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Bucky ferrocene and ruthenocene: serendipity and discoveries

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Abstract

An idea of making a ferrocene/fullerene hybrid, "bucky ferrocene", has intrigued chemists for some time, but the compounds remained to be hypothetical. The synthesis of such hybrid molecules as $Fe(C_{60}Me_5)Cp$, $Ru(C_{60}Me_5)Cp$ and $Fe(C_{70}Me_3)Cp$ as well as their functionalized derivatives from [60] and [70]fullerenes has been achieved in recent years. With their esthetically pleasing structures and the dual character of metallocene and graphite, these molecules may stimulate the interest of both chemists and non-chemists.
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1. Introduction

Every organometallic chemist would agree that ferrocene discovered half a century ago [1] ($Fe(C_5H_5)_2$, Scheme 1 left) is among the most historical organometallics for its scientific and educational values. This 18-electron organometallic is composed of a pair of η^5-6π-electron aromatic pentagonal carbon ligands (cyclopentadienide = Cp) and a 6d-electron iron(II) atom. [60]Fullerene (Scheme 1 center) discovered 35 years later [2] has secured an even more important position in science and technology, as it has stimulated the imagination of scientists and engineers alike, recreating the whole new world of the science of carbon. The notion of combining ferrocene and fullerene together through face-to-face fusion of the two molecules (Scheme 1 right) has been in the mind of chemists for some time, but no one could materialize the concept until recently. Though such a molecule would enjoy the rich scientific heritage of both ferrocene and fullerene, it is expected to be very unstable first because of the lack of suf-

ficient numbers of 2p-electron in a fullerene pentagon (only five while six required to make ferrocene), and second because of the curvature of the fullerene surface [3].

In 2002, we reported the first successful synthesis of ferrocene/fullerene hybrid molecules [4], where a fullerene pentagon acts as a η^5-6π-electron donor ligand to the 6d-electron iron(II) atom [5–11]. The crystal structures of the [60] and [70]fullerene derivatives of bucky ferrocenes are shown in Scheme 2. (A purist may say that these are not exactly "bucky ferrocene" since methylated fullerenes are not fullerenes, as toluene is not exactly benzene.)

A considerable variety of structures are now available and the repertoire is expanding rapidly [12]. In Scheme 3 are illustrated representative structures. The initial synthetic route gave an access only to pentamethylated fullerene derivatives, but recent development allowed us to synthesize pentahydrogenated derivatives [13] from which we can synthesize compounds having functional groups (e.g., imide, ester, etc.) amenable to further chemical transformations. Ruthencene/fullerene hybrid molecules are now also available [14].
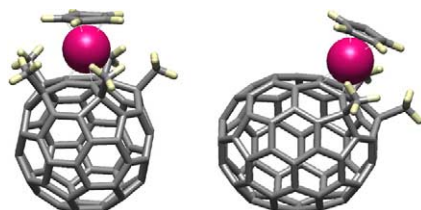
As is usually the case in any research, our bucky ferrocene project needed careful planning, hard work, and,

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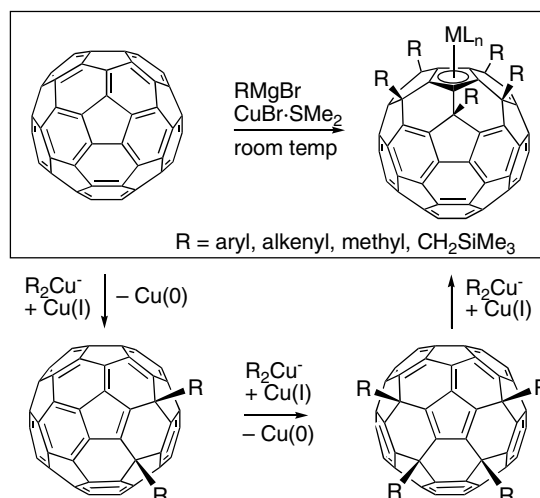*E-mail address:* nakamura@chem.s.u-tokyo.ac.jp.
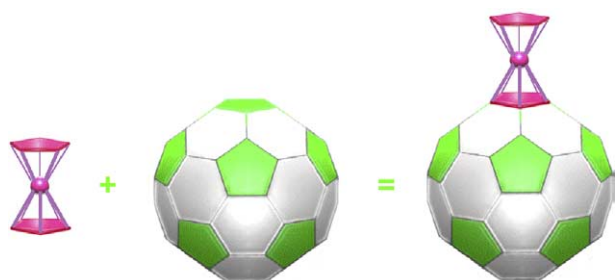
Scheme 1. Ferrecene + [60]fullerene = bucky ferrocene.

Scheme 2. Crystal structures of bucky ferrocenes derived from [60] and [70]fullerenes.

Scheme 4. Quantitative penta-addition of RCu in a stepwise manner.

among others, serendipitous discoveries. The five-electron nature of the fullerene pentagon seemed to be an insurmountable problem at the beginning. This issue was resolved by the use of methylated fullerenes, which became available through an unexpected discovery that an organocopper reagent (RCu) adds five times to [60]fullerene ($C_{60}R_5H$) [5] and three times to [70]fullerene ($C_{70}R_3H$) [10] (Schemes 4 and 6). Introduction of

the required Fe(II) atom was difficult by the standard methods but could be achieved easily through discovery of an unexpected C–H bond activation reaction of a Fe(I)Cp complex. The versatility of the RCu method notwithstanding, the variety of the R groups was limited largely to hydrocarbon groups. The third serendipitous discovery allowed us to construct $Fe(C_{60}H_5)(Cp)$ (Scheme 3) directly from [60]fullerene.

Throughout this review, we employ an acronym RFCp as a generic name to represent the $C_{60}R_5$-cyclopentadienyl ligand [e.g., Fe(MeFCp)(Cp) for $Fe(C_{60}\text{-}Me_5)(C_5H_5)$] and FCp for the fullerene-cyclopentadienyl
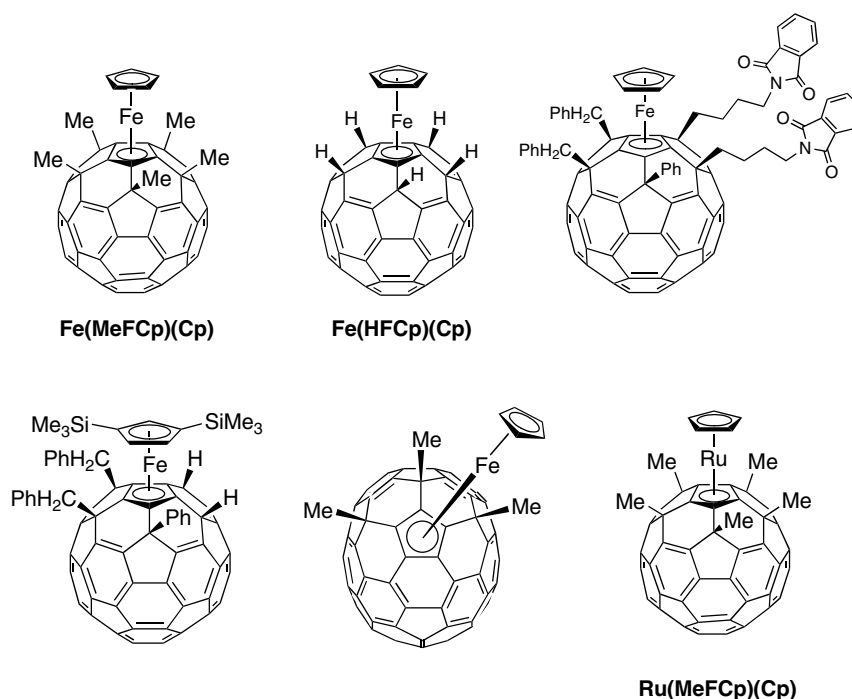
Scheme 3. Representative bucky ferrocene Fe(FCp)(Cp) and ruthenocene Ru(FCp)(Cp) molecules (see text for the use of FCp abbreviation).

ligand in general (including [70]fullerene derivatives). Owing to the wide structural variety available, these simple acronyms have failed already for the two structurally complex C_1-[60]fullerene derivatives listed in Scheme 2. Nonetheless, we consider these acronyms worthwhile for identifying the major structural features of the fullerene-cyclopentadienyl ligands as contrasted with those of Cp and Cp*.

2. Discovery #1: quantitative multiple addition to fullerenes

The access to a series of η^5-fullerene metal complexes through the fivefold addition of an RCu(I) reagent to [60]fullerene was discovered serendipitously [5]. The reaction was found by Dr. Masaya Sawamura, now at Hokkaido University, and Hitoshi Iikura, then a third-year graduate student. Being careful enough, Hitoshi identified $C_{60}Ph_5H$ forming in 3% yield in one of his disparate trial reactions between PhCu and [60]fullerene: Intensive experimentation for a few months after the discovery improved the yield to 90%, and after a few years to 95–100% yield on a 10-g scale [6].

The synthesis of the methyl analog (R = Me) necessitated incorporation of a small trick (the use of N-methylimidazolidone additive), and gave $C_{60}Me_5H$ in 95% yield [8]. Penta-silylmethyl[60]fullerene [15] derivatives became also available later by the effort of Dr. Yutaka Matsuo and Ayako Muramatsu.

How did we make the discovery? The compound such as $C_{60}Ph_5H$ had once appeared in our conversations prior to the experiment, and Hitoshi Iikura was mindful enough to watch for a high molecular weight region of the liquid chromatography chart, and to perform well-informed mass spectrum analysis. Admittedly, such a reaction might have taken place in the reaction flasks in every laboratory in the world devoted to fullerene chemistry, but had apparently escaped proper attention. For instance, similar findings were made by the Sussex group during chlorination of [60]fullerene before our discovery (generating $C_{60}Cl_6$) [16], and, after ours, by the Kyoto group ($C_{60}Ar_5H$, Ar = fluorenyl) [17], but the potential of these products was not pursued in full.
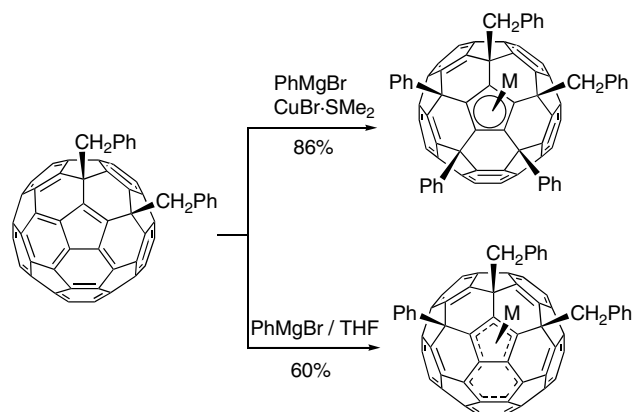

Scheme 5. Selective mono- and tri-addition to dibenzylfullerene.

The fullerene functionalization reaction that takes place with 100% selectivity and 100% yield was unprecedented in the chemistry of fullerenes and nanotubes. With its perfectly isotropic structure, the large molecular weight, and the generally low solubility of [60]fullerene, the reactions of fullerene had rarely been connected to the words like "high regioselectivity, high yield and large-scale" in a sense commonly used in modern catalysis and organic synthesis. This reaction and a related oxidative tetra-amination that we discovered later [18] represent the only two classes of reactions known in fullerene chemistry that take place in quantitative yield. With such high efficiency of synthesis, the products have prove to be useful not only in organometallic chemistry as described below, but in materials [15,19–26] and biological sciences [27,28].

What could be the mechanism of this reaction? We still know very little partly because of the inhomogeneity of the reaction mixture. It is obvious that the penta-addition takes place in a stepwise manner as shown in Scheme 4. On the basis of some experimental data, we consider that the formation of the first di-adduct is the most difficult step, from which the addition of the three remaining R groups takes place rapidly.

Thus, if we treat dibenzylated fullerene with a phenyl-copper reagent (Scheme 5), a dibenzyltriphenyl compound forms in 86% yield [29]. On the other hand, the addition take place only once when a phenyl Grignard
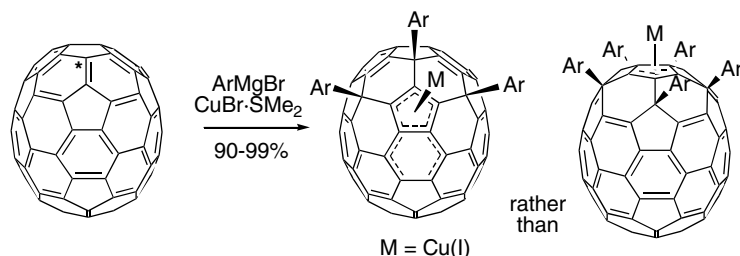
Scheme 6. Selective tri-addition of RCu to [70]fullerene. The most strained carbon is marked with an asterisk.

reagent is used instead of a phenyl copper reagent to afford a C_1-symmetric dibenzyl monophenyl compound in 60% yield.

The profile of the reaction changes with [70]fullerene (Scheme 6). One would expect that the addition gives a penta-adduct by sacrificing the most strained the top part. In reality, the reaction afforded a tri-addition product to give an indenyl metal complex [10]. We speculate that the phenylcopper addition to a C–C double bond took place in such a manner that the first addition reaction generates an sp^3 center at the most strained sp^2 atom (marked with an asterisk), and to generate a more planar and hence better conjugated anion as the first intermediate.

3. Discovery #2: C–H bond activation route to bucky ferrocene

With a series of $C_{60}R_5H$ (or FCpH) compounds in hand, we had only one step ahead of us to the target bucky ferrocene, e.g., Fe(FCp)(Cp). This one step took us a long time to achieve in satisfactory yield. The target molecule being composed of Fe(II), FCp, and Cp, there are a priori two synthetic routes; "FCp + FeCp" and "FeFCp + Cp". The most obvious route in the first approach was the reactions of an FCp anion and an Fe(II)Cp halide, while the second route was then unfeasible since we could not synthesize necessary the Fe(FCp) compounds.

The target molecule Fe(MeFCp)(Cp) was first obtained by Yoichiro Kuninobu, now at Okayama University, rather easily but only in 10% [4] from FeBrCp(CO)$_2$ and Tl(MeFCp) [5,8]. We could however neither improve the yield nor scale up the reaction. While Yoichiro struggling, a rescue came from an unexpected direction. Motoki Toganoh, now at Kyushu University, discovered a more expeditious, C–H bond activation route that directly replaces the cyclopentadienyl hydrogen atom with the FeCp fragment of a Fe(I)(!) complex. Heating $C_{60}Me_5H$ and [FeCp(CO)$_2$]$_2$ together in benzonitrile at 180 °C for 8 h produced Fe(MeFCp)(Cp) in 52% isolated yield (Scheme 7). The success critically depended on the use of benzonitrile (a solvent discovered by serendipity). The bucky ferrocene compound was obtained in two steps from [60]fullerene in 45% overall
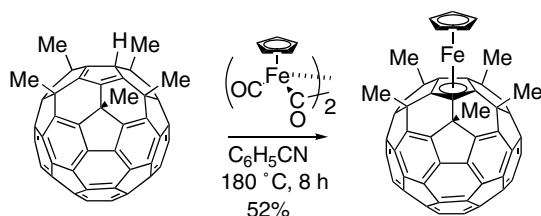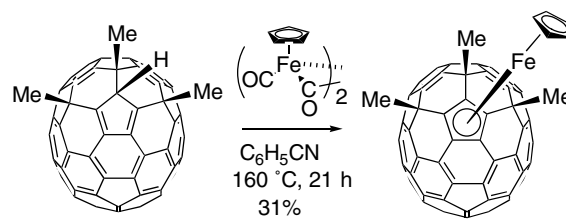
Scheme 8. Synthesis of a [70]fullerene bucky ferrocene.

yield on a multi-gram scale. The compound was found to be very stable: No decomposition took place after standing for many months in air, after 24 h at 200 °C in vacuo, or after irradiation with a high-pressure mercury lamp under nitrogen for 15 h.

The tri-methyl adduct obtained from [70]fullerene was also converted to "bucky ferrocene"; this time, the ferrocene moiety is directly conjugated with the fullerene π-system [30]. The metathesis approach (e.g., the reaction between an FCp anion and a Fe(II) halide complex) failed entirely in this case. Instead, we treated $C_{70}Me_3H$ with [FeCp(CO)$_2$]$_2$ in benzonitrile at 160 °C for 21 h to obtained the desired compound in 31% isolated yield as a dark brown solid (Scheme 8). An overall yield of the two-step synthesis from [70]fullerene was 27%.

Ruthenium has a larger atomic radius and is more electron-rich than iron, and hence "bucky ruthenocene" (Ru(MeFCp)(Cp)) caught our next interest (Scheme 9). The synthesis required different synthetic methods, now back to more conventional ones. We employed a $C_{60}Me_5Ru(II)$ compound [31] as a starting material rather than CpRu(I) as in the ferrocene synthesis. Thus, Yutaka Matsuo first synthesized Ru(η^5-$C_{60}Me_5$)Cl-(CO)$_2$ from [RuCl$_2$(CO)$_3$]$_2$ and $C_{60}Me_5K$. This chloride complex was then allowed to react with sodium cyclopentadienide in THF to give first an unstable η^1-cyclopentadienyl complex, Ru(η^5-$C_{60}Me_5$) (η^1-C_5H_5)(CO)$_2$ in 90% yield. Upon heating at 90 °C, it afforded the desired bucky ruthenocene in 12% yield [14].

4. Discovery #3: transfer hydrometalation route to ferrocene/hydrofullerene hybrid

Ever since we discovered the RCu-route to $C_{60}R_5H$, we searched from time to time for a way to introduce hydrogen atoms as R groups. We also wanted to introduce functionalized R groups so as to prepare functionalized bucky ferrocenes. The first problem looked especially difficult since the literature reactions of fullerene polyhydrogenation invariably gave a mixture of products. Motoki Toganoh came out again to discover a new reaction, transfer hydrometalation, and solved the two problems at once.

He first found rhenium-templated transfer hydrogenation of [60]fullerene by the use of 9,10-dihydoanthracene

Scheme 7. Synthesis of a bucky ferrocene Fe(MeFCp)(Cp).
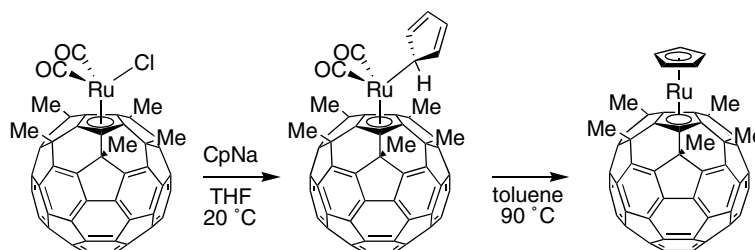
Scheme 9. Synthesis of bucky ruthenocene.
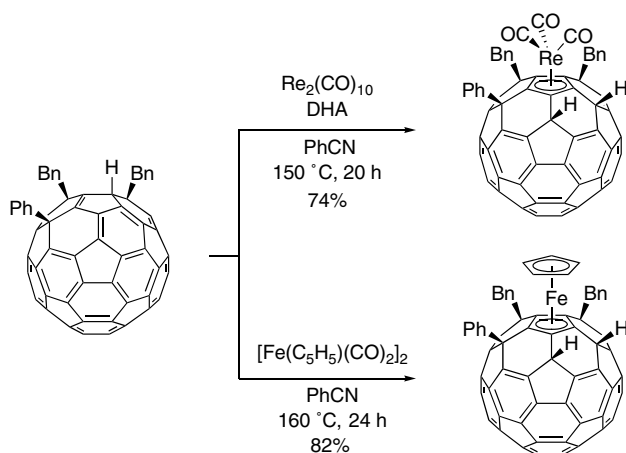
Scheme 10. Transfer hydrogenation.

(DHA) as a reducing agent [32]. The reaction of a dibenzylphenyl fullerene with DHA in the presence of $Re_2(CO)_{10}$ afforded a rhenium complex **2** (Scheme 10). Similarly but now without DHA, the reaction of $[Fe(C_5H_5)(CO)_2]_2$ with $C_{60}(PhCH_2)_2$ [33] in benzonitrile at 160 °C afforded the desired hydroferrated product in 82% yield [13]. The cyclopentadiene liberated from $[Fe(C_5H_5)(CO)_2]_2$ acts as the hydrogen source in this reaction.

The reaction permitted us to synthesize a bucky ferrocene directly from [60]fullerene (Scheme 11); for instance, $Fe(C_{60}H_5)(Cp)$ (i.e., Fe(HFCp)(Cp)) in 25% yield from [60]fullerene). In addition, it was found that we can deprotonate the hydrofullerene [34] and alkylate the resulting anion regioselectively with an alkyl halide. For instance, the addition of Bu_4NOH to Fe(HFCp)(Cp) in benzonitrile at ambient temperature causes color change from light red to dark red within

a few seconds, and was in situ alkylated in good yield with an excess of an alkyl halide.

5. Conclusion

The chemistry of bucky metallocenes and related metal complexes has just begun. We therefore do not know exactly the future of this chemistry. It is clear however that they will benefit from their dual properties: They are organometallics and graphitic materials at the same time. We expect it possible to synthesize higher analogs with respect to the graphitic part, for instance, the nanotube derivatives of ferrocene. Applications of FCp metal complexes to catalysis seem to be obvious and we have already found some interesting cases where the selectivity of a catalytic reaction is affected by the use of the FCp ligand instead of a conventional Cp ligand [35]. More unforeseeable is the applications to the fields outside of the conventional chemistry. It has been demonstrated that the $C_{60}R_5$-type molecules form vesicles and DNA-complexes in water [21–23,27,28], liquid crystals [15,19], layer structures on a solid surface [24] and found use in solar cell applications [25,26]. There is therefore every reason to believe that the metal complexes [31,36] can be incorporated into higher-order structures such as a liquid crystalline phase and adds to the diversity of the fullerene-based materials. Given the drastically reduced price of fullerenes because of the establishment of a mass production plant [37], the compounds such as Fe(FCp)(Cp) can be made relatively cheaply on a large scale, and hence they have become potential targets of high-tech materials development. Though we would not claim that bucky ferrocenes will become as important as their parents, we are hoping
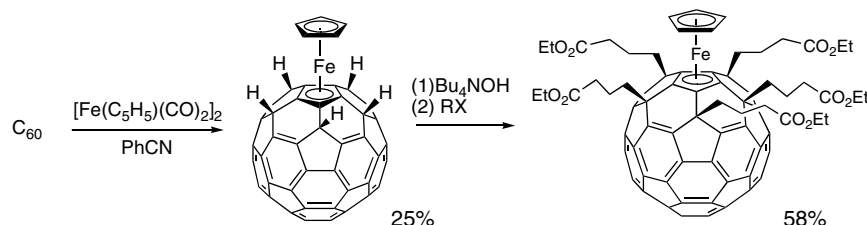
Scheme 11. Transfer hydrometalation followed by alkylation under mildly basic conditions.

that they will find some places to live long in the field of organometallic chemistry.

Acknowledgements

References

[1] (a) T.J. Kealy, P.L. Pauson, Nature 168 (1951) 1039;
(b) S.A. Miller, J.A. Tebboth, J.F. Tremaine, J. Chem. Soc. (1952) 632;
(c) G. Wilkinson, M. Rosenblum, M.C. Whiting, R.B. Woodward, J. Am. Chem. Soc. 74 (1952) 2125;
(d) E.O. Fischer, W.Z. Pfab, Z. Naturforsch. 7B (1952) 377.

[2] (a) H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, Nature 318 (1985) 162;
(b) E. Osawa, Kagaku 25 (1970) 854;
Chem. Abst. 74 (15): 75698v.

[3] E.D. Jemmis, M. Manoharan, P.K. Sharma, Organometallics 19 (2000) 1879.

[4] M. Sawamura, Y. Kuninobu, M. Toganoh, Y. Matsuo, M. Yamanaka, E. Nakamura, J. Am. Chem. Soc. 124 (2002) 9354.

[5] M. Sawamura, H. Iikura, E. Nakamura, J. Am. Chem. Soc. 118 (1996) 12850.

[6] M. Sawamura, H. Iikura, T. Ohama, U.E. Hackler, E. Nakamura, J. Organomet. Chem. 599 (2000) 32.

[7] M. Sawamura, N. Nagahama, M. Toganoh, E. Nakamura, J. Organomet. Chem. 652 (2002) 31.

[8] M. Sawamura, M. Toganoh, Y. Kuninobu, S. Kato, E. Nakamura, Chem. Lett. (2000) 270.

[9] M. Toganoh, K. Suzuki, R. Udagawa, A. Hirai, M. Sawamura, E. Nakamura, Org. Biomol. Chem. 1 (2003) 2604.

[10] M. Sawamura, H. Iikura, A. Hirai, E. Nakamura, J. Am. Chem. Soc. 120 (1998) 8285.

[11] M. Sawamura, Y. Kuninobu, M. Toganoh, Y. Matsuo, M. Yamanaka, E. Nakamura, J. Am. Chem. Soc. 124 (2002) 9354.

[12] (a) E. Nakamura, Pure Appl. Chem. 75 (2003) 427;
(b) E. Nakamura, M. Sawamura, Pure Appl. Chem. 73 (2001) 355.

[13] M. Toganoh, Y. Matsuo, E. Nakamura, J. Am. Chem. Soc. 125 (2003) 13974.

[14] Y. Matsuo, Y. Kuninobu, S. Ito, E. Nakamura, Chem. Lett. 33 (2004) 68.

[15] Y. Matsuo, A. Muramatsu, R. Hamasaki, N. Mizoshita, T. Kato, E. Nakamura, J. Am. Chem. Soc. 126 (2004) 432.

[16] (a) P.R. Birkett, A.G. Avent, A.D. Darwish, H.W. Kroto, R. Taylor, D.R.M. Walton, J. Soc. Chem., Chem. Commun. (1993) 1230;
(b) P.R. Birkett, P.B. Hitchcock, H.W. Kroto, R. Taylor, D.R.M. Walton, Nature 357 (1992) 479.

[17] Y. Murata, M. Shiro, K. Komatsu, J. Am. Chem. Soc. 119 (1997) 8117.

[18] H. Isobe, N. Tomita, E. Nakamura, Org. Lett. 2 (2000) 3663.

[19] M. Sawamura, K. Kawai, Y. Matsuo, K. Kanie, T. Kato, E. Nakamura, Nature 419 (2002) 702.

[20] R. Hamasaki, Y. Matsuo, E. Nakamura, Chem. Lett. 33 (2004) 328.

[21] M. Sawamura, N. Nagahama, M. Toganoh, U.E. Hackler, H. Isobe, E. Nakamura, S.-Q. Zhou, B. Chu, Chem. Lett. (2000) 1098.

[22] S.-Q. Zhou, C. Burger, B. Chu, M. Sawamura, N. Nagahama, M. Toganoh, U.E. Hackler, H. Isobe, E. Nakamura, Science 291 (2001) 1944.

[23] E. Nakamura, H. Isobe, Acc. Chem. Res. 36 (2003) 807.

[24] T. Shimada, H. Nakatani, K. Ueno, A. Koma, Y. Kuninobu, M. Sawamura, E. Nakamura, J. Appl. Phys. 90 (2001) 209.

[25] A. Fujii, T. Umeda, H. Isobe, E. Nakamura, K. Yoshino, Jpn. J. Appl. Phys. 40 (2001) L1390.

[26] T. Shirakawa, T. Umeda, Y. Nishihara, A. Fujii, H. Isobe, E. Nakamura, K. Yoshino, Synth. Met. 137 (2003) 1415.

[27] E. Nakamura, H. Isobe, N. Tomita, M. Sawamura, S. Jinno, H. Okayama, Angew. Chem. Int. Ed. 39 (2000) 4254.

[28] H. Isobe, N. Tomita, S. Jinno, H. Okayama, E. Nakamura, Chem. Lett. (2001) 1214.

[29] M. Sawamura, M. Toganoh, K. Suzuki, A. Hirai, H. Iikura, E. Nakamura, Org. Lett. 2 (2000) 1919.

[30] H. Iikura, S. Mori, M. Sawamura, E. Nakamura, J. Org. Chem. 62 (1997) 7912.

[31] Y. Matsuo, E. Nakamura, Organometallics 22 (2003) 2554.

[32] M. Toganoh, Y. Matsuo, E. Nakamura, Angew. Chem. Int. Ed. 42 (2003) 3530.

[33] R. Subramanian, K.M. Kadish, M.N. Vijayashree, X. Gao, M.T. Jones, M.D. Miller, K.L. Krause, T. Suenobu, S. Fukuzumi, J. Phys. Chem. 100 (1996) 16327.

[34] (a) M.S. Meier, R.G. Bergosh, M.E. Gallagher, H.P. Spielmann, Z. Wang, J. Org. Chem. 67 (2002) 5946;
(b) Y. Rubin, P.S. Ganapathi, A. Franz, Y.-Z. An, W. Qian, R. Neier, Chem. Eur. J. 5 (1999) 3162.

[35] M. Toganoh, Y. Matsuo, E. Nakamura, J. Organomet. Chem. 683 (2003) 295.

[36] M. Sawamura, Y. Kuninobu, E. Nakamura, J. Am. Chem. Soc. 122 (2000) 12407.

[37] Frontier Carbon Corporation: http://www.f-carbon.com/.