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Synthesis of C_{60}-attached SCS pincer palladium(II) complexes☆

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Dedicated to Prof. Dr. Martin Bennett on the occasion of his retirement in admiration of his skills in and contribution to the field of organometallic chemistry

Abstract

The synthesis of C_{60}-attached SCS ligands ($[C_6H_2(CH_2SPh)_2$-2,6-R-4$]^-$) is described. Starting from 4-formyl-SCS-H (**2**), 1,2-methanofullerene and fulleropyrrolidine SCS ligands were obtained. Subsequent palladation with $[Pd(MeCN)_4](BF_4)_2$ afforded the corresponding palladium(II) complexes.

Keywords: Palladium(II) complexes; SCS ligand; Methanofullerene

1. Introduction

The attachment of organometallic complexes to fullerenes is an important area within fullerene chemistry [1]. Covalently bound fullerene organometallic complexes have found applications in artificial photosynthesis and macromolecular synthesis [2,3]. As model studies for the modification of carbon nanotubes with catalytically active materials, we have reported on the derivatization of C_{60} with various monoanionic, potentially terdentate coordinating bisaminoarene ligands ($[C_6H_2(CH_2NMe_2)_2$-2,6-4-R$]^-$ or NCN) [4]. In particular, the metalation of these ligands was found to be hampered by the reactivity of the fullerene moiety. However, methanofullerene NCN-palladium(II) complexes were obtained by electrophilic palladation of methanofullerene NCN-$SiMe_3$ ligands. These complexes were tested in Lewis acid catalysis. Recently, the application of 4-substituted SCS pincer-type palladium complexes (SCS = $[C_6H_3(CH_2SPh)_2$-2,6$]^-$) in the assembly of metallodendrimers and as catalysts in the Heck reaction was reported [5,6]. In these and other studies, it was found that palladium could be easily introduced into the SCS ligand via direct palladation [7]. Thus, we anticipated the usefulness of this approach in the preparation of fullerene-based metal complexes. Here, we report on the functionalization of C_{60} with SCS ligands and show preliminary results concerning the subsequent palladation methods.

2. Experimental

2.1. General

All experiments were conducted under a dry dinitrogen atmosphere using standard Schlenk techniques. Solvents were dried over appropriate materials and distilled prior to use. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 298 K (unless stated otherwise) on a Varian Inova 300 MHz or on a Varian Mercury 200 MHz NMR spectrometer. All NMR chemical shifts are in ppm referenced to residual solvent signal. Starting material, 3,5-bis(bromomethyl)bromobenzene [8], was prepared according to literature procedures. C_{60} (Hoechst, Gold Grade) was used as received. MALDI-TOF mass spectra were acquired using a Voyager-DE BioSpectrometry Workstation mass spectrometer

☆ A new method is presented for the introduction of a metal center into SCS-derivatized fullerene ligands. This method comprises direct palladation with $[Pd(MeCN)_4](BF_4)_2$.

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equipped with a nitrogen laser emitting at 337 nm. Sample solutions with an approximate concentration of 1 g l^{-1} in CH_2Cl_2 were prepared. The matrix was 9-nitroanthracene (9-NA) with an approximate concentration of 40–50 g l^{-1}. A 0.5 μl aliquot of the sample solution and 0.5 μl of the matrix solution were combined on a golden MALDI target and analyzed after evaporation of the solvent. Elemental analyses were performed by Dornis und Kolbe, Mikroanalytisches Laboratorium (Mülheim, Germany).[1]

2.2. 3,5-Bis(phenylsulfidomethyl)bromobenzene (*1*)

To a solution of 3,5-bis(bromomethyl)bromobenzene (17.31 g, 50.49 mmol) in THF (80 ml) at 0 °C was added K_2CO_3 (14.8 g, 106 mmol), 18-crown-6 (1.4 g, 5.1 mmol) and thiophenol (10.6 ml, 103 mmol). The reaction mixture was stirred for 5 h, filtered and all volatiles were evaporated in vacuo. The remaining yellow oil was dissolved in Et_2O (100 ml), washed with a 2 M solution of NaOH (2 × 100 ml), a saturated NaCl solution (100 ml), dried over $MgSO_4$ and filtered. The crude product was distilled in vacuo, affording **1** as a yellow solid (17.29 g, 85%). ^{1}H NMR ($CDCl_3$): δ 7.26 (m, 12H, Ar*H*), 7.13 (s, 1H, Ar*H*), 4.01 (s, 4H, CH_2S). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 139.9, 135.4, 130.5, 130.3, 128.9, 127.9, 126.8, 122.2 (aryl *C*), 38.6 (CH_2S). Anal. Calc. for $C_{20}H_{17}BrS_2$: C, 59.85; H, 4.27. Found: C, 60.03; H, 4.36%.

2.3. 3,5-Bis(phenylsulfidomethyl)benzaldehyde (*2*)

To a solution of **1** (7.66 g, 19.1 mmol) in Et_2O (100 ml) at −78 °C was added 26 ml of a 1.5 M t-BuLi solution in pentane (39 mmol). The reaction mixture was stirred at −70 °C for 1 h and DMF (3.3 ml, 38 mmol) was added (Scheme 1). The reaction mixture was allowed to warm up to room temperature overnight and water (100 ml) was added. The organic layer was separated, washed with 2 M NaOH solution (2 × 50 ml), a saturated NaCl solution (100 ml), dried over $MgSO_4$, filtered and evaporated in vacuo, yielding **2** as a dark yellow oil (4.98 g, 74%). ^{1}H NMR ($CDCl_3$): δ 9.90 (s, 1H, C*H*O), 7.62 (s, 2H, Ar*H*), 7.47 (s, 1H, Ar*H*), 7.25 (m, 10H, Ar*H*), 4.09 (s, 4H, CH_2S). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 191.7 (*C*O), 139.2, 136.7, 135.1, 130.5, 128.9, 128.8, 128.7, 126.9 (aryl *C*), 38.7 (*C*H_2SPh). Anal. Calc. for $C_{21}H_{18}OS_2$: C, 71.96; H, 5.18. Found: C, 72.11; H, 5.23%.

[1] No correct elemental analysis of the fullerene-derivatized SCS-H ligands and the corresponding palladium complexes have been obtained yet due to the introduction of small amounts of impurities during the required extensive column chromatographic purification of the compounds. However, these contaminations did not influence the subsequent palladation of the obtained C_{60}-SCS-H ligands.

2.4. N-methyl-2-[3′,5′-bis(phenylsulfidomethyl)phenyl]-3,4-fulleropyrrolidine (*3*)

A solution of C_{60} (0.86 g, 1.2 mmol), **2** (0.21 g, 0.60 mmol) and *N*-methyl glycine (54 mg, 0.61 mmol) in toluene (1 l) was heated at 110 °C for 20 h. Silica gel (9 g) was added to the reaction mixture and all volatiles were removed in vacuo. The product was purified by column chromatography using toluene/hexane (1/2 to 3/1, v/v gradient) as eluens, affording unreacted C_{60} (0.55 g) and crude product. This was washed with Et_2O (5 × 25 ml) and dried in vacuo, affording **3** as a brown solid (0.23 g, 35%, 49% based on reacted C_{60}). ^{1}H NMR (CS_2/C_6D_6, 3/1 (v/v)): δ 7.55 (s, 2H, Ar*H*), 6.94 (m, 11H, Ar*H*), 4.68 (d, ^2J = 9.6 Hz, 1H, C*H*N), 4.65 (s, 1H, C*H*N), 4.01 (s, 4H, CH_2S), 3.99 (d, ^2J = 9.6 Hz, 1H, C*H*N), 2.49 (s, 3H, NCH_3). ^{13}C{^{1}H} NMR (CS_2/C_6D_6, 3/1 (v/v)): δ 156.71, 154.47, 153.85, 153.77, 147.89, 147.29, 147.04, 146.94, 146.88, 146.85, 146.79, 146.74, 146.63, 146.55, 146.36, 146.24, 146.19, 146.12, 146.02, 145.90, 145.85, 145.77, 145.34, 145.22, 145.01, 143.78, 143.66, 143.32, 143.23, 142.91, 142.86, 142.79, 142.68, 142.55, 142.38, 142.30, 142.24, 140.86, 140.79, 140.59, 140.15, 138.95, 138.33, 137.47, 137.27, 137.14, 136.55, 136.41, 130.25, 129.42, 126.79 (C_{60}–*C* and aryl *C*), 88.6 (*C*H_2N), 77.6 (C_{60}-sp^3), 70.4 (*C*HN), 69.5 (C_{60}-sp^3), 40.3 (N*C*H_3), 39.5 (*C*H_2S).

2.5. 3,5-Bis(phenylsulfidomethyl)benzaldehyde hydrazone (*4*)

A solution of **2** (1.92 g, 5.48 mmol) and $N_2H_4 \cdot H_2O$ (0.50 ml, 11 mmol) in anhydrous EtOH (40 ml) was heated at 78 °C for 2 h. All volatiles were removed in vacuo. The crude product was dissolved in Et_2O (30 ml), dried over $MgSO_4$ and filtered. All volatiles were removed in vacuo, yielding **4** as a yellow solid (2.00 g, 100%). ^{1}H NMR ($CDCl_3$): δ 7.62 (s, 1H, *H*CN_2H_2), 7.36 (s, 2H, Ar*H*), 7.28 (m, 11H, Ar*H*), 5.53 (s, 2H, N_2H_2), 4.07 (s, 4H, CH_2S). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 142.2, 138.1, 136.0, 135.6, 129.8, 129.4, 128.8, 126.3, 125.4 (aryl *C*), 38.7 (*C*H_2SPh). Anal. Calc. for $C_{21}H_{20}S_2N_2$: C, 69.19; H, 5.53. Found: C, 68.71; H, 5.32%.

2.6. 1,2-Dihydro-61-(3′,5′-bis(phenylsulfidomethyl)-phenyl)-1,2-methano[60]fullerene (*5*)

To a solution of **4** (0.35 g, 0.96 mmol) in Et_2O (75 ml) was added NiO_2 (0.44 g, 4.9 mmol) and Na_2SO_4 (0.68 g, 4.8 mmol). The reaction mixture was stirred for 20 h, filtered and slowly added to a solution of C_{60} (0.70 g, 0.96 mmol) in toluene (800 ml). The reaction mixture was stirred for 4 days. Then silica gel (9 g) was added and all volatiles were removed in vacuo. The product

was purified by column chromatography using toluene/hexane (1/5 to 1/1, v/v gradient) as eluens, affording **5** as a dark brown solid (0.25 g, 24%). ^{1}H NMR (CS_2/C_6D_6, 3/1 (v/v)): δ 7.59 (s, 2H, Ar*H*), 7.00 (m, 11H, Ar*H*), 4.98 (s, 1H, C*H*), 3.88 (s, 4H, CH_2S). ^{13}C{^{1}H} NMR (CS_2/C_6D_6, 3/1 (v/v)): δ 149.73, 147.54, 145.79, 145.66, 145.41, 145.36, 145.33, 145.32, 144.98, 144.90, 144.70, 144.62, 144.42, 143.97, 143.91, 143.30, 143.27, 143.22, 143.18, 142.90, 142.51, 142.37, 142.32, 141.32, 141.11, 138.80, 138.62, 136.63, 136.48, 133.59, 130.41, 129.84, 129.72, 129.08, 126.54 (C_{60}–*C* and aryl *C*), 75.5 (C_{60}-sp^3), 43.5 (bridgehead-*C*), 38.8 (*C*H_2SPh).

2.7. 3,5-Bis(phenylsulfidomethyl)benzyl alcohol (*6*)

A solution of **2** (2.46 g, 7.02 mmol) in dry Et_2O (25 ml) was slowly added to a suspension of $LiAlH_4$ (3.03 g, 79.8 mmol) in Et_2O (75 ml). The reaction mixture was stirred for 3 days and carefully quenched with a saturated NaCl solution (90 ml). The reaction mixture was filtered, and the organic layer was isolated and washed with a saturated aqueous NaCl solution (50 ml). The aqueous layers were combined and were extracted with Et_2O (2×50 ml). The organic fractions were combined, dried over $MgSO_4$ and filtered. All volatiles were removed in vacuo yielding **6** as a yellow oil (2.33 g, 94%). ^{1}H NMR ($CDCl_3$): δ 7.27 (m, 13H, Ar*H*), 4.55 (d, $^3J = 6.0$ Hz, 2H, OCH_2), 4.05 (s, 4H, CH_2S), 2.16 (t, $^3J = 5.9$ Hz, 1H, O*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 141.8, 138.2, 136.4, 130.1, 129.1, 128.9, 126.7, 126.5 (aryl *C*), 65.0 (*C*OH), 39.1 (*C*H_2S). Anal. Calc. for $C_{21}H_{20}OS_2$: C, 71.55; H, 5.72. Found: C, 71.63; H, 5.78%.

2.8. 1-[3,5-Bis(phenylsulfidomethyl)benzyloxy]-3-ethoxymalonate (*7*)

To a solution of **6** (1.01 g, 2.87 mmol) in CH_2Cl_2 (75 ml) was added pyridine (0.24 ml, 2.9 mmol). A solution of ethyl malonyl chloride (0.40 ml, 3.1 mmol) in CH_2Cl_2 (10 ml) was slowly added at 0 °C. The reaction mixture was allowed to warm up to room temperature overnight and water (50 ml) was added. The organic fraction was separated, washed with 0.05 M solution of Na_2CO_3 (50 ml), dried over $MgSO_4$ and evaporated in vacuo, yielding **7** as an orange oil (1.29 g, 100%). ^{1}H NMR ($CDCl_3$): δ 7.19 (m, 13H, Ar*H*), 5.07 (s, 2H, OCH_2), 4.05 (s, 4H, CH_2S), 4.19 (q, $^3J = 10.8$ Hz, 2H, OEt), 3.39 (s, 2H, OCCH_2CO), 1.25 (t, $^3J = 10.8$ Hz, 3H, OEt). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.8 (*C*O), 137.7, 135.6, 135.4, 129.3, 128.8, 128.4, 126.9, 125.9 (aryl *C*), 66.1 (O*C*H_2), 61.0 (OEt), 41.0 (CO*C*H_2CO), 38.0 (*C*H_2S), 13.6 (OEt). Anal. Calc. for $C_{26}H_{26}O_4S_2$: C, 66.92; H, 5.62. Found: C, 67.10; H, 5.62%.

2.9. 1,2-Dihydro-61-ethoxycarbonyl-61-[3′,5′-bis(phenylsulfidomethyl)benzyloxycarbonyl]-1,2-methano[60]fullerene (*8*)

A solution of C_{60} (0.47 g, 0.66 mmol), I_2 (0.17 g, 0.66 mmol), DBU (1,8-diazabicyclo[5.4.0]undec-7-ene; 0.20 g, 1.3 mmol) and **7** (0.31 g, 0.66 mmol) in dry toluene (600 ml) was stirred for 22 h (Scheme 2). Then silica gel (9 g) was added and all volatiles were removed in vacuo. Column chromatography using toluene/hexane as eluens (1/5 to 1/0, v/v gradient) afforded unreacted C_{60} (0.25 g), and the crude product, which was washed with Et_2O (3×25 ml) and dried in vacuo, yielding **8** as a brown solid (0.18 g, 23%, 52% based on reacted C_{60}). ^{1}H NMR (CS_2/C_6D_6, 3/1 (v/v)): δ 7.02 (m, 13H, Ar*H*), 5.12 (s, 2H, OCH_2), 4.20 (q, $^3J = 6.9$ Hz, 2H, OEt), 3.79 (s, 4H, CH_2S), 1.09 (t, $^3J = 7.2$ Hz, 3H, OEt). ^{13}C{^{1}H} NMR (CS_2/C_6D_6, 3/1 (v/v)): δ 163.1, 163.0 (*C*O), 145.98, 145.87, 145.85, 145.80, 144.77, 145.45, 145.28, 145.22, 144.52, 143.71, 143.62, 142.85, 142.46, 141.58, 139.97, 139.68, 138.97, 137.21, 136.01, 130.35, 130.25, 129.53, 128.62, 126.92 (C_{60}–*C* and aryl *C*), 72.3 (C_{60}-sp^3), 68.6 (O*C*H_2), 63.7 (OEt), 52.8 (bridgehead-*C*), 39.3 (*C*H_2S), 14.8 (OEt).

2.10. N-methyl-2-[4′-[chloropalladio]-3′,5′-bis(phenylsulfidomethyl)phenyl]-3,4-fulleropyrrolidine (*9*)

To a solution of **3** (106 mg, 97 μmol) in toluene (100 ml) was added a solution of $[Pd(CH_3CN)_4](BF_4)_2$ (48 mg, 108 μmol) in CH_3CN (25 ml). The reaction mixture was heated at 80 °C for 3 h, after which a solution of LiCl (60 mg, 1.4 mmol) in MeOH (30 ml) was added. The reaction mixture was cooled down to room temperature, stirred for another 1.5 h and evaporated in vacuo. The residue was washed with MeOH (2×40 ml) and extracted with CS_2 (3×60 ml). The organic fraction was evaporated in vacuo, yielding **9** as dark brown solid (77 mg, 64%). Due to the poor solubility of **9** in common NMR solvents, no ^{13}C{^{1}H} NMR spectrum could be obtained. ^{1}H NMR (CS_2/C_6D_6, 3/1 (v/v)): δ 7.53, 7.16, 7.04 (m, 12H, Ar*H*), 4.73 (d, $^2J = 9.6$ Hz, 1H, C*H*N), 4.68 (s, 1H, C*H*N), 4.15 (s, 4H, CH_2S), 4.08 (d, $^2J = 9.6$ Hz, 1H, C*H*N), 2.64 (s, 3H, NCH_3). MALDI-TOF (9-NA): $m/z = 1202.1$ ($[M-Cl]^+$).

2.11. 1,2-Dihydro-61-{4′-(chloropalladio)-3′,5′-(bisphenylsulfidomethyl)phenyl}-1,2-methano-[60]fullerene (*10*)

Complex **10** was synthesized in a similar way as **9**, using **5** (99 mg, 94 μmol), $[Pd(CH_3CN)_4](BF_4)_2$ (53 mg, 119 μmol) and LiCl (60 mg, 1.4 mmol), yielding **10** as a brown solid (69 mg, 61%). ^{1}H NMR ($CDCl_3$): δ 7.89, 7.59, 7.40 (m, 12H, Ar*H*), 5.27 (s, 1H, C*H*), 4.75 (s, 4H,

CH_2S). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 149.82, 149.69, 147.65, 145.80, 145.62, 145.41, 144.97, 144.65, 144.49, 143.97, 143.34, 143.30, 142.93, 142.54, 142.33, 141.36, 141.17, 138.61, 136.70, 132.35, 131.79, 130.22, 129.99, 125.15 (C_{60}–*C* and aryl *C*), 75.4 (C_{60}-sp^3), 52.1 (CH_2S), 43.0 (bridgehead-*C*). MALDI-TOF (9-NA): m/z = 1160.0 ($[M-Cl]^+$).

2.12. 1,2-Dihydro-61-ethoxycarbonyl-61-[4′-(chloropalladio)-3′,5′-bis(phenylsulfidomethyl)benzyloxycarbonyl]-1,2-methano[60]fullerene (**11**)

Complex **11** was synthesized in a similar way as **9**, using **8** (99 mg, 83 μmol), $[Pd(CH_3CN)_4](BF_4)_2$ (51 mg, 114 μmol) and LiCl (60 mg, 1.4 mmol), yielding **11** as a brown solid (84 mg, 63 μmol, 76%). ^1H NMR ($CDCl_3$): δ 7.84 (m, 4H, Ar*H*), 7.39 (m, 6H, Ar*H*), 7.12 (m, 2H, Ar*H*), 5.41 (s, 2H, OCH_2), 4.60 (OEt), 4.53 (CH_2S), 1.25 (OEt). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 163.78, 163.63 (CO), 149.98, 145.54, 145.47, 145.37, 145.33, 145.23, 145.16, 145.03, 144.95, 144.89, 144.83, 144.13, 144.11, 143.51, 143.34, 143.30, 143.18, 142.45, 142.38, 142.10, 141.91, 141.25, 139.77, 138.54, 132.36, 131.94, 130.27, 130.01, 123.51 (C_{60}–*C* and aryl *C*), 71.6 (C_{60}-sp^3), 68.6 (OCH_2), 63.8 (OEt), 52.2 (CH_2S), 52.1 (bridgehead-*C*), 14.1 (OEt). MALDI-TOF (9-NA): m/z = 1289.9 ($[M-Cl]^+$).

3. Results and discussion

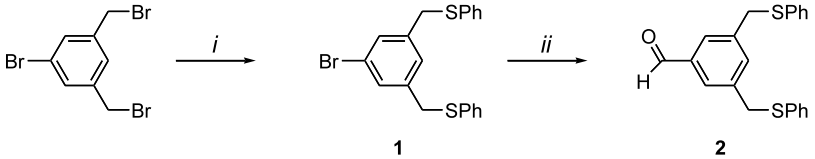
The most frequently used methods for fullerene derivatization are Bingel reaction [9], the addition of 1,3-dipolar diazo compounds [4] and Prato reaction [10]. Interestingly, the mutual precursor compound required for these reactions contains in all cases an aldehyde functionality. Therefore, we prepared 4-formyl SCS ligand **2** as starting SCS-H compound (Scheme 1).

Treatment of 3,5-bis(bromomethyl)bromobenzene with thiophenol and K_2CO_3 in THF afforded **1** in 85% yield. This was reacted at low temperature with 2 equiv. of t-BuLi in Et_2O and subsequently quenched with an excess of DMF giving **2** after aqueous work-up.

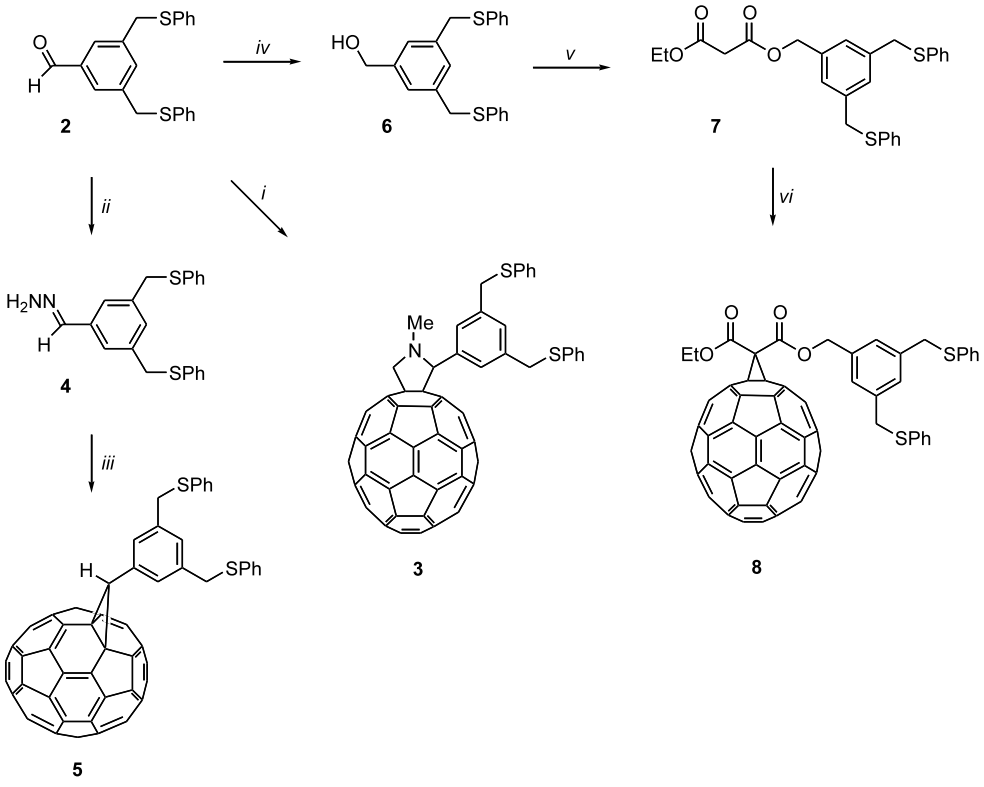
Aldehyde **2** reacted readily with *N*-methyl glycine and C_{60} to form SCS-H-substituted fulleropyrrolidine **3** in 49% yield based on reacted C_{60} (Scheme 2). In addition, **2** was also converted to the corresponding hydrazone ligand **4** with $N_2H_4 \cdot H_2O$ in EtOH. Reaction of **4** with NiO_2 afforded the corresponding diazo compound, which was added to C_{60}, resulting in the formation of methanofullerene **5**. Remarkably, although the crude reaction product contained both [5,6]- and [6,6]-isomers of **5**, only the [6,6]-closed isomer of **5** was isolated by column chromatography (silica gel) of the crude reaction mixture, as was confirmed by NMR spectroscopy. The methine bridge proton of **5** was observed at 4.98 ppm (^1H NMR), while the diagnostic resonance at 75.5 ppm in the $^{13}C\{^1H\}$ NMR spectrum was attributed to the C_{60}-sp^3 carbons of the 1,2-methanofullerene. For derivatization of C_{60} with an SCS-H ligand via Bingel reaction, the formyl functionality of **2** was reduced with $LiAlH_4$ to the corresponding benzyl alcohol (**6**) and connected to ethyl malonyl chloride in the presence of pyridine, giving **7** in quantitative yield. Subsequent reaction of **7**, I_2, C_{60} and DBU in toluene afforded methanofullerene SCS ligand **8** in 52% yield based on reacted C_{60}.

The incorporation of palladium was achieved by reaction of SCS ligands **3**, **5** and **8** with $[Pd(MeCN)_4](BF_4)_2$ in toluene/MeCN solution, yielding palladium complexes **9**–**11** in moderate yields (61–76%, Scheme 3). The palladium(II) complexes were insoluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, benzene and CS_2. Formation of the palladium complexes was confirmed by NMR and MALDI-TOF mass spectroscopy. Downfield shifts in ^1H NMR spectra were observed for the resonances attributed to the benzylic and aromatic protons of sulfur donor arms. Ion fragments of m/z = 1202.1, 1160.0 and 1289.9 for **9**, **10** and **11** were observed, respectively, corresponding to the molecular ions minus chloride, which is a commonly observed phenomenon for pincer-type metal complexes.[2]

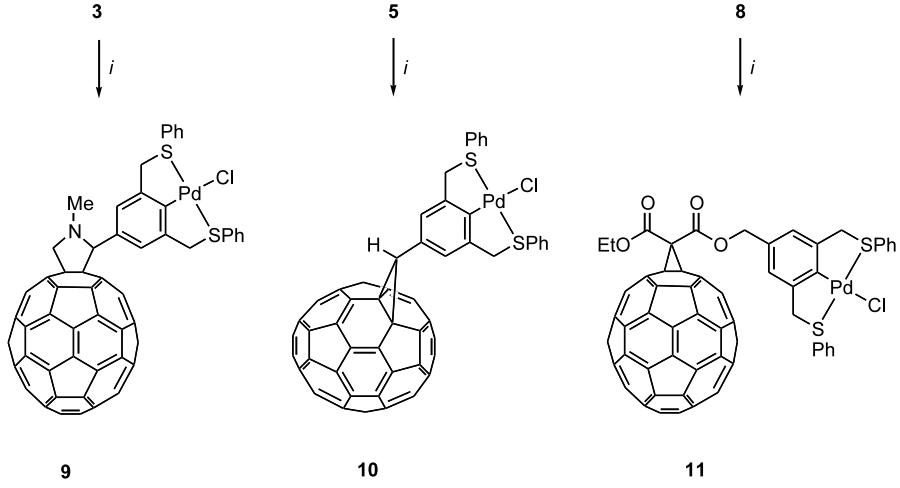
[2] The calculated mass for the molecular ion minus chloride for **11** is m/z = 1291.6. We attributed the difference between the observed mass (m/z = 1289.9) and the calculated mass to an incorrect reference setting of the spectrometer.



Scheme 1. Synthesis of precursor SCS ligand **2**. Reagents and conditions: (i) PhSH, K_2CO_3/18-crown-6, THF and (ii) 2 equiv. t-BuLi, Et_2O, −70 °C, then DMF.



Scheme 2. Synthesis of SCS-derivatized C_{60} ligands. Reagents and conditions: (i) C_{60}, *N*-methyl glycine, toluene, 110 °C, 20 h; (ii) $N_2H_4 \cdot H_2O$, EtOH, 78 °C, 2 h; (iii) NiO_2 followed by C_{60}, toluene; (iv) $LiAlH_4$, Et_2O, 3 days; (v) ethyl malonyl chloride, pyridine, 24 h and (vi) C_{60}, I_2, DBU, toluene, 22 h.



Scheme 3. Formation of palladium complexes **9**–**11**. Reagents and conditions: $[Pd(MeCN)_4](BF_4)_2$, MeCN/toluene, 3 h, then LiCl, MeOH.

In conclusion, synthetic routes toward the attachment of SCS ligands to C_{60} starting from 4-formyl SCS, followed by subsequent palladation has been shown. Especially, the convenient one-pot formation of the fulleropyrrolidine compound **3** and subsequent palladation affording **9** is a promising pathway for the synthesis of novel structures comprising catalytically active organometallic moieties and C_{60}.

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