic mixture of enantiomers.

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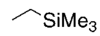
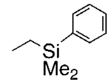
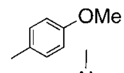
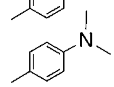
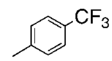
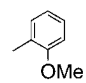
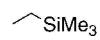
(7) Tzirakis, M. D.; Orfanopoulos, M. *J. Am. Chem. Soc.* **2009**, *131*, 4063–4069.
(8) (a) MeOTf is a more efficient alkylating reagent than iododmethane by the factor of $\sim 10^4$; see: Boche, G. *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: New York, 1995; Vol. 5, pp 3617−3622. (b) Stang, P. J; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, *8*, 5–126.
(9) The color of the monoanion (dark green) persisted until the end of the reaction .

Table 1. Scope and Limitation[a]

entry	R ($C_{60}RH$)	solvent	product	yield/%[b]
1		PhCN	**3a**	63
2		PhCN	**3b**	80
3		PhCN	**3c**	78
4		PhCN	**3d**	75
5		PhCN	**3e**	77
6		PhCN	**3f**	62
7		CH_3CN	**3g**	32[c]

[a] The reaction conditions are described in Scheme 1 (bottom scheme). [b] Isolated yield. [c] 60% recovery of starting material **1**.

The 1,4-addition pattern was unambiguously determined by the X-ray crystallographic analysis of **3c** (Figure 1). Single crystals of imino[60]fullerene **3c** were successfully obtained by slow diffusion of methanol into a *o*-dichlorobenzene solution of **3c**. The orientation of the imine group relative to the fullerene π-surface exposes the nitrogen lone pair in such a direction that a suitable metal atom may be able to coordinate both to the lone pair and to the fullerene π-surface.

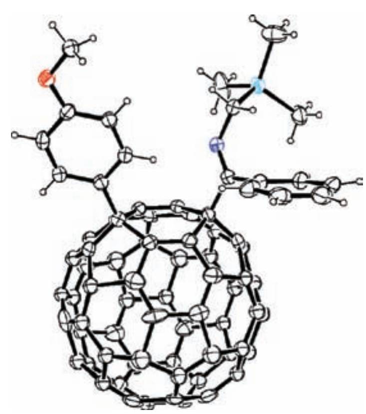


Figure 1. Molecular structure of **3c**. The ORTEP drawing with 30% level of probability level ellipsoids. The oxygen, nitrogen, and silicon atoms are marked in red, blue, and sky blue, respectively. The solvent molecule in the unit cell (**3c**:*o*-dichlorobenzene = 1:1) is omitted for clarity.

The cyclic voltammogram of **3c** exhibited two reversible one-electron reduction processes at $E_{1/2}^{red} = -1.02$ and -1.61 V vs Fc/Fc^+ (Figure S1, Supporting Information). The reduction potential values of **3c** shifted toward the positive side of the corresponding 1,4-di(organo)[60]fullerene, $C_{60}(CH_2SiMe_2Ph)_2$ ($E_{1/2}^{red}$ = −1.06 and −1.63 V vs Fc/Fc$^+$),[5] as one may expect in light of the electron-withdrawing property of the imino moiety.[10]

It has been reported that Me_3SiCH_2OTf reacts slowly with a nitrile (in several days at 25 °C),[11] and the resulting nitrilium salt reacts readily with nucleophiles.[11,12] Thus, we assume (Scheme 2) that Me_3SiCH_2OTf slowly reacted with the nitrile solvent to form in situ the corresponding nitrilium salt, which reacted with the mono(organo)[60]fullerene anion to produce the imino[60]fullerene **3**. We can ascribe the difference between Me_3SiCH_2OTf, Me_3SiCH_2I, and MeOTf to the hardness/softness of the electrophiles (OTf vs I) and to the steric and electron-withdrawing effects of the silyl group (Me_3SiCH_2OTf vs MeOTf).

In summary, we have found an efficient method to introduce an imine group to a monoadduct of [60]fullerenes to produce a 1-imino-4-organo[60]fullerene. The simple and mild reaction conditions (25 °C), the exclusive 1,4-regioselectivity, and the synthetically useful yield are attractive attributes of the reaction. The present synthesis is a useful addition to the repertoire of the synthesis of 1,4-dialkyl [60]fullerene derivatives that is less widely known than 1,2-relative compounds that are available through a variety of cycloaddition reactions including Prato and Bingel−Hirsch reactions.[13,14] We expected that the presence of the imine group will give us ample opportunity to explore the coordination chemistry of this class of compounds as well as the applications to materials research.[15]

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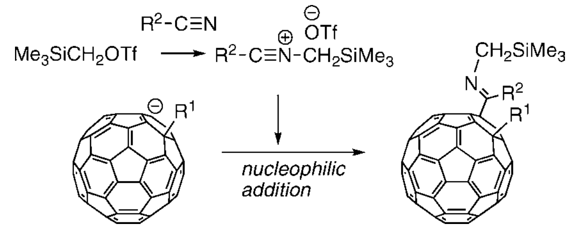
Scheme 2. Proposed Reaction Mechanism



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Supporting Information Available: Experimental procedures, spectroscopic data for all new compounds, and CV data and CIF file for **3c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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