



New routes toward metallated methanofullerene terdentate bisaminoaryl ligands

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Dedicated to Professor Dr K. Vrieze on the occasion of his 65th birthday, while thanking him for all the great years of collaboration and support in Science and 'University' affairs

Abstract

The preparation of a series of new ligands, comprising a NCN ligand ($C_6H_2(CH_2NMe_2)_2-2,6-X-4$, X = H, Br, I) substituted on the *para* position with a [1,2]-methanofullerene group is described. Metallation of these ligands is achieved via an oxidative addition reaction of nickel(0) or palladium(0) complexes. The first step of this reaction comprises the formation of a π -complex between the metal center and the fullerene moiety of the ligand, which upon heating in a subsequent step is followed by oxidative addition of the NCN-halide bond to the metal center. The nickel(II) complex $C_{60}-C(Me)-NCN-NiBr$ (**9**) was isolated in pure form. Low temperature NMR spectroscopy and theoretical calculations showed that the NCN moiety in **9** rotates about the (Me)C–NCN bond at room temperature. UV–Vis spectroscopic measurements of **9** suggest that binding a metal center via a covalent metal–carbon bond to the NCN moiety does not lead to a substantial change in the electronic structure of the fullerene moiety. The cyclic voltammograms of **9** showed the absence of a Ni(II)/Ni(III) oxidation/reduction process, while the second and fourth C_{60} reduction potentials were anodically shifted. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Metallated methanofullerene; Bisaminoaryl ligands; NCN moieties

1. Introduction

Fullerene chemistry has evolved rapidly since the development of the gram-scale synthesis of these carbon allotropes [1]. In particular, the use of the highly symmetrically structured Buckminsterfullerene (C_{60}) has been widely reported in organic synthesis, organometallic chemistry, biochemistry, and material science [2–5]. The combination of its unique properties, i.e. the ability to accommodate up to six electrons in its LUMO [6], its readily accessible excited-state (photo)chemistry, and its symmetric topology, make C_{60} an interesting component in new materials. For example, C_{60} is used in superconducting alkali-metal intercalated fullerides [2f,7] or as a molecular building

block in the synthesis of new supra-molecular structures, such as a molecular engine reported by Sauvage and coworkers [8]. In a large number of reports, C_{60} is used as an electron acceptor or as a photosensitizer in donor–acceptor systems in order to develop molecular electronics and photoactive devices [9]. For this purpose, organic donors were attached to C_{60} , such as dimethylaniline, tetrathiafulvalene, and a carotenoid tail [10–12]. Also, ligated organometallic C_{60} dyads were prepared and characterized: C_{60} –ferrocenyl complexes [11d,13], C_{60} –ruthenium bipyridyl/terpyridyl ligated complexes [14], and several C_{60} –porphyrine/phthalocyanine structures containing nickel or zinc [9a,c,15,16].

Part of our research is focussed on the use of monoanionic terdentate bisamino-, bisphosphino-, and bisulfido-aryl (pincer) ligands [$C_6H_2(CH_2Y_2)_2-2,6-R-4$][−], commonly abbreviated for R = H as NCN (Y = NR₂) [17], PCP (Y = PR₂) [18], and SCS (Y = SR') [19],

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for application in homogeneous catalysis [20] (e.g. as metallo-dendritic catalysts [21]) and in materials with new physicochemical properties. The hard Lewis-donor property of the nitrogen atoms of the monoanionic NCN ligand enhance the nucleophilic character of Ni(II) and Pt(II)-centers and stabilize higher oxidation states of the metal center, like in stable Ni(III) and Pt(IV) NCN complexes [22]. The NCN ligand was used to synthesize new donor–acceptor systems with novel electronic, photochemical and sensing properties, e.g. [PtI(NCN)(η^1 -I₂)] and [PtX(NCN)(η^1 -SO₂)] [22b,23]. In addition, the NCN ligand provides several possibilities for ligand modification via the *para* position (to the metal–carbon bond), which allows linking to supports [21,24] or further tuning of the redox properties of the metal center [25]. Recently, we became interested to explore the synthesis of C₆₀-attached pincer metal complexes as mimics for metal complexes bound to a carbon support. The synthesis of two methanofullerene NCN ligands, **1** and **2**, which were reported in preliminary form [26], will be described in this paper in detail. In particular, the metallation of these ligands, which is complicated due to the reactivity of the C₆₀ core, is discussed. The first examples are presented of metalated methanofullerene terdentate bisaminoaryl ligands.

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, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded at 298 K (unless stated otherwise) in a Varian Inova 300 MHz or in a Varian Mercury 200 MHz NMR spectrometer. All NMR chemical shifts are in ppm referenced to residual solvent signal (¹H and ¹³C{¹H}) or to H₃PO₄ (³¹P{¹H}). Starting materials 3,5-bis[(dimethylamino)methyl]bromobenzene (**3**) [27] and 4-bromo-3,5-bis[(dimethylamino)methyl]acetophenone (**6**) [25] were prepared according to literature procedures. C₆₀ (Hoechst, Gold Grade) was used as received. UV–Vis spectra were measured in a Varian Cary 1 UV–Vis spectrophotometer in degassed, N₂ saturated CH₂Cl₂ at ambient temperature at a concentration of 1 × 10⁻⁵ M. MALDI-TOF mass spectra were acquired using a Voyager-DE BioSpectrometry Workstation mass spectrometer (PerSeptive Biosystems Inc., Framingham, MA, USA). Sample solutions with an approximate concentration of 10 mg ml⁻¹ in CH₂Cl₂ were prepared. The matrix was 9-nitroanthracene (9-NA) with an approximate concentration of 40–50 mg ml⁻¹. An 0.2 μl amount of the sample solution and 0.2 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).

2.2. Synthesis of

3,5-bis[(dimethylamino)methyl]benzaldehyde (**4**)

To a solution of **3** (5.41 g, 20.0 mmol) in Et₂O (40 ml) was added 27 ml of a 1.5 M t-BuLi solution in pentane (40 mmol) at -78 °C. The resulting yellow suspension was stirred at -78 °C for 1 h followed by addition of dimethylformamide (1.6 ml, 21 mmol). The reaction mixture was allowed to warm up to room temperature (r.t.) in 17 h and quenched with water (50 ml). The organic layer was separated, and the remaining water layer extracted with Et₂O (2 × 50 ml). The organic fractions were dried over MgSO₄, filtered, and evaporated in vacuo. The residue was distilled in vacuo, giving **4** as a yellow oil (3.77 g, 86% yield). ¹H NMR (C₆D₆): δ 9.81 (s, 1H, COH), 7.68 (s, 2H, ArH), 7.62 (s, 1H, ArH), 3.18 (s, 4H, CH₂N), 2.03 (s, 12H, NCH₃), ¹³C{¹H} NMR (C₆D₆): δ 191.1 (CHO), 140.6, 136.9, 134.6, 128.4 (Ar–C), 63.3 (CH₂N), 44.8 (NCH₃). *Anal.* Calc. for C₁₃H₂₀N₂O: C, 70.87; H, 9.15; N, 12.72. Found: C, 70.81; H, 9.22; N, 12.85%.

2.3. Synthesis of 3,5-bis[(dimethylamino)-methyl]benzaldehyde hydrazone (**5**)

To a solution of **4** (2.02 g, 9.17 mmol) in ethanol (30 ml) was added N₂H₄·H₂O (4.59 g, 91.7 mmol). The reaction mixture was heated at 80 °C for 2 h whereafter all volatile components were evaporated in vacuo. The product was dissolved in CH₂Cl₂ (25 ml), dried over MgSO₄, filtered, and evaporated in vacuo yielding **5** as a light-yellow oil, which solidified upon standing (2.13 g, quantitatively). ¹H NMR (C₆D₆): δ 7.66 (s, 2H, ArH), 7.44 (s, 1H, ArH), 7.25 (s, 1H, CHN₂H₂), 4.90 (s, 2H, N₂H₂), 3.30 (s, 4H, CH₂N), 2.10 (s, 12H, NCH₃). ¹³C{¹H} NMR (C₆D₆): δ 141.4, 139.9, 136.0, 129.3 (ArC), 125.4 (CN₂H₂), 64.1 (CH₂N), 45.1 (NCH₃). *Anal.* Calc. for C₁₃H₂₂N₄: C, 66.63; H, 9.46; N, 23.91. Found: C, 66.46; H, 9.38; N, 23.76%.

2.4. Synthesis of 4-bromo-3,5-bis[(dimethylamino)-methyl]acetophenone hydrazone (**7**)

To a solution of **6** (1.34 g, 4.28 mmol) in dry ethanol (25 ml) was added N₂H₄·H₂O (2.14 g, 42.8 mmol). The reaction mixture was heated at 80 °C for 2 h. Subsequently, all volatile components were removed in vacuo, yielding **7** as a white solid (1.41 g, quantitatively). ¹H NMR (C₆D₆): δ 8.02 (s, 2H, ArH), 4.83 (s, 2H, N₂H₂), 3.57 (s, 4H, CH₂N), 2.16 (s, 12H, NCH₃), 1.63 (s, 3H, CN₂H₂CH₃). ¹³C{¹H} NMR (C₆D₆): δ

144.0, 138.6, 138.3, 125.8 (ArC), 126.2 (CN₂H₂), 63.7 (CH₂N), 45.1 (NCH₃), 10.2 (CN₂H₂CH₃). Anal. Calc. for C₁₄H₂₃BrN₄: C, 51.38; H, 7.08; N, 17.12. Found: C, 51.26; H, 6.94; N, 17.21%.

2.5. Synthesis of 1,2-dihydro-61-(3,5-bis[(dimethylamino)methyl]phenyl)-1,2-methano[60]fullerene (**1**)

A suspension of **5** (0.33 g, 1.42 mmol), MnO₂ (1.23 g, 14.2 mmol), Na₂SO₄ (2.03 g, 14.2 mmol), and a freshly prepared saturated solution of KOH in ethanol (0.5 ml) in Et₂O (50 ml) was stirred in the dark for 20 h. The reaction mixture was filtered over a G4 glass frit and slowly added to a solution of C₆₀ (1.02 g, 1.42 mmol) in toluene (1 l). The reaction mixture was stirred for 5 h and evaporated in vacuo. The remaining product was chromatographed over silica gel. Elution with toluene and toluene/MeOH (95:5 v/v %) gave unreacted C₆₀ (0.41 g) and the crude product as a mixture of [5,6]- and [6,6]-isomers (0.58 g, 40, 68% based on reacted C₆₀), respectively. A part of this mixture (0.44 g) was dissolved in toluene (500 ml) and heated at 110 °C until the isomerization of the [5,6]-isomer to the [6,6]-isomer was complete (monitored by ¹H NMR spectroscopy, 5 days). The crude product was chromatographed over silica gel using toluene/MeOH (95:5 v/v %) as eluents, then dissolved in CS₂ (20 ml), precipitated by addition of pentane (300 ml), and dried in vacuo, yielding **1** as a brown solid (0.38 g, 86, 58% overall yield based on reacted C₆₀). ¹H NMR (CS₂/C₆D₆ (3:1)): δ 7.78 (s, 2H, ArH), 7.29 (s, 1H, ArH), 5.17 (s, 1H, bridgehead-CH), 3.39 (s, 4H, CH₂N), 2.16 (s, 12H, NCH₃). ¹³C{¹H} NMR (CDCl₃): δ 149.75, 147.81, 145.66, 145.56, 145.10, 145.05, 145.02, 145.00, 144.75, 144.60, 144.48, 144.33, 144.28, 144.05, 143.68, 143.62, 143.01, 142.95, 142.89, 142.83, 142.66, 142.22, 142.07, 142.02, 140.98, 140.71, 139.45, 138.15, 137.77, 136.40, 133.10, 130.57, 129.81 (C₆₀-C and ArC), 75.55 (C₆₀-sp³), 64.11 (CH₂N), 45.41 (NCH₃), 43.47 (bridgehead-C). MALDI-TOF MS (9-NA); *m/z*: 925.3 (*M*⁺). Anal. Calc. for C₇₃H₂₀N₂: C, 94.79; H, 2.18; N, 3.03. Found: C, 94.58; H, 2.31; N, 2.99%.

2.6. Synthesis of 1,2-dihydro-61-methyl-61-(3,5-bis[(dimethylamino)methyl]-4-bromophenyl)-1,2-methano[60]fullerene (**2**)

Compound **2** was synthesized similar to **1** starting from **7** (0.21 g, 0.65 mmol), MnO₂ (0.57 g, 6.5 mmol), Na₂SO₄ (0.93 g, 6.5 mmol), and C₆₀ (0.94 g, 1.3 mmol). Column chromatography of the reaction mixture afforded unreacted C₆₀ (0.64 g) and the crude product as a mixture of [5,6]- and [6,6]-isomers (0.39 g, 59, 93% based on reacted C₆₀). A part of this mixture (0.18 g) was dissolved in toluene (100 ml) and heated at 110 °C until the isomerization of the [5,6]-isomer to the [6,6]-

isomer was complete (monitored by ¹H NMR spectroscopy, 6 days). The crude product was chromatographed over Al₂O₃-90 using CHCl₃ as eluent, yielding **2** as a brown solid (0.11 mg, 60, 56% overall yield based on reacted C₆₀). ¹H NMR (CS₂/C₆D₆ (3:1)): δ 7.99 (s, 2H, ArH), 3.54 (s, 4H, CH₂N), 2.41 (s, 3H, CH₃), 2.18 (s, 12H, NCH₃). ¹³C{¹H} NMR (CDCl₃): δ 148.79, 147.92, 145.93, 145.17, 145.13, 145.11, 145.07, 145.03, 144.78, 144.73, 144.65, 144.43, 144.34, 143.97, 143.74, 143.70, 143.08, 142.98, 142.92, 142.14, 142.10, 141.98, 140.96, 140.71, 138.73, 138.26, 138.04, 137.20, 131.86, 126.07 (C₆₀-C and ArC), 80.63 (C₆₀-sp³), 63.80 (CH₂N), 47.19 (bridgehead-C), 45.54 (NCH₃), 22.00 (CH₃). MALDI-TOF MS (9-NA); *m/z*: 1017.84 (*M*⁺). Anal. Calc. for C₇₄H₂₁BrN₂: C, 87.32; H, 2.08; N, 2.75. Found: C, 87.46; H, 2.18; N, 2.84%.

2.7. Synthesis of 1,2-dihydro-61-methyl-61-((4-chloro-nickel-3,5-bis[(dimethylamino)methyl]benzene)-1,2-methano[60]fullerene (**9**)

2.7.1. Reaction of **2** with Ni(COD)₂

To a solution of **2** (137 mg, 0.137 mmol) in degassed toluene (60 ml) was added a solution of Ni(COD)₂ (48 mg, 0.18 mmol) in toluene (20 ml) at 0 °C. A dark green precipitate was formed. The reaction mixture was slowly heated to 45 °C and stirred for 20 h, filtered through a G4 glass frit, and evaporated in vacuo. The remaining solid was washed with pentane (40 ml) and dried in vacuo, yielding **9** as a brown solid (76 mg, 52%).

2.7.2. Reaction of **2** with Ni(PPh₃)₄

To a solution of **2** (70 mg, 0.069 mmol) in degassed toluene (60 ml) was added a solution of Ni(PPh₃)₄ (84 mg, 0.076 mmol) in toluene (20 ml) at 0 °C. The dark-green colored reaction mixture was slowly heated to 45 °C and stirred for 20 h, and evaporated in vacuo. The resulting brown solid was extracted with benzene (20 ml). To this solution was added acetone (60 ml) and the precipitate was collected by centrifugation/decantation. This procedure was repeated once. The product was washed with pentane and dried in vacuo, yielding **9** as a brown solid (41 mg, 55%). ¹H NMR (C₆D₆): δ 7.04 (s, 2H, ArH), 3.02 (s, 4H, CH₂N), 2.44 (s, 12H, NCH₃), 2.35 (s, 3H, CH₃). ¹³C{¹H} NMR (CS₂/CD₂Cl₂ (1:1)): δ 152.01, 149.36, 148.57, 147.15, 146.16, 145.49, 145.45, 145.39, 145.32, 145.21, 145.16, 145.05, 144.96, 144.71, 144.61, 144.31, 144.03, 143.37, 143.32, 143.26, 142.60, 142.48, 142.45, 142.42, 141.25, 141.04, 138.27, 137.97, 136.41, 129.31, 128.61, 128.53, 121.62, 121.54 (C₆₀-C and ArC), 81.51 (C₆₀-sp³), 73.84 (CH₂N), 66.11 (bridgehead-C), 52.38 (NCH₃), 23.23 (CH₃). Anal. Calc. for C₇₄H₂₁BrN₂Ni: C, 82.56; H, 1.97; N, 2.60. Found: C, 82.38; H, 2.15; N, 2.58%.

2.8. Synthesis of 4-bromo-3,5-bis[(dimethylamino)-methyl]acetophenone ethylene acetal (**10**)

A solution of **6** (6.07 g, 19.4 mmol), *p*-toluenesulfonic acid monohydrate (9.21 g, 48.5 mmol), ethylene glycol (2.2 ml, 39 mmol) in benzene (100 ml) was heated at 80 °C in a Dean–Stark setup for 20 h. NEt₃ (10 ml) was added to the reaction mixture, and all volatiles were removed in vacuo. The remaining solid was extracted with Et₂O (2 × 100 ml). The organic fraction was washed with a 4 M NaOH solution (2 × 50 ml), dried over MgSO₄, filtered, and evaporated in vacuo, yielding **10** as a white solid (5.20 g, 75%). ¹H NMR (CDCl₃): δ 7.40 (s, 2H, ArH), 3.98 (m, 2H, acetal), 3.72 (m, 2H, acetal), 3.50 (s, 4H, CH₂N), 2.26 (s, 12H, NCH₃), 1.61 (s, 3H, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 141.7, 138.5, 128.2, 126.3 (ArC), 108.4 (CCH₃), 64.3 (acetal), 63.9 (CH₂N), 45.5 (NCH₃), 27.4 (CCH₃). Anal. Calc. for C₁₆H₂₅BrN₂O₂: C, 53.79; H, 7.05; N, 7.84. Found: C, 53.88; H, 7.11; N, 7.86%.

2.9. Synthesis of 3,5-bis[(dimethylamino)-methyl]-4-iodoacetophenone (**11**)

To a solution of **10** (3.22 g, 9.01 mmol) in hexanes (50 ml) at –78 °C was added 11 ml of a 1.7 M *t*-BuLi solution in pentane (19 mmol). The solution was allowed to warm up to 0 °C in 3 h, and a solution of I₂ (2.50 g, 9.85 mmol) in THF (20 ml) was added. The reaction mixture was stirred at ambient temperature for 1 h. A 2 M HCl solution (40 ml) was added to the solution and the aqueous layer isolated. The organic layer was extracted with a 1 M HCl solution (40 ml). The aqueous layers were combined, and a 4 M NaOH solution (100 ml) was added. The solution was extracted with Et₂O (3 × 75 ml). The organic fractions were combined, dried over MgSO₄, filtered, and evaporated in vacuo. The remaining product was distilled in vacuo, yielding **11** as a yellow oil (2.32 g, 71%). ¹H NMR (CDCl₃): δ 7.77 (s, 2H, ArH), 3.49 (s, 4H, CH₂N), 2.55 (s, 3H, COCH₃), 2.25 (s, 12H, NCH₃). ¹³C{¹H} NMR (CDCl₃): δ 197.6 (CO), 142.4, 136.1, 128.0, 113.4 (ArC), 68.6 (CH₂N), 45.3 (NCH₃), 26.6 (COCH₃). Anal. Calc. for C₁₄H₂₁IN₂O: C, 46.68; H, 5.88; N, 7.78. Found: C, 46.55; H, 6.05; N, 7.71%.

2.10. Synthesis of 3,5-bis[(dimethylamino)-methyl]-4-iodoacetophenone hydrazone (**12**)

Compound **12** was synthesized similar to **5**, starting from **11** (0.81 g, 2.2 mmol) and N₂H₄·H₂O (0.11 g, 2.2 mmol), yielding **12** as a white solid (0.64 g, 76%). ¹H NMR (CDCl₃): δ 7.56 (s, 2H, ArH), 5.33 (s, 2H, N₂H₂), 3.54 (s, 4H, CH₂N), 2.30 (s, 12H, NCH₃), 2.12 (s, 3H, CCH₃). ¹³C{¹H} NMR (CDCl₃): δ 146.3, 141.5, 138.6, 107.0 (ArC), 126.2 (CN₂H₂), 68.9 (CH₂N), 45.4 (NCH₃), 11.6 (CCH₃). Anal. Calc. for C₁₄H₂₃IN₄: C,

44.93; H, 6.19; N, 14.97. Found: C, 45.08; H, 6.25; N, 15.06%.

2.11. Synthesis of 1,2-dihydro-61-methyl-61-(3,5-bis[(dimethylamino)methyl]-4-iodophenyl)-1,2-methano[60]fullerene (**13**)

Compound **13** was synthesized similar to **1** starting from **12** (0.22 g, 0.57 mmol), MnO₂ (0.75 g, 8.5 mmol), Na₂SO₄ (1.21 g, 8.51 mmol), a freshly prepared saturated solution of KOH in EtOH (0.5 ml) and C₆₀ (0.61 g, 0.85 mmol). Column chromatography of the reaction mixture afforded unreacted C₆₀ (0.36 g) and the crude product as a mixture of [5,6]- and [6,6]-isomers (0.35 mg). This was dissolved in 400 ml toluene and heated to reflux until the isomerization of the [5,6]-isomer to the [6,6]-isomer was complete (monitored by ¹H NMR spectroscopy, 4 days). The crude product was chromatographed over silica gel using toluene/MeOH (95:5 v/v %) as eluents, yielding **13** as a brown solid (0.29 g, 48, 78% based on reacted C₆₀). ¹H NMR (CS₂/C₆D₆ (3:1)): δ 7.92 (s, 2H, ArH), 3.50 (s, 4H, CH₂N), 2.42 (s, 3H, CH₃), 2.18 (s, 12H, NCH₃). ¹³C{¹H} NMR (CDCl₃): δ 149.06, 148.14, 146.22, 145.48, 145.45, 145.35, 145.08, 145.04, 144.95, 144.72, 144.70, 144.32, 144.04, 144.02, 143.41, 143.35, 143.30, 143.26, 142.59, 142.46, 142.44, 142.33, 141.32, 141.06, 139.11, 138.32, 137.61, 131.54, 106.49 (C₆₀–C and ArC), 81.0 (C₆₀–sp³), 69.1 (CH₂N), 47.5 (bridgehead-C), 45.6 (NCH₃), 22.3 (CH₃). MALDI-TOF MS (9-NA); *m/z*: 1065.0 (*M*⁺). Anal. Calc. for C₇₄H₂₁IN₂: C, 83.46; H, 1.99; N, 2.63. Found: C, 83.37; H, 1.84; N, 2.65%.

2.12. Electrochemistry

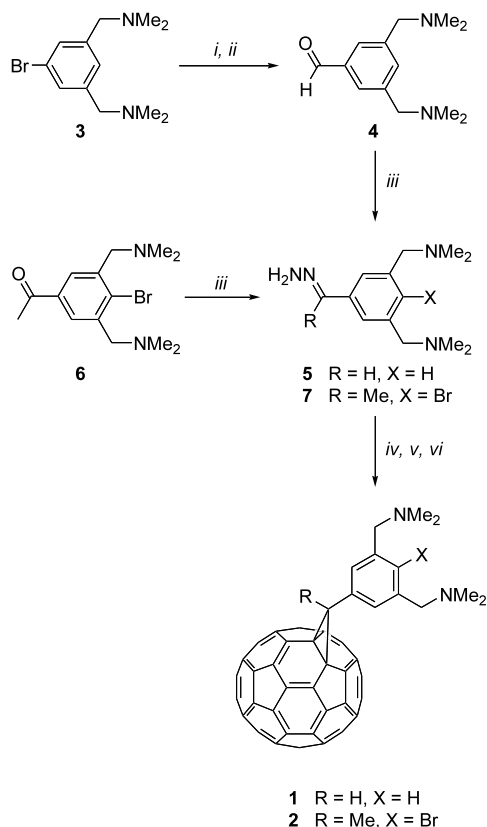
Cyclic voltammetry measurements were performed in a glovebox under dinitrogen atmosphere using an Autolab PGStat 100 electrochemical analyzer. The spectra were recorded at a scan rate of 100 mV s^{–1}, using a platinum disc as the working electrode, a Ag/AgNO₃ reference electrode and a platinum counter electrode. Tetrabutylammonium hexafluorophosphate ((*n*-Bu)₄N(PF₆)) was employed as the supporting electrolyte in 0.1 mol l^{–1} concentration. A freshly prepared mixture of toluene and acetonitrile (5:2 v/v %) was used as solvent (both solvents were distilled prior to use).

3. Results and discussion

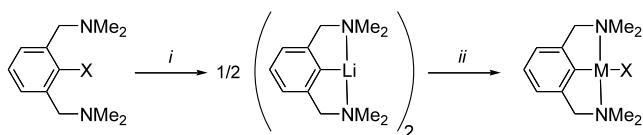
3.1. Synthesis of the free methanofullerene NCN ligands

[1,2]-Methanofullerene NCN ligand **1** (C₆₀–CH–NCN–H) and its corresponding bromide **2**

(C_{60} -C(Me)-NCN-Br) were synthesized via addition of 4-diazo substituted pincer ligands to C_{60} (Scheme 1 [26]). 3,5-Bis[(dimethylamino)methyl]bromobenzene (**3**) and 4-bromo-3,5-bis[(dimethylamino)methyl]acetophenone (**6**), were converted into the corresponding hydrazone compounds **5** and **7**, respectively. Subsequently, **5** and **7** were transformed to the corresponding diazo compounds with MnO_2 , and reacted in situ with C_{60} . This led in both cases to the formation of a mixture of the [5,6]-fulleroid, the kinetically more stable isomer, together with small amounts (10–15%) of the thermodynamically more stable [6,6]-methanofullerene. Complete isomerization to the [6,6]-methanofullerene took place in refluxing toluene in 5–6 days.



Scheme 1. Synthesis of methanofullerenes **1** and **2**. Reagents and conditions: (i) 2 *t*-BuLi, Et_2O , $-78\text{ }^\circ\text{C}$, 1 h; (ii) DMF, $-78\text{ }^\circ\text{C}$ to r.t., 17 h; (iii) $N_2H_4 \cdot H_2O$, EtOH, reflux, 2 h; (iv) MnO_2 , Et_2O , 20 h; (v) C_{60} , toluene, 5 h; (vi) toluene, $110\text{ }^\circ\text{C}$, 5–6 days.



Scheme 2. Metallation pathway of NC(X)N ligands via lithiation and transmetalation. Reagents and conditions: (i) For X = H: *n*-BuLi, hexanes, $0\text{ }^\circ\text{C}$. For X = Br: Li, Et_2O ; (ii) For example: $[PtCl_2(SEt_2)_2]$ [28], $[PdCl_2(SEt_2)_2]$ [28], $[NiCl_2(PEt_3)_2]$ [21b], or $[RuCl_2(PPh_3)_3]$ [30].

During this conversion, small amounts of insoluble side products were formed. Monitoring of the conversion by 1H NMR spectroscopy also revealed the appearance of a new set of signals grouped around the resonances of the NMe_2 groups and benzylic protons of the desired [6,6]-methanofullerene, pointing to the formation of several soluble side products. As primary, secondary, and tertiary amines do react with C_{60} itself, these side products probably result from intermolecular reactions of the amine donor groups with fullerene moieties, leading to the formation of oligomeric amine–fullerene donor–acceptor compounds [28].

Unfortunately, the use of higher temperatures in order to accelerate the isomerization reaction also led to an increase of the formation of side products. Therefore, the isomerization reaction was carried out in dilute solutions ($< 1\text{ mg ml}^{-1}$) to suppress side reactions. This could not prevent that isolation of pure compounds still required an additional chromatographic purification step in the work-up procedure.

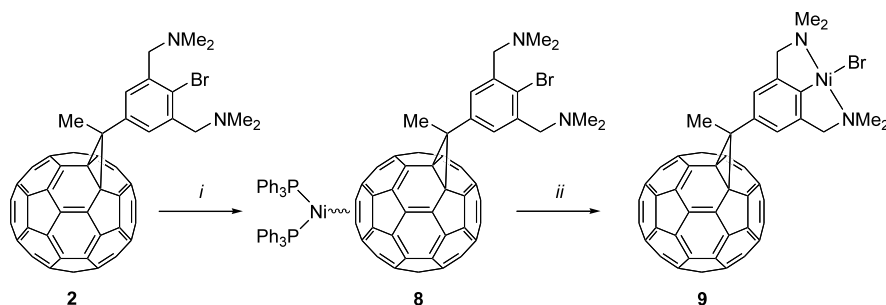
3.2. Metallation procedure of **1** and **2**

The established way of synthesizing pincer metal complexes involves either direct lithiation of the C(2)–H bond in $C_6H_4(CH_2NMe_2)_2$ -1,3, or proceeds via lithium–bromide exchange at the C(2)–Br bond in 2-Br- $C_6H_3(CH_2NMe_2)_2$ -1,3 (Scheme 2). Subsequent transmetalation of the corresponding aryllithium compound with an appropriate transition-metal halide gives the pincer metal–halide complex and lithium halide [21b,29,30].

However, facile reaction of C_{60} itself with various organolithium reagents obstructs the use of this route [31–33]. Indeed, reaction of **1** and **2** with either *n*-BuLi or *t*-BuLi leads to formation of insoluble black solids. Therefore, other routes were investigated without the involvement of organolithium reagents or intermediates. Alternative direct metallation routes are the cyclometallation of NCN–H with $RhCl_3 \cdot H_2O$ [34], and $Pd(OAc)_2$ [35,36], the oxidative addition of NCN–Br with Ni^0 and Pd^0 complexes [25,37] or the electrophilic metallation of NCN–SiMe₃ with $Pd(OAc)_2$ or $Li_2[PdCl_4]$ [36]. Direct metallation of **1** with $RhCl_3 \cdot H_2O$ or $Pd(OAc)_2$ failed; only starting material and insoluble products were isolated. However, the addition of either Ni^0 or Pd^0 complexes to **2** showed the formation of new complexes.

3.3. Oxidative addition of nickel(0) complexes to **2**

Reaction of Ni^0 complexes such as $[Ni(COD)_2]$ and $[Ni(PPh_3)_4]$ with 2-Br- $C_6H_3(CH_2NMe_2)_2$ -1,3 led to the oxidative addition of the aryl bromide bond to the Ni^0 complex, thus forming the corresponding colorless NCN·NiBr complex [25]. However, upon addition of



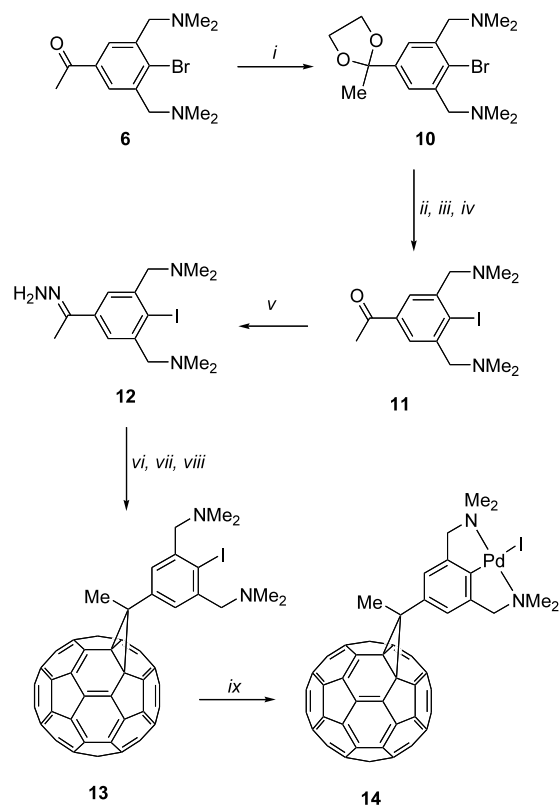
Scheme 3. Synthesis of **9**. Reagents and conditions: (i) [Ni(PPh₃)₄], toluene, 0 °C to r.t., 1 h; (ii) toluene, 45 °C, 20 h.

[Ni(COD)₂] to a dark-red solution of **2** in toluene at 0 °C, an immediate formation of a dark-green material was observed. This color change corresponds to the formation of a π-complex between the zerovalent nickel center and C₆₀ [38,39]. Similarly, addition of [Ni(PPh₃)₄] to a toluene solution of **2** at 0 °C also gave a clear dark-green reaction mixture. Spectroscopic investigation of this reaction mixture by ³¹P NMR spectroscopy showed a broad resonance signal at 25.5 ppm (C₆D₆), pointing to the presence of the π-complex (**8**, Scheme 3) between the nickel(0) center and the fullerene part of **2**. This proposal is supported by the fact that for similar complexes, such as (PPh₃)₂PdC₆₀ and (PPh₃)₂PtC₆₀, these resonances are found at 25.4 ppm (CDCl₃) [38] and 27.0 ppm (THF-d₈) [39], respectively. Upon heating these (C₆₀-C(Me)-NCN-Br)·NiL_{*n*} π-complexes (L = PPh₃ or COD) for 20 h at 45 °C, the color of the reaction mixture changed from dark-green back to deep-red. After subsequent removal of all volatiles, washing of the residue and extraction with benzene, a new product was isolated, which was identified with NMR spectroscopy as the oxidative addition product, i.e. the C₆₀-C(Me)-NCN·NiBr complex **9**.

3.4. Reactivity of palladium(0) complexes toward **2**

The addition of Pd(dba)₂ to **2** afforded a gray solid, insoluble in common organic solvents. This result resembles the formation of a C₆₀-palladium polymer upon reaction of Pd(dba)₂:dba·CHCl₃ with C₆₀ [40]. Heating this gray solid did not result in subsequent rearrangement and formation of the desired C₆₀-C(Me)-NCN·PdBr complex as was the case for nickel. Upon addition of [Pd(PPh₃)₄] to **2**, the green colored π-complex **2**·Pd(PPh₃)₂ was formed (³¹P NMR, δ = 26.2). Heating a benzene solution of **2**·Pd(PPh₃)₂ at reflux in order to force palladium insertion into the NCN C-Br bond did not result in the formation of the expected oxidative product. Instead, decomposition took place under formation of **2**, palladium black, PPh₃ and other (unidentified) side products. As Pd⁰ complexes are more prone to oxidatively add to aryl iodides, the corresponding methanofullerene NCN-I

compound, **13**, was prepared. The synthesis, shown in Scheme 4, started with the protection of the carbonyl group in ketone **6** with glycol using *p*-toluenesulfonic acid as catalyst in benzene. In this way, ketal **10** was obtained in good yield within 20 h. Subsequently, **10** was reacted with 2 equiv. of *t*-BuLi in hexanes, followed by a quench reaction with I₂ in THF. The acetal protection was removed by acid-base work-up of the reaction mixture, yielding the corresponding acetophenone **11** in 72% overall yield. Similar to the synthesis of **1** and **2**, **11** was converted to the corresponding hydra-



Scheme 4. Synthesis route toward **14**. Reagents and conditions: (i) glycol, *p*-TosOH, benzene, reflux, 20 h; (ii) 2 *t*-BuLi, Et₂O, -78 °C, 30 min; (iii) I₂, THF, -78 °C to r.t.; (iv) HCl, Et₂O, then NaOH, Et₂O; (v) N₂H₄·H₂O, EtOH, reflux, 2 h; (vi) MnO₂, Et₂O, 20 h; (vii) C₆₀, toluene, 5 h; (viii) toluene, 110 °C, 5 days; (ix) Pd(PPh₃)₄, benzene, 80 °C, 4 days.

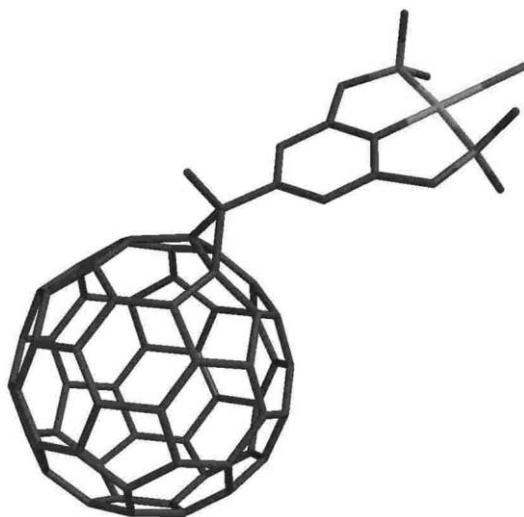


Fig. 1. PM3(tm) optimized structure of **9** (ground state rotamer), hydrogen atoms are omitted for clarity.

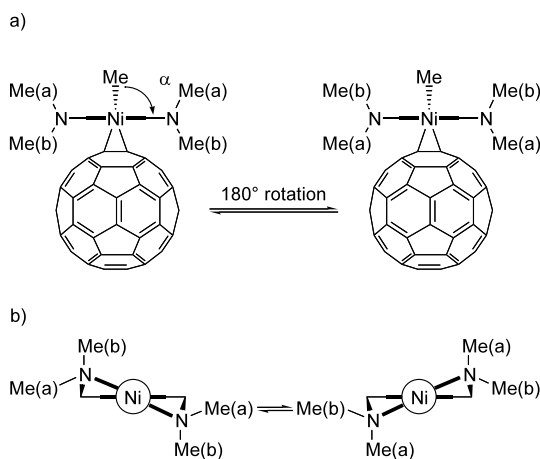


Fig. 2. (a) Newman projection along the C(Me)–NCN–Ni axis showing α , the angle between the planes through CH₃–C–C(NCN) and the NCN group and rotation (180°) about the methano–NCN C–C bond. (b) Wagging of the puckered chelate rings.

zone compound **12** with a stoichiometric amount of hydrazine hydrate in refluxing EtOH.¹ Coupling to C₆₀ was achieved via oxidation of the hydrazone functionality to the corresponding diazo compound with MnO₂, followed by cycloaddition to C₆₀ and isomerization of the obtained mixture of regioisomers to the pure methanofullerene **13**.

A mixture of **13** and Pd(PPh₃)₄ in toluene was heated at 80 °C for 4 days. ¹H and ³¹P NMR spectra of the reaction mixture revealed that partial formation of the desired C₆₀–C(Me)–NCN·PdI complex **14** had occurred, but attempts to isolate **14** from the reaction

¹ The use of more than 1 equivalent of N₂H₄·H₂O in this reaction leads to removal of the iodine atom in **12**, and formation of the corresponding NC(H)N compound.

mixture in pure form failed. As a result of the long reaction time and high reaction temperature needed various decomposition compounds were formed. Although addition of excess amounts of Pd(PPh₃)₄ to the reaction mixture enhanced the rate of formation of **14**, also more side products were found. To this moment, successful synthesis of methanofullerene NCN metal complexes via an oxidative addition pathway seems viable for nickel only. In this case, the reactivity of the π -complex formed between Ni⁰ and **2** toward the aryl C–Br bond in **2** offered an interesting new pathway toward the preparation of C₆₀–C(Me)–NCN·NiBr complex **9**.

3.5. Properties of C₆₀–C(Me)–NCN·NiBr (**9**)

Attempts to obtain crystals of **9** suitable for X-ray crystal structure determination were unsuccessful. Therefore, **9** was studied in more detail using molecular modeling [41]. The semi-empirical (PM3(tm)) optimized structure (Fig. 1) shows that the ground state conformation (rotamer) contains a methano-methyl group which is anti-planar positioned with respect to the plane of the NCN·NiBr unit. The structural features of the latter unit corresponds with those obtained from X-ray crystal structure determinations of parent NCN·Ni complexes [42]. Furthermore, also the structural features of the [1,2]-methanofullerene part of **9** are similar to the known distances and bond lengths of [1,2]-methanofullerenes [43]. From the PM3 calculation, a shortest intramolecular nickel–fullerene distance of 6.5 Å was derived.

The ¹H NMR spectroscopy of the new bulky-ligands **1**, **2**, **13**, and the nickel complex **9** showed a single resonance pattern for the NMe₂ and benzylic protons, pointing to the presence of a single species in solution. Comparison of the ¹H NMR chemical shifts of **9** in C₆D₆ with those of the parent ligand **2** showed a downfield shift for the NMe₂ groups ($\Delta\delta = 0.60$ ppm), while the benzylic signal were found upfield shifted ($\Delta\delta = 0.28$ ppm), which is a common observation for NCN·Ni complexes. The largest change was observed for the aromatic protons, which shifted highfield from 8.22 to 7.04 ppm (C₆D₆). Interestingly, similar values were found for the aromatic protons in other 4-substituted NCN·Ni complexes [25]. The large deshielding effect of the fullerene unit in the parent ligand **2** is apparently compensated for by the electronic effect of the nickel center in **9**. The PM3(tm) model of **9** shows that as the N(Me₂) and C(H₂) centers cannot be situated in a single molecular symmetry plane, the methyl groups and benzylic protons are diastereotopic. The single resonance pattern indicates that the 4-substituent, which is the origin of the dissymmetry, is either too far away or that an intramolecular fluxional processes on the NMR time scale takes place, rendering

these diastereotopic groups enantiotopic. Two fluxional processes can be responsible for this: (i) rotation about the (Me)C–NCN bond (Fig. 2(a)), and (ii) wagging of the aryl ring about the C–Ni axis causing inversion of ring puckering in the two fused five-membered chelate rings (Fig. 2(b)). To test this hypothesis, variable temperature ^1H NMR spectroscopic experiments were performed. The ^1H NMR spectrum of ligands **1**, **2** and **13** in toluene remained unchanged in a temperature range of 298–173 K. However, for nickel complex **9**, the singlet resonance for the NMe_2 groups decoalesced on cooling into two singlet signals while simultaneously the signal of the benzylic protons started to decoalesce in an AB pattern (CD_2Cl_2). The ΔG^\ddagger values, calculated from the observed chemical shift differences and coalescence temperatures T_c , for the (dimethylamino) methyl groups and the benzylic protons are 44.5 kJ mol^{-1} ($T_c = 215 \text{ K}$) and 44.0 kJ mol^{-1} ($T_c = 210 \text{ K}$), respectively, indicating that both effects result from the same process. Previous work showed that the wagging process leading to inversion of the chelate ring puckering in NCN-metal complexes has a lower barrier [44], i.e. is still in the fast exchange limit. This leaves the rotation of the NCN·Ni unit about the (Me)C–NCN bond in **9** as the origin for the observed fluxional process in the molecule, i.e. rotation between the ground state rotamers (Fig. 2(a)). This process is only observable in **9** due to the stable coordination of the nitrogen donor atoms to nickel (on the NMR time scale), which leads to a fixation of the benzylic and NMe_2 groups with respect to the NCN-aryl plane. In **1**, **2**, and **13** more

rotational freedom is present in the nitrogen donor arms due to the lack of spatial fixation as a result of such a coordination. Although the rotation of the NCN-moiety about the (Me)C–NCN bond in these free ligands is supposed to be blocked at low temperature as well, this was not observed with NMR spectroscopy at 173 K.

Interestingly, the same energy barrier for rotation about the (Me)C–NCN bond in **9** was also estimated by a theoretical method. A range of semi-empirical calculations (PM3(tm)) was performed for **9**. The heat of formation was calculated for various rotamers of **9** as function of the dihedral angle, α , between the Me–C–C(NCN) and the NCN-aryl plane. The energy difference between the rotamer with the lowest energy ($\alpha = 90^\circ$) and the one with the highest energy ($\alpha = 0^\circ$) amounted to 44 kJ mol^{-1} . This is in excellent agreement with the observed energy barriers found by NMR spectroscopy.

The UV–Vis spectra of **2** and **9** in CH_2Cl_2 (Fig. 3) revealed absorption bands present at 258, 327, 431 and a very broad band centered at 480 nm, which are well-known bands for 1,2-methano[60]fullerene compounds. Since the two spectra do not differ substantially from each other, there seems to be no influence of the nickel center in **9** on the absorption behavior of the fullerene unit in the ground state.

The redox potentials of C_{60} , **2**, and **9**, respectively, were measured by cyclic voltammetry in toluene/acetonitrile solution (5:2 v/v %) with $[(n\text{-Bu})_4\text{N}(\text{PF}_6)]$ (0.1 M) as the supporting electrolyte (Table 1). The first

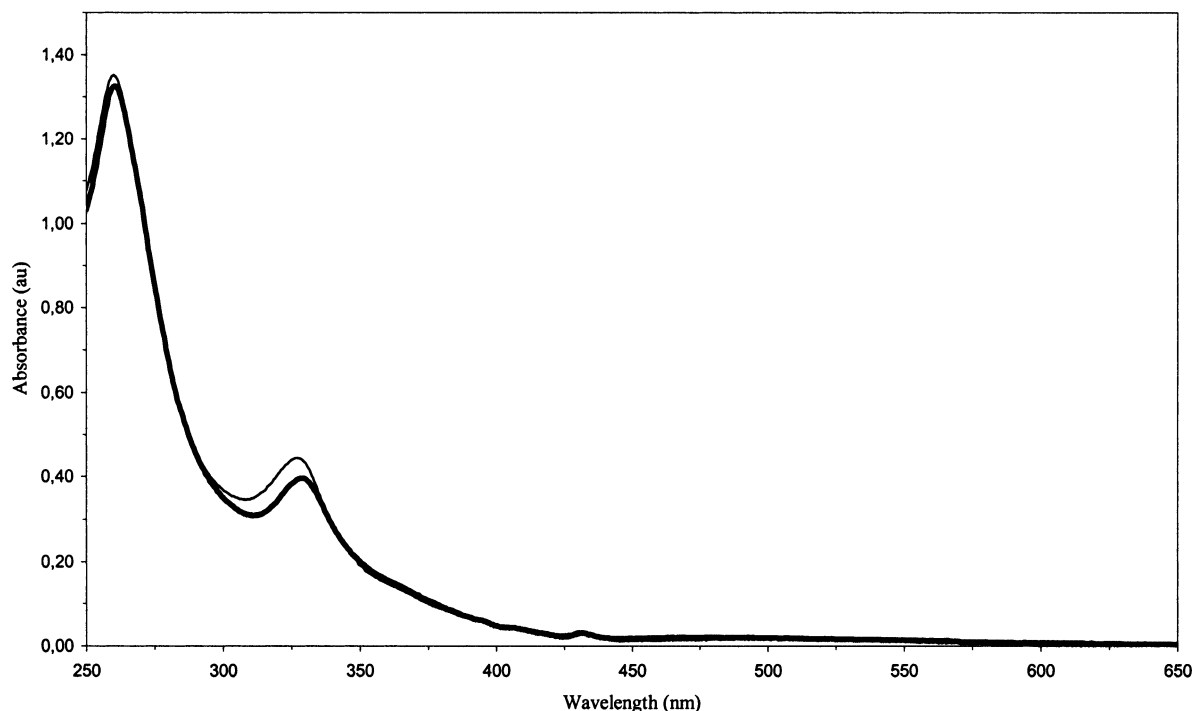


Fig. 3. UV–Vis spectra (CH_2Cl_2 , $1 \times 10^{-5} \text{ M}$) of **2** (bold line) and **9** (normal line).

Table 1
Electrochemical data for C₆₀, **2** and **9**^{a,b}

C ₆₀	−2.21	−1.64	−1.14	−0.71	
2	−2.21	−1.77	−1.19	−0.81	0.81 ^c
9	−2.25	−1.78	−1.25	−0.82	0.83 ^c

^a In toluene/acetonitrile (5:2) solution, with [(n-Bu)₄N(PF₆)] (0.1 M) as supporting electrolyte, measured at 0.1 V s^{−1}.

^b E_{1/2} potentials are in volts vs. the Fc/Fc⁺ couple in the same solvent.

^c Irreversible wave, the peak potentials E_p^{ox} are given.

(fullerene) reduction wave of **2** is anodically shifted by 100 mV with respect to C₆₀, which is commonly observed for methanofullerenes [5]. The reductions are accompanied by an irreversible ligand oxidation at 0.81 V. While parent NCN·Ni complexes can be oxidized (chemically) reversible to the corresponding NCN·Ni(III) complexes [22], we did not observe a similar reversible oxidation/reduction process for the NCN·NiBr moiety in **9**. Only an irreversible oxidation was observed at 0.83 V. The absence of a Ni(II)/Ni(III) redox couple indicates that the nickel(II) center in **9** is influenced by the presence of the fullerene moiety. Likewise, the nickel center causes small, but measurable anodic shifts of some of the fullerene reduction potentials: with respect to **2**, the second and fourth fullerene reduction potentials of **9** were shifted 60 and 40 mV, respectively, whereas the other potentials were barely shifted (~10 mV). The influence of the C₆₀ moiety on the redox potentials of NCN–Ni in **9** (and vice versa) is presently not understood. One might speculate that the absence of the Ni(II)/Ni(III) couple is due to slow electrode kinetics. Therefore, we will attempt to prepare the nickel(III) complex of **9** through chemical oxidation. This will be a subject for further investigations.

Acknowledgements

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