Supporting information for

Pentaarylfullerenes as non-coordinating cyclopentadienyl anions

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Experimental section

General considerations. All manipulations of air and moisture sensitive compounds were performed under nitrogen atmosphere using standard Schlenk and vacuum line techniques or in an MBraun glovebox. Solvents (THF, pentane) were dried by percolation under nitrogen atmosphere over columns of alumina, molecular sieves, and supported copper oxygen scavenger (BASF R3-11), or by distillation from Na/K alloy (cyclohexane, toluene-$d_8$ and THF-$d_8$) or CaH$_2$ (1,2-dichlorobenzene). Reagents were purchased from commercial providers and used without purification unless stated otherwise. Ph$_5$C$_{60}$H$^1$ and [Zr(NMe$_2$)$_4$]$^2$ were prepared following literature procedures. NMR spectra were recorded on Varian Inova 500, Varian Gemini VXR 400, Varian VXR 300, and Varian Gemini 200 instruments. $^1$H chemical shifts are referenced to residual protons in deuterated solvents and are reported relative to tetramethylsilane. Elemental analyses were performed by the Microanalytical Department at the University of Groningen. Reported values are the averages of two independent determinations. Crystals suitable for a single-crystal X-ray analysis were grown as described. A crystal was mounted on a glass fiber inside a drybox and transferred under an inert atmosphere to the cold nitrogen stream of a Bruker SMART APEX CCD diffractometer. Intensity data were corrected for Lorentz and polarization effects, scale variation, decay, and absorption: a multiscan absorption correction was applied, based on the
intensities of symmetry-related reflections measured at different angular settings (SADABS), and reduced to $F_0^2$. The structures were solved by Patterson methods, and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF. The positional and anisotropic displacement parameters for the non-hydrogen atoms were refined. Final refinement on $F^2$ was carried out by full-matrix least-squares techniques.

(4-$n$PrC$_6$H$_4$)$_5$C$_{60}$H (1b). To a yellowish-green suspension, generated by addition of 4-$n$PrC$_6$H$_4$MgBr in THF (11 mL 0.74 M; 8.1 mmol) to a white suspension of [CuBr(SMe$_2$)] (2.0 g; 9.5 mmol) in THF (25 mL), a dark purple solution of C$_{60}$ (0.40 g; 0.56 mmol) in 1,2-dichlorobenzene (25 mL) was added. The resulting dark green reaction mixture was stirred for 2 h and quenched with a concentrated aqueous solution of NH$_4$Cl (2 mL). The THF and dimethylsulfide were removed under reduced pressure and the concentrated reaction mixture was diluted with toluene (50 mL). The dark red reaction mixture was filtered through a pad of silica gel and the toluene was removed by rotary evaporation. Addition of pentane (100 mL) and cooling to -30 °C afforded 550 mg (0.417 mmol, 75 %) of red crystals identified as (4-$n$PrC$_6$H$_4$)$_5$C$_{60}$H. The compound was recrystallized from toluene, affording crystals suitable for a single-crystal X-ray analysis. $^1$H NMR (toluene-$d_8$, RT) δ 7.69 (d, 8Hz, 4H, Ph), 7.62 (d, 8Hz, 4H, Ph), 7.45 (d, 8Hz, 2H, Ph), 7.02 (d, 8Hz, 4H, Ph), 6.95 (d, 8Hz, 4H, Ph), 6.91 (d, 8Hz, 2H, Ph), 5.31 (s, 1H, CpH), 2.41 (overlapping, 8H, CH$_2$), 2.38 (m, 2H, CH$_2$), 1.52 (overlapping, 8H, CH$_2$), 1.45 (m, 2H, CH$_2$), 0.85 ppm (overlapping, 15H, CH$_3$); $^{13}$C($^1$H) NMR (toluene-$d_8$, RT) δ 156.91, 153.32, 153.03, 152.51, 149.26, 149.22, 148.94, 148.77, 148.65, 148.62, 148.59, 148.27, 147.71, 147.63, 146.84, 146.54, 146.31, 146.04, 145.07, 145.02, 144.94, 144.84, 144.75, 144.66, 144.43, 144.02, 143.74, 142.16, 141.96, 141.70, 138.10, 138.03, 130.96, 130.34, 129.38, 129.24, 128.59, 128.31, 127.71, 125.46, 63.78, 61.47, 59.40, 59.36, 37.90, 37.86 (2 overlapping signals), 24.84, 24.82, 24.76, 13.96, 13.85, 13.83 ppm. Anal. Calcd. for C$_{105}$H$_{56}$: C, 95.72; H, 4.28. Found: C, 94.59 H, 4.35.$^3$

[Li(THF)$_4$][Ph$_5$C$_{60}$] (2a). THF (5 mL) was added to a mixture of 1a (69.5 mg; 0.114 mmol) and LiNMe$_2$ (5.8 mg; 0.11 mmol). After stirring for 3 h, the volatiles were removed under reduced pressure. The compound was extracted with THF (2 x 1 mL) and triturated with pentane (2 mL). The supernatant
was decanted and the reddish-brown solid was dried, affording 91.0 mg (0.064 mmol, 57%) of [Li(THF)]_4[Ph_5C_60]. ^1H NMR (THF-d_8, RT) δ 7.8 (m, 10H, o-Ph), 7.0 ppm (m, 15H, m-Ph and p-Ph); ^13C{^1H} NMR (THF-d_8, RT) δ 160.0, 149.4, 149.3, 147.3, 146.6, 146.3, 143.2, 129.4, 128.9, 128.1, 126.1, 62.4 ppm. Anal. Calcd. for C_{106}H_{57}LiO_4: C, 90.84; H, 4.10. Found: C, 90.54; H, 3.71.

[Zr(NMe_2)_3(THF)_2][Ph_5C_60] (2b). Compound 2b was prepared analogous to 2a, using 1b (62.9 mg; 0.0477 mmol) and LiNMe_2 (2.5 mg; 0.049 mmol). This afforded 63.5 mg (0.0394 mmol, 83%) of 2b. The compound was recrystallized from THF/cyclohexane, affording crystals suitable for a single-crystal X-ray analysis. ^1H NMR (THF-d_8, RT) δ 7.79 (d, 8 Hz, Ph), 6.88 (d, 8 Hz, Ph), 2.51 (t, 7 Hz, CH_2), 1.59 (ps. sext, 7 Hz, CH_2), 0.91 ppm (t, 7 Hz, CH_3); ^13C{^1H} NMR (THF-d_8, RT) δ 160.4, 149.6, 149.3, 147.2, 146.5, 143.8, 143.1, 140.0, 129.4, 129.1, 128.2, 38.5, 25.7, 14.2 ppm. Anal. Calcd. for C_{121}H_{87}LiO_4: C, 90.16; H, 5.44. Found: C, 90.44; H, 5.37.

[Zr(NMe_2)_3(THF)_2][(4-nPrC_6H_4)_5C_60] (3a). THF (15 mL) was added to a mixture of 1a (305 mg; 0.275 mmol) and [Zr(NMe_2)_4] (75 mg; 0.28 mmol). The reaction mixture was frequently shaken over a period of 2 h during which a dark, reddish-brown solution was formed. The reaction mixture was degassed to remove the dimethylamine and filtered. The volatiles were removed in vacuo and the resulting brown solid was washed with pentane (2 x 5 mL). Evaporation of the pentane afforded 360 mg (0.222 mmol, 81%) of a brown solid identified as [Zr(NMe_2)_3(THF)_2][Ph_5C_60](THF)_2]. The compound was recrystallized from chlorobenzene/cyclohexane, affording crystals suitable for a single-crystal X-ray analysis. ^1H NMR (THF-d_8, RT) δ 7.8 (m, 10H, o-Ph), 7.0 (m, 15H, m-Ph and p-Ph), 2.87 ppm (s, 18H, NMe_2); ^13C{^1H} NMR (THF-d_8, RT) δ 160.2 (s), 149.5 (s), 149.4 (s), 147.4 (s), 146.6 (s), 146.3 (s), 143.3 (s), 129.4 (d, 158 Hz), 128.9 (s), 128.2 (d, 152 Hz), 126.2 (d, 157 Hz), 62.4 (s), 44.7 (q, 132 Hz) ppm. Anal. Calcd. for C_{112}H_{75}N_3O_4Zr: C, 83.14; H, 4.67; N, 2.60. Found: C, 82.76; H, 4.38; N, 2.80.

[Zr(NMe_2)_3(THF)_2][(4-nPrC_6H_4)_5C_60] (3b). This compound was prepared analogues to 3a, using 1b (130 mg; 0.0987 mmol) and [Zr(NMe_2)_4] (28 mg; 0.10 mmol). This afforded 128 mg (0.0729 mmol, 74% of 3b. ^1H NMR (THF-d_8, RT) δ 7.79 (d, 8 Hz, o-Ph), 6.88 (d, 8 Hz, m-Ph), 2.95 (s, 18H, NMe_2), 2.51 (t, 7 Hz, CH_2), 1.59 (ps. sext, 7 Hz, CH_2), 0.91 ppm (t, 7 Hz, CH_3); ^13C{^1H} NMR (THF-d_8, RT) δ
160.5, 149.7, 149.4, 147.3, 146.6, 144.1, 143.2, 140.0, 129.5, 129.3, 128.1, 38.6, 25.4, 13.9 ppm. Anal. Calcd. for C_{123}H_{97}N_{3}O_{3}Zr: C, 84.11; H, 5.57; N, 2.39. Found: C, 84.60; H, 5.29; N, 2.23.

[Zr(NMe_{2})_{3}(THF)_{n}][BPh_{4}] (4, 4'). THF (10 mL) was added to a mixture of [Zr(NMe_{2})_{4}] (96 mg; 0.36 mmol) and [PhNMe_{2}H][BPh_{4}] (144 mg; 0.350 mmol). The volatiles were pumped off, affording 208 mg (0.303 mmol, 87 %) of a white crystalline material, after washing with pentane (2 x 10 mL), which was identified as the title compound. The compound was recrystallized from both THF/cyclohexane and chlorobenzene/THF affording crystals suitable for a single-crystal X-ray analysis. In the case of the first, crystals were obtained of the tris(THF) adduct, [Zr(NMe_{2})_{3}(THF)_{3}][BPh_{4}], and in the case of the second, crystals were obtained of the bis(THF) adduct, [Zr(NMe_{2})_{3}(THF)_{2}][BPh_{4}]. \(^1\)H NMR (THF-\textit{d}_{8}, RT) \(\delta\) 7.23 (br, 8 H, \textit{m}-CH), 6.82 (t, 7 Hz, 8H, \textit{o}-CH), 6.67 (t, 7 Hz, 4H, \textit{p}-CH), 2.89 ppm (s, 18 H, NMe_{2}); \(^{13}\)C NMR (THF-\textit{d}_{8}, RT) \(\delta\) 137.1 (BPh_{4}), 125.7 (BPh_{4}), 121.8 (BPh_{4}), 44.8 ppm (NMe_{2}). Anal. Calcd. for C_{42}H_{62}N_{3}O_{3}Zr: C, 66.46; H, 8.23; N, 5.54. Found: C, 65.82; H, 8.17; N, 5.98.

References

3 Despite many attempts, elemental analyses consequently result in low carbon values, even when crystalline material was used.