ELSEVIER

Journal of Organometallic Chemistry 652 (2002) 31–35

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Regioselective penta-addition of 1-alkenyl copper reagent to [60]fullerene. Synthesis of penta-alkenyl FCp ligand

Masaya Sawamura *, Noriaki Nagahama, Motoki Toganoh, Eiichi Nakamura *

Department of Chemistry, The University of Tokyo, Bunkyo-Ku, Hongo, 7-3-1 Tokyo, Japan

Received 31 August 2001

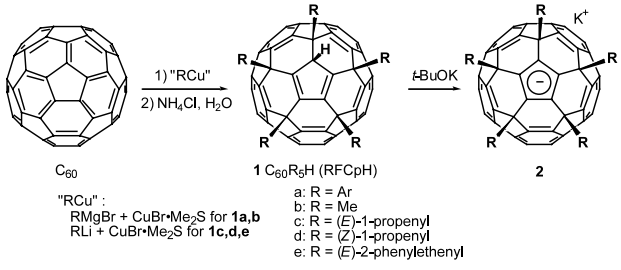
Abstract

We have found the conditions to achieve penta-addition of an alkenyl group to [60]fullerene in good yield with the aid of an RCu-type reagent prepared from the corresponding alkenyllithium reagent. The addition took place regioselectively at the five double bonds surrounding a pentagon in the fullerene and with retention of the stereochemistry of the alkenylcopper reagent. The reaction thus produced a cyclopentadiene embedded in the fullerene core that bears five 1-alkenyl groups (**1c**–**e**). © 2002 Published by Elsevier Science B.V.

Keywords: Fullerene; Organocopper reagent; Multiple addition; Alkenyl; Cyclopentadiene; Cp ligand

1. Introduction

Regioselective penta-addition of an organocopper reagent (RCu) to one of the 12 pentagons of [60]fullerene takes place to produce a new class of cyclopentadiene **1** that is embedded in the fullerene core (Eq. (1)) [1]. The reaction takes place with complete regioselectivity and in essentially quantitative yield to give $C_{60}Ar_5H$ (**1a**) and $C_{60}Me_5H$ (**1b**) from aryl and methyl copper reagents, respectively, prepared by the reaction of the corresponding Grignard reagent and $CuBr \cdot Me_2S$. The anion prepared by deprotonation of **1** represents a new class of ligand (denoted as FCp ligand, or RFCp where R may be the group derived from the RCu reagent), wherein the cyclopentadienyl anion is conjugated with the remaining fullerene π-system through the endohedral π-lobes [2]. Upon treatment with a base such as *t*-BuOK, the cyclopentadiene **1** becomes the cyclopentadienide **2**, which is C_{5v} symmetric as observed in solution by NMR. η^5-Organometallic complexes including a η^5-$Rh(CO)_2$ complex of MeFCp have been prepared and used for catalysis [3]. Indenyl-type complexes have been synthesized by the use of a related tri-addition product [4]. The potential of the FCp molecules in nanoscience has also been demonstrated: the potassium complex of PhFCp (**2a**) has been shown to self-assemble to form a new class of vesicles in aqueous solution [5] and MeFCpH (**1b**) formed monolayer epitaxial films on H–Si(111) and MoS_2(0001) surfaces [6].



(1)

With such rapid expansion of the FCp science and applications, the limited availability of the R groups surfaced as a problem; namely, we have not been able to synthesize alkyl-substituted derivatives (except for MeFCpH (**1b**)), which will be useful for further studies on self-assembly properties and on catalysis. To this end, we sought to perform penta-addition of a 1-alkenyl copper reagent as a surrogate having steric bulk similar to an alkyl group. As shown in Fig. 1 for the (*E*)-1-

* Corresponding authors. Present address: Department of Chemistry, Hokkaido University, Kita-ku, Sapporo 060-0810, Japan (M.S.).

E-mail address: sawamura@chem.s.u.-tokyo-ac.jp (M. Sawamura).

0022-328X/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S0022-328X(02)01305-0

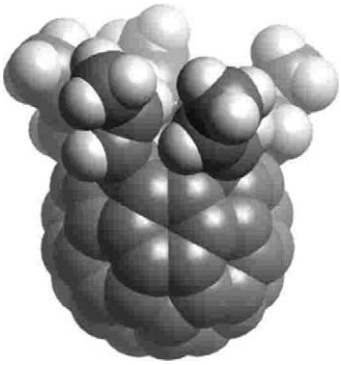


Fig. 1.

propenyl derivative (**1c**), the alkenyl substituent will extend upward from the fullerene core (the most stable structure obtained by Monte–Carlo structural search with MM2* force field implemented in the MACROMODEL program) [7]. An expected merit of the 1-alkenyl group is its *E*–*Z* isomerism, with which one may control the gross shape of the FCp molecule—a property needed to be controlled in supramolecular applications. We report here that one can synthesize the 1-alkenyl compounds by the use of the copper reagent prepared from the corresponding lithium reagent instead of the Grignard reagent so far employed for the synthesis of arylated and methylated analogs. The *E* and the *Z* isomers of the alkenyllithium reagents react with retention of the stereochemistry to give the corresponding *E* and *Z* adducts (**1c** and **1d**).

2. Results and discussion

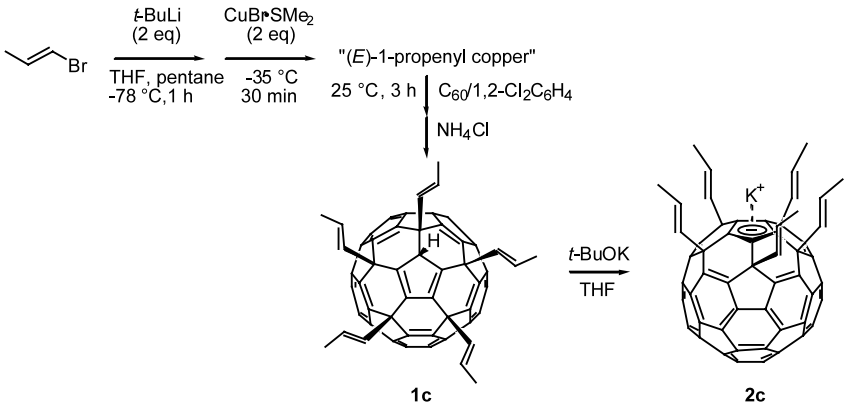
We previously established the conditions to quantitatively convert [60]fullerene to the penta-addition products **1a** and **1b** with aryl and methyl copper reagents that are prepared from equimolar amounts of the corresponding Grignard reagent and $CuBr \cdot Me_2S$ (Eq. (1)) [1]. The reaction conditions for the arylation and methylation reactions were similar to each other except that the latter needs the presence of a polar additive (e.g. *N*,*N*-dimethylimidazolidinone) [1c]. It was necessary to use 25 equivalents of the copper reagents partly because Cu(I) species oxidizes the intermediary copper–fullerene adducts and get reduced eventually to metallic copper. Oxidative dimerization of the organocopper reagent also takes place. In contrast, long chain alkyl copper reagents proved entirely ineffective (much recovery of fullerene).

The penta-addition to [60]fullerene so far successfully took place only for organocopper reagents stable at room temperature, and an apparent problem with the long chain alkylcopper reagents is the thermal instability of the reagents [8]. For instance, it takes 24 h at 60 °C for complete decomposition of the phenylcopper reagent (PhMgBr and CuCl) in THF, and 15 h at 25 °C for the methylcopper reagent (MeMgBr and CuCl). In contrast, it takes only 3 h at 2 °C for ethylcopper reagent in ether [9]. 1-Propenylcopper reagent (*E*–*Z* mixture) prepared from the corresponding Grignard reagent is as stable as the methylcopper reagent [10] and hence appears to be suitable for the reaction with [60]fullerene.

Thus, in an attempt to prepare **1e**, we prepared 2-phenylethenyl copper reagent from (*E*)-2-phenylethenyl bromide via a Grignard reagent, and allowed it to react with [60]fullerene, and found two problems. The reaction was slow and full consumption of fullerene could not be achieved. In addition, the product was a mixture of *E* and *Z* isomers owing to *cis*/*trans* isomerization during the reaction of the starting alkenyl bromide with metallic magnesium. An obvious remedy to the latter issue is the preparation of the Grignard reagent through initial bromine–lithium exchange carried out on the alkenyl bromide [11] followed by Li-to-Mg and then Mg-to-Cu transmetallation reactions. We found, however, that the Li-to-Mg transmetallation is unnecessary and the copper reagent prepared directly from the lithium reagent is more effective than the Grignard-derived copper reagent. The findings stands in contrast to our previous observations for the methyl and aryl copper reagents that the Grignard-derived copper reagents are more efficacious than the lithium-based reagents.

The procedure optimized after a series of experimentation is described for the synthesis **1c** from (*E*)-1-propenyl bromide (Scheme 1). The (*E*)-bromide in THF was first treated at −78 °C with two equivalents of *t*-BuLi in pentane [11], and the lithium reagent was subsequently allowed to react with two equivalents of $CuBr \cdot Me_2S$ at −35 °C (less than two equivalents of the copper salt led to decreased yield). A 1,2-dichlorobenzene solution of [60]fullerene (1/25 molar equivalent to the bromide) was added to the copper reagent and the mixture was warmed immediately to 25 °C, and quenched after 3 h by addition of aqueous NH_4Cl. This procedure give the desired penta-adduct **1c** isolated in 85% yield with over 95% purity after precipitation with methanol. The product was composed of 99% all *E* product. From the reasons yet unclear, immediate warming of the reaction mixture after mixing the copper reagent and the fullerene is essential to minimize the recovery of the fullerene as well as the formation of mono- or multi-addition side products.

The product $C_{60}[(E)\text{-1-propenyl}]_5H$ (**1c**) was C_s symmetrical as found by NMR studies, and, upon conversion to $C_{60}[(E)\text{-1-propenyl}]_5K$ (**2c**) by treatment with *t*-BuOK, became C_{5v} symmetric-an observation typical for the FCpH compounds [1]. This observation combined with other physical properties including mass spectrum established the identity of the product. Application of the same procedure to (*Z*)-1-propenyl bromide



Scheme 1.

(containing ca. 5% *E*-isomer) afforded the corresponding (*Z*)-adduct **1d**. The retention of the *E*- or Z-geometry of the olefin during the reaction could be readily discerned by the coupling constant for the olefinic protons (determined for **2c**: $J = 15.2$ Hz, **2d**: $J = 11.4$ Hz). Comparison of NMR spectrum with the (*E*)-adduct indicated that the (*Z*)-adduct was composed of 82% all *Z* product.

Starting with (*E*)-2-phenylethenyl bromide, we obtained the corresponding adduct **1e** in 83% yield with > 93% purity with retention of the *E* geometry ($J = 15.6$ Hz determined for **2e**). The reaction of various types of alkenylcopper reagents, however, afforded a complex mixture instead of the desired penta-alkenylated fullerene. The reason for this complexity is unclear at this time.

The alkenyl adducts **1c**–**e** are stable in solid kept in air but are oxidized slowly in solution exposed to air. The stability falls between $C_{60}Me_5H$ (**1b**) and $C_{60}Ph_5H$ (**1a**: the latter being more resistant to oxidation). The chemical shift of the proton attached directly to the fullerene core is 4.60 ppm for C_{60}[(*E*)-1-propenyl]$_5$H, which falls between $C_{60}Ph_5H$ (5.30 ppm) and $C_{60}Me_5H$ (4.46 ppm). The chemical shift must reflect the electron-withdrawing and/or the magnetic anisotropic effects of the substituents.

In conclusion, we have found the conditions to achieve the penta-addition of an alkenyl group to [60]fullerene in good yield with the aid of an RCu-type reagent prepared from the corresponding alkenyllithium reagent. The addition took place regioselectively at the five double bonds surrounding a pentagon in the fullerene and with retention of the stereochemistry of the alkenylcopper reagents. In this and the previous studies, we thus noted significant effects of inorganic (e.g. Mg vs. Li) and organic compounds (e.g. polar additives) that do not appear on the overall chemical equation, but their mechanistic roles still remain unclear in spite of recent advance in organocopper reaction mechanisms [12].

3. Experimental

3.1. General

All reactions were carried out in an oven-dried reaction vessel under argon or nitrogen and were analyzed by HPLC (column: Buckyprep, 4.6 × 250 mm, Nacalai tesque; flow rate: 1.0 ml min^{-1}; eluent: toluene–2-propanol = 7/3; detector: SPD-M10Avp, Shimadzu). Purity of products was determined by integrated area ratios of products at 350 nm absorption. Common organic solvents as well as aqueous solutions used for work up procedures were deoxygenated by freeze-thaw cycles (over three times) or by bubbling nitrogen (over 30 min).

All ^{1}H-NMR spectra were taken at 400 MHz (JEOL EX-400), and ^{13}C-NMR spectra at 100 MHz. Spectra are reported in part per million from internal tetramethylsilane. IR spectra were recorded on a JASCO IR-420 instrument; absorptions are reported in cm^{-1}. Mass spectra were measured with a Shimadzu LCMS-QP8000 (APCI mode) equipped with a Buckyprep column. Preparative HPLC was performed on a Buckyprep column (20 × 250 mm) using toluene–2-propanol = 7/3 as eluent (flow rate 12–20 ml min^{-1}, detected at 350 nm with an UV spectrophotometric detector, Shimadzu SPD-6A). Recycle preparative HPLC was performed on a Japan Analytical Industry LC-908 machine equipped with GPC columns (JAIGEL 1H and 2H) and an RI detector RI-5HC ($CHCl_3$ as eluent, flow rate: 3.5 ml min^{-1}) or on a Japan Analytical Industry LC908-C60 machine equipped with GPC columns (JAIGEL 2H and 3H), a UV detector 3702 and an RI detector RI-5 (toluene as eluent, flow rate: 3.5 ml min^{-1}).

3.2. Solvents

Anhydrous tetrahydrofuran (THF) was purchased from Kanto Chemical Co, Inc. (free from stabilizer).

1,2-Dichlorobenzene was distilled under reduced pressure from CaH_2 and stored over molecular sieves 4A. The water content of the solvent was determined in every experiment with a Karl–Fisher Moisture Titrator (MK-210, Kyoto Electronics Company) to be less than 10 ppm.

3.3. Materials

All commercially available reagents were distilled or recrystallized before use. *t*-Butyllithuim in pentane were purchased from Kanto Chemical Co, Inc. and titrated prior to use. *t*-BuOK in THF was purchased from Aldrich Inc. and used as received. $CuBr \cdot SMe_2$ was freshly prepared from CuBr (washed with methanol prior to use) and Me_2S and precipitated twice from Me_2S and pentane.

3.4. Computational method

Molecular mechanics calculations were performed for **1c** and **1d** with a MACROMODEL program version 6, implemented with MM2* and a BATCHMIN program capable of a Monte–Carlo sted of the generation and minimization of 500 structures, with each conformer being kept when it fell within 10 kJ mol^{-1} of the current global minimum and did not duplicate any previously stored conformers. This process was repeated twice, each time starting from an arbitrary conformer which was minimized by MM2* in advance. All the minimization was converged using Polak–Ribiere conjugate gradient minimization. In Fig. 1 is shown the most stable structure of **1c**, to which the structure of **1d** was similar.

3.4.1. $C_{60}[(E)$-1-propenyl$]_5H$ (**1c**)

To a solution of (*E*)-1-propenyl bromide (0.30 ml, 3.5 mmol, *E*:*Z* > 99:1) in 20 ml of THF was added *t*-BuLi (1.62 M in pentane, 4.7 ml, 7.0 mmol) at −78 °C. After stirring for 1 h 1.4 g of $CuBr \cdot SMe_2$ (7.0 mmol) was added at this temperature and the resulting suspension was stirred for 30 min at −35 °C. To the mixture was added 100 mg of C_{60} in 20 ml of 1,2-dichlorobenzene (0.14 mmol) and then the temperature was quickly raised to 25 °C. After stirring for 3 h at 25 °C, 0.2 ml of saturated aqueous NH_4Cl solution was added and the mixture was diluted with 200 ml of toluene. The crude mixture was filtered by passing through a pad of Al_2O_3–Na_2SO_4, through which a MeOH–toluene mixture was passed prior to the filtration. The filtrate was evaporated under reduced pressure to a small volume, and diluted quickly with MeOH to precipitate the title compound as brown solid (109 mg, 85% yield). This sample was judged to be >95% purity by HPLC and NMR analysis and suitable for further synthetic operations. Geometrical purity was over 99% as judged by ^{1}H-NMR for the area ratio of Cp–H peaks. Identification of the compound was also achieved by deprotonation of the cyclopentadienyl proton with *t*-BuOK as described in the following section and stereochemistry was unambiguously determined by coupling constant of olefinic proton in this stage (**2c**: *J* = 15.2 Hz, **2d**: *J* = 11.4Hz). Further purification was achieved with preparative HPLC. IR (KBr disk) 2925 (s), 2853 (m), 1738 (m), 1541 (w), 1458 (m), 1380 (w), 1261 (m), 1096 (br s), 960 (w), 803 (br s), 758 (w), 725 (w), 660 (w), 637 (w), 617 (w), 560 (w), 538 (w), 469 (w), 431 (w), 410 (w); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.86 (d, *J* = 1.6 Hz, 3H), 1.88 (d, *J* = 2.8 Hz, 6H), 1.90 (d, *J* = 2.8 Hz, 6H), 4.60 (s, 1H), 6.00–6.35 (m, 10H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 18.06, 18.12 (2C), 18.14 (2C), 56.79, 57.56 (2C), 58.98, 59.49 (2C), 125.28, 126.64 (2C), 127.18 (2C), 130.60 (2C), 130.84 (2C), 135.70, 142.74 (2C), 142.87 (2C), 143.56 (2C), 143.82 (2C), 143.85 (2C), 144.04 (2C), 144.14 (2C), 144.31 (2C), 145.11 (2C), 145.40 (2C), 145.42 (2C), 145.66 (2C), 146.48, 146.68 (2C), 146.74 (2C), 147.52 (2C), 147.57 (2C), 147.67 (2C), 147.77 (2C), 147.92 (2C), 148.00 (2C), 148.30 (2C), 148.37 (1C+2C),151,54 (2C), 151.57 (2C), 151.91 (2C), 155.29 (2C); UV–vis λ_{max} 279, 285, 349, 396, 472 nm; MS *m*/*z* 926 [M^+].

3.4.2. $C_{60}[(E)$-1-propenyl$]_5K$ (**2c**)

To a solution of **1c** (10 mg, 11 μmol) in 0.60 ml of degassed THF-d_8 in an NMR tube was added 13 μl of a *t*-BuOK solution (1.0 M in THF, 13 μmol) under an argon atmosphere. Immediately the color of the solution changed from orange to dark brown, which indicated a generation of cyclopentadienyl anion: ^{1}H-NMR (400 MHz, THF-d_8) δ 1.81 (dd, *J* = 2.0, 6.4 Hz, 15H), 6.15 (dq, *J* = 6.0, 15.2 Hz, 5H), 6.40 (dd, *J* = 2.0, 15.2 Hz, 5H); ^{13}C-NMR (100 MHz, THF-d_8) δ 18.34 (5C), 60.99 (5C), 122.28 (5C), 127.69 (5C), 138.08 (5C), 143.14 (10C), 146.32 (5C), 147.22 (10C), 148.57 (10C), 148.93 (5C), 158.87 (10C).

3.4.3. Synthesis of $C_{60}[(Z)$-1-propenyl$]_5H$ (**1d**)

This compound was synthesized by a procedure similar to that for the preparation of C_{60}[(*E*)-1-propenyl]$_5$H except that 0.30 ml (3.5 mmol) of (*Z*)-1-propenyl bromide (*E*:*Z* = 95:5) was used instead of (*E*)-1-propenyl bromide. Ninety nine milligram of the title compound (77% yield) was obtained as brown solid. This sample was judged to be >98% purity (as to the penta adduct) by HPLC and NMR analysis and suitable for further synthetic operations (Geometrical purity was 82% as judged by ^{1}H-NMR for the area of Cp–H peaks.). Identification of the compound was also achieved in the same manner as described in Section 3.4.1. Further purification was achieved with preparative HPLC. IR (KBr disk) 3009 (s), 2917 (m), 1732 (br s), 1649 (br m), 1457 (s), 1398 (m), 1364 (w), 1326 (m), 1235 (m), 1199 (m), 1126 (w), 1034 (w), 965 (m), 805 (w), 750 (m), 706 (s), 544 (s), 500 (w); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.91 (dd, *J* = 1.8 Hz, 7.4 Hz, 3H), 1.98 (dd,

$J = 1.8$ Hz, 7.4 Hz 6H), 2.01 (dd, $J = 1.8$ Hz, 7.4 Hz, 6H), 4.68 (s, 1H), 5.72–5.86 (m, 5H), 6.02 (dq, $J = 1.8$ Hz, 11.2 Hz, 4H), 6.19 (dq, $J = 1.6$ Hz, 11.6 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.59, 14.76 (2C+2C), 56.25, 56.34, 58.26 (2C), 60.37 (2C), 124.30, 126.44 (2C), 126.67 (2C), 128.08 (2C), 128.29 (2C), 133.18, 142.73 (2C), 142.98 (2C), 143.52 (2C), 143.65 (2C), 143.70 (2C), 143.81 (2C), 143.96 (2C), 144.30 (2C), 144.86 (2C), 145.25 (2C), 145.67 (2C), 145.72 (2C), 146.47, 146.59 (2C), 146.82 (2C), 146.92 (2C), 147.54 (2C), 147.76 (2C), 147.78 (2C), 148.02 (2C), 148.08 (2C), 148.39 (2C), 148.46 (1C + 2C), 151,70 (2C), 151.87 (2C), 152.21 (2C), 155.64 (2C); MS *m/z* 926 [M^+].

3.4.4. C_{60}[(*Z*)-1-propenyl]$_5$K (**2d**)

To a solution of **1d** (10 mg, 11 μmol) in 0.60 ml of degassed THF-d_8 in an NMR tube was added 13 μl of a *t*-BuOK solution (1.0 M in THF, 13 μmol) under an argon atmosphere. Immediately the color of the solution changed from orange to dark brown that indicated generation of cyclopentadienyl anion: ^{1}H-NMR (400 MHz, THF-d_8) δ 1.97 (dd, $J = 2.0$, 7.2 Hz, 15H), 5.50 (dq, $J = 7.2$, 11.4 Hz, 5H), 6.27 (dd, $J = 2.0$, 11.4 Hz, 5H); ^{13}C-NMR (100 MHz, THF-d_8) δ 15.21 (5C), 79.44 (5C), 121.90 (5C), 129.02 (5C), 131.48 (5C), 136.22 (10C), 143.12 (5C), 146.62 (10C), 147.43 (10C), 148.51 (5C), 149.16 (10C).

3.4.5. C_{60}[(*E*)-2-phenylethenyl]$_5$H (**1e**)

This compound was synthesized by a procedure similar to that for the preparation of C_{60}[(*E*)-1-propenyl]$_5$H except that 0.45 ml (3.5 mmol) of (*E*)-2-phenylethenyl bromide (*E*:*Z* > 99:1) was used instead of (*E*)-1-propenyl bromide. 141 mg of the title compound (83% yield) was obtained as brown solid. This sample was judged to be >93% purity by HPLC and NMR analysis and suitable for further synthetic operations. Geometrical purity was over 99% as judged by ^{1}H-NMR for the area of Cp–H peaks. Stereochemistry was estimated by coupling constant of olefinic proton ($J = 15.6$ Hz) in **2e** after deprotonation of **1e** as shown below. Further purification was achieved with preparative HPLC. IR (KBr disk) 3034 (w), 2925 (s), 2857 (s), 1496 (m), 1448 (s), 960 (s), 742 (br m), 691 (s), 553 (w), 524 (w); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.96 (s, 1H), 6.96–7.08 (m, 5H), 7.11–7.15 (m, 5H), 7.25–7.56 (m, 25H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 56.74, 57.45 (2C), 58.96, 59.41 (2C), 126.36 (4C), 126.38 (4C), 126.39 (2C), 127.67 (2C), 127.72 (2C), 127.75, 128.34 (4C), 128.38 (2C), 128.41 (4C), 128.63 (2C), 128.70 (2C), 129.93, 131.01 (2C), 131.46 (2C), 133.35, 135.86, 136.07 (2C), 136.09 (2C), 142.97 (2C+2C), 143.37 (2C), 143.90 (2C), 143.93 (2C), 144.03 (2C), 144.12 (2C), 144.18 (2C), 144.67 (2C), 144.93 (2C), 145.17 (2C), 145.42 (2C), 146.36, 146.57 (2C), 146.63 (2C), 146.96 (2C), 147.46 (2C), 147.64 (2C), 147.74, 147.87 (2C), 147.97 (2C), 148.31 (2C+2C), 148.38 (2C), 150.86 (2C), 151.37 (2C), 151.58 (2C), 154.92 (2C); UV–vis λ_{max} 277, 294, 354, 397, 470 nm; MS *m/z* 1236 [M^+].

3.4.6. C_{60}[(*E*)-2-phenylethenyl]$_5$K (**2e**)

To a solution of **1e** (14 mg, 11 μmol) in 0.60 ml of degassed THF-d_8 in an NMR tube was added 13 μl of *t*-BuOK solution (1.0 M in THF, 13 μmol) under an argon atmosphere. Immediately the color of the solution changed from orange to dark brown that indicated a generation of cyclopentadienyl anion: ^{1}H-NMR (400 MHz, THF-d_8) δ 7.08 (t, $J = 7.6$ Hz, 5H), 7.19 (t, $J = 7.6$ Hz, 10H), 7.27 (d, $J = 15.6$ Hz, 5H), 7.33 (d, $J = 15.6$ Hz, 5H), 7.46 (d, $J = 7.6$ Hz, 10H); ^{13}C-NMR (100 MHz, THF-d_8) δ 61.28 (5C), 127.02 (5C) 127.12 (10C), 127.55 (5C), 128.30 (5C), 128.84 (10C), 136.33 (5C), 139.48 (5C), 143.44 (10C), 146.44 (5C), 147.41 (10C), 148.61 (10C), 149.09 (5C), 158.52 (10C).

Acknowledgements

We thank Monbukagakusho for financial support (Grant-in-Aid for Scientific Research). M.T. thanks Japan Society for Promotion of Science for predoctoral fellowship.

References

[1] (a) M. Sawamura, H. Iikura, E. Nakamura, J. Am. Chem. Soc. 118 (1996) 12850;
(b) M. Sawamura, H. Iikura, T. Ohama, U.E. Hackler, E. Nakamura, J. Organomet. Chem. 599 (2000) 32;
(c) M. Sawamura, M. Toganoh, Y. Kuninobu, S. Kato, E. Nakamura, Chem. Lett. (2000) 270.
[2] H. Iikura, S. Mori, M. Sawamura, E. Nakamura, J. Org. Chem. 62 (1997) 7912.
[3] M. Sawamura, Y. Kuninobu, E. Nakamura, J. Am. Chem. Soc. 122 (2000) 12407.
[4] (a) M. Sawamura, H. Iikura, A. Hirai, E. Nakamura, J. Am. Chem. Soc. 120 (1998) 8285;
(b) M. Sawamura, M. Toganoh, K. Suzuki, A. Hirai, H. Iikura, E. Nakamura, Org. Lett. 2 (2000) 1919.
[5] (a) M. Sawamura, N. Nagahama, M. Toganoh, U.E. Hackler, H. Isobe, E. Nakamura, S. Zhou, B. Chu, Chem. Lett. (2000) 1098;
(b) S. Zhou, C. Burger, B. Chu, M. Sawamura, N. Nagahama, M. Toganoh, U.E. Hackler, H. Isobe, E. Nakamura, Science 291 (2001) 1944.
[6] T. Shimada, H. Nakatani, K. Ueno, A. Koma, Y. Kuninobu, M. Sawamura, E. Nakamura, J. Appl. Phys. 90 (2001) 209.
[7] F. Mohamadi, N.G.J. Richards, W.C. Guida, R. Liskamp, C. Caufield, G. Chang, T. Hendrickson, W.C. Still, J. Comp. Chem. 11 (1990) 440.
[8] G.H. Posner, Org. React. 22 (1975) 253.
[9] M. Tamaru, J.K. Kochi, Bull. Chem. Soc. Jpn. 44 (1971) 3063.
[10] T. Kauffmann, W. Sahm, Angew. Chem. 79 (1967) 101.
[11] H. Neumann, D. Seebach, Tetrahedron Lett. 52 (1976) 4839.
[12] E. Nakamura, S. Mori, Angew. Chem. Int. Ed. 39 (2000) 3750.