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Preparation and ESR characterization of polyalkyl-*s*-indacenyl anion-radicals from polyalkyl-1,5-dilithio-*s*-indacenes

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ABSTRACT

Polyalkyl-(or chloropolyalkyl)-*s*-indacenyl anion radicals were obtained from the organodilithium derivatives of the corresponding substituted-1,5-dihydro-*s*-indacenes by three different methods: (i) UV photolysis, (ii) oxidation by a ferrocenium salt, (iii) single electron transfer reaction from an electron rich olefin. The last reaction (iii) involves transient formation of an unstable polyalkyl-lithio-*s*-indacenyl imidazolidinium salt. The same salt, obtained by another way by reacting 1,3-dimethylimidazolidinium chloride with the polyalkyl-1,5-dilithio-*s*-indacene, also leads to the corresponding lithium polyalkyl-*s*-indacenyl anion radical. All lithium polyalkyl-*s*-indacenyl anion radicals studied were characterized from their ESR spectra. They present a characteristic symmetrical spin distribution. On the contrary a Rhodium-COD polyalkyl-*s*-indacene radical presents a non symmetrical spin distribution.

1. Introduction

Because of their potential use as ligands or spacers in the synthesis of binuclear complexes, conducting polymers and biological compounds, polyalkyl-*s*-indacenes and polyalkyl-1,5-dihydro-*s*-indacenes, as well as some of their radical anions, radical cations or radicals have been prepared and studied [1–10].

Here we report the lithium anion-radicals $(Ar)^{-\cdot}$ Li^{+} of various polyalkyl-*s*-indacenes or halopolyalkyl-*s*-indacenes which have been prepared by three different ways and then characterized by ESR.

2. Experimental section

All reactions were performed under nitrogen using standard Schlenk tube and dry solvents. NMR spectra were recorded on Bruker AC 80 (^{1}H, 80 MHz), ARX400 (^{1}H, 400.13 MHZ); AC 200 (^{13}C, 50.32 MHz), ARX 400 (^{13}C, 100.62 MHz) spectrometers. Mass and gas chromatography (GC/mass) and mass spectra were recorded with a Hewlett Packard HP5989 in electron impact mode (Ei, 70 Ev), or a Rybermag R10-10 spectrometer operating in Ei mode, or by chemical desorption (DCi/CH_4 or NH_3). Infrared spectra were recorded on a Perkin–Elmer 1600FT spectrometer. ESR spectra were recorded on a Brüker spectrometer EPR ELFXSYS E 500. *g* Values were calculated by the Brüker Xepr software using the frequencemeter integrated to the ER049X microwave bridge. The magnetic field was controlled by the NMR teslameter Brüker and verified against dpph. Elemental analyses were done by the "Centre de Microanalyses de l'Ecole Nationale Supérieure de Chimie de Toulouse". All Density Functional (DF) calculations reported here were performed with the Amsterdam Density Functional package, ADF 2006.01 [11]. All the structures were fully optimized (without any geometry constrain) via analytical energy gradient techniques employing the Local Density Approximation [12] (LDA), and the Generalized Gradient Approximation (GGA) method using Vosko, Wilk and Nusair's local exchange correlations [13], with nonlocal exchange corrections by Becke [14], and non local electronic correlations by Perdew [15]. We used uncontracted type IV basis set used Triple-ξ accuracy sets of Slater-Type Orbitals [16] (STO) with a single polarization function added for the main group elements (2p on H and 3d on C). Frozen Core approximation [17] was applied to the inner orbitals of the constituent atoms: the C core up to 1s, Cl up to 2p and Rh up to 3d. For recrystallized compounds, melting points were measured on a Leitz microscope.

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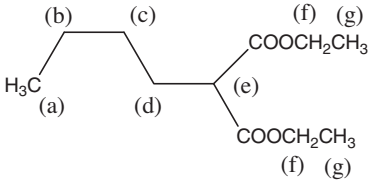
2.1. Preparation of **Ic**

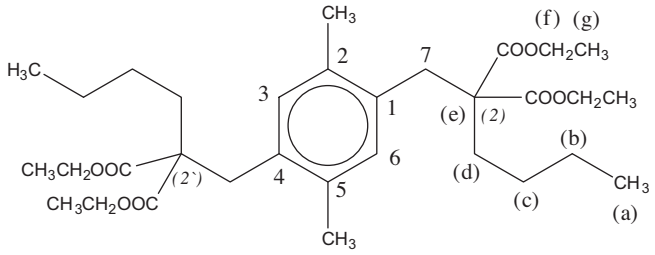
Ligand **Ic** was synthesized following the multi step process of Dahrouch et al. [3], using reagents **A–F** prepared as follow.

2.1.1. Diethyl 2-butyl-malonate **A**



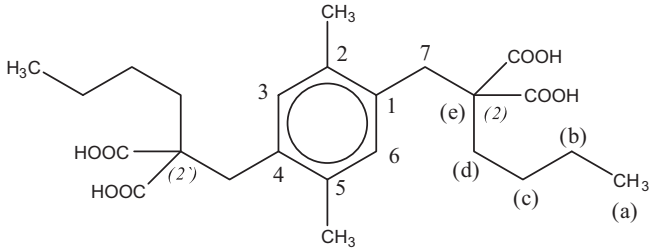
To 100 mL of ethanol in a 300 mL round-bottomed flask was added Na pieces (3.91 g, 0.17 mol) with stirring at room temperature. When all Na was consumed, diethylmalonate (28.03 g, 0.175 mol) was added slowly. After 30 min stirring at room temperature, 1-bromobutane (23.96 g, 0.175 mol) was added and the solution heated at reflux for 3 h. The excess of ethanol was distilled. To the refreshed residue (0 °C) was added water and diethylether. After stirring and decantation, the two phases were separated. The solvent of the organic phase was removed on a rotary evaporator affording a liquid which was purified by distillation in vacuum, yielding 31 g (82%) of **A**. Bp: 67 °C/0.8 mm Hg, conforming to [18]. ^{1}H NMR ($CDCl_3$) δ 0.71 (t, 3H, CH_3 (a), $^3J_{ab}$ = 7.1 Hz); 1,00–1.30 (m, 10H, CH_2 (b,c) and CH_3 (g)); 1.81 (q, 2H, CH_2 (d), $^3J_{cd} = {}^3J_{de}$ = 7.5 Hz); 3.23 (t, 1H, CH (e), $^3J_{de}$ = 7.5 Hz); 4.12 (q, 4H, CH_2 (f), $^3J_{fg}$ = 7.1 Hz) conform to [19]; $^{13}C\{^1H\}$ NMR ($CDCl_3$): 13.35 (CH_3 (a)); 13.8, 13.9 (CH_2 (b,c)); 28.23 (CH_2 (d)); 29.26 (CH_3 (g)); 51.81 (CH (e)); 60.94 (CH_2 (f)); 169.32 (CO). *Anal.* Calc. for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 61.28; H, 9.28%.

2.1.2. Preparation of **B**: tetraethyl 2,2′-(2,5-dimethyl-1,4-phenylene)bis(methylene)bis(2-butylmalonate)



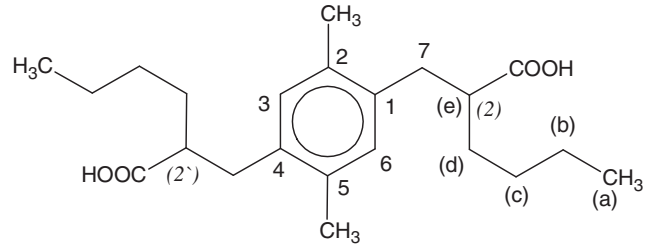
Following the same procedure, but using ethanol (100 mL), Na (3.17 g, 0.14 mol), butyldiethylmalonate (30.00 g, 0.14 mol), and 1.4-bis bromomethyl-2,5-dimethylbenzene (20.22 g, 0.069 mol) 35.83 g of **B** were obtained. Yield 92%. m.p: 69 °C. ^{1}H NMR ($CDCl_3$): 0.86 (t, 6H, CH_3(a), $^3J_{ab}$ = 7.1 Hz); 1.10–1.25 (m, 8H, CH_2(b,c)); 1.18 (t, 12H, CH_3 (g)), $^3J_{fg}$ = 7.0 Hz); 1.77 (m, 4H, CH_2 (d)); 2.14 (s, 6H, CH_3(in 2,5)); 3.17 (s, 4H, CH_2(7)); 4.11 (m, 8H, CH_2 (f)), 6.78 (s, 2H, CH (3,6)). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 13.7 (CH_3 (a)); 13.9 (CH_3 (g)); 19.2 (CH_3 in 2,5); 22.8, 26.4 (CH_2 (b,c)); 32.3 (CH_2 (d)); 34.0 (CH_2 (7)); 58.6 C (e)); 60.9 (CH_2 (f)); 132.1 (CH (3,6)); 133.1, 134.0 (C(1,2,4,5)); 171.6 (CO). IR (KBr pellet, cm^{-1}) ν 1730 (C═O). MS (Ei, m/z (%): $M^{+\cdot}$ 562 (12); ($M^{+\cdot}$ – BuC($COOEt)_2$ 347 (100) and (M^+347 – HCOOEt) 273 (81); ($M^{+\cdot}$ – 2 BuC($COOEt)_2$) 132 (31). *Anal.* Calc. for $C_{32}H_{50}O_8$: C, 68.30; H, 8.96. Found: C, 68.10; H, 8.79%.

2.1.3. Preparation of **C**: 2,2′-(2,5-dimethyl-1,4-phenylene) bis(methylene)bis(2-butylmalonic acid)



To a solution of KOH (180 g, 3.21 mol) in 75 mL of 1/1 EtOH/H_2O placed in a round-bottomed flask with a nitrogen inlet, was added **B** (53.8 g, 0.096 mol).The reaction was exothermic and was heated further until the ester was completely dissolved. This solution was poured into a mixture of water and ice. Then HCl (37%) was added until a pH of 3 was reached. The resulting compound, insoluble in water, was filtered, washed with water and then dried at 60 °C under low pressure giving 29.41 g of **C**. Yield 68%. m.p.: 189 °C; ^{1}H NMR: (DMSO): δ 0.85 (t, 6H, CH_3 (a); $^3J_{ab}$ = 6.8 Hz); 1.23 (m, 8H, CH_2(b,c)); 1.62 (bs, 4H, CH_2(d)); 2.14 (s, 6H, CH_3 (in 2,5)); 3.02 (s, 4H, CH_2(7)); 6.84 (s, 2H, CH_{ar} (3,6)); 12.86 (s, 4H, COOH). $^{13}C\{^1H\}$ NMR (DMSO): δ 14.6 (CH_3 (a)); 19.7 (CH_3 in 2,5); 22.6, 23.0 (CH_2 (b,c)); 32.1 (CH_2(d)); 34.5 (CH_2 (7)); 57.7 (C(e)); 132.1 (CH (3,6)); 132.9, 134.3 (C(1,2,4,5); 176.98 (CO). IR (KBr pellet, cm^{-1}) ν: 3339, 3239 (OH); 1738 (C═O). *Anal.* Calc. for $C_{24}H_{34}O_8$ C, 63.98; H, 7.61. Found: C, 63.89; H, 7.53%.

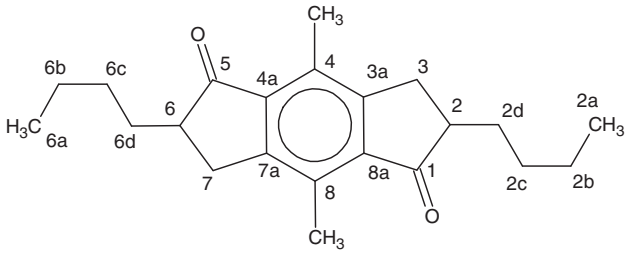
2.1.4. Preparation of **D**: 2,2′(2,5-dimethyl-1,4-phenylene)bis (methylene)dihexanoic acid



Compound **C** (27.08 g, 0.060 mol) was placed in a round-bottomed flask (500 mL) fitted with a nitrogen inlet and melted (190–200 °C) releasing CO_2. The cooled residue (21.18 g) was a white solid identified as **D**. Yield 97%; m.p.: 132 °C. ^{1}H NMR: (DMSO): δ 0.79 (t, 6H, CH_3 (a), $^3J_{ab}$ = 7.0 Hz); 1.20 (m, 8H, CH_2 (b,c)); 1.43 (m, 4H, CH_2 (d)); 2.13 (s, 6H, CH_3 in 2,5); 2.41 (m, 4H, CH_2(7)); 2.70 (m, 2H, CH (e)); 6.82 (s, 2H, CH(3,6)); 11.70 (s, 2H, COOH). $^{13}C\{^1H\}$ NMR (DMSO): δ 13.8 (CH_3 (a)); 18.6 (CH_3 in 2,5); 22.1, 29.1 (CH_2 (b,c)); 31.6 (CH_2 (d)); 34.8 (CH_2 (7)); 45.7 (CH (e)); 131.1 (CH (3,6)); 132.7, 135.5 (C(1,2,4,5)); 176.6 (COOH). IR (KBr pellet, cm^{-1}) ν 1704 (C═O), 2975 (OH).

MS (Ei, *m/z* (%)): $M^{+\cdot}$ 362 (14); ($M^{+\cdot}$ – BuCHCOOH) 247 (100); ($M^{+\cdot}$ – 2BuCHCOOH) 132 (16); *Anal.* Calc. for $C_{22}H_{34}O_4$: C, 72.89; H, 9.45. Found: C, 73.20; H, 9.51%.

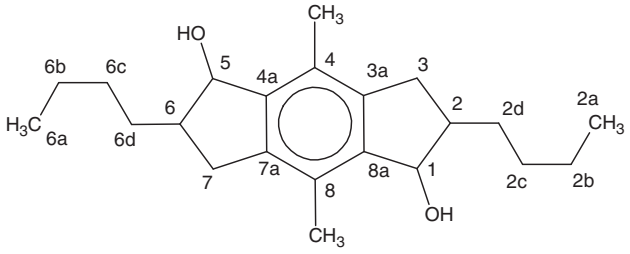
*2.1.5. Preparation of **E**: 2,6-dibutyl-4,8-dimethyl-2,3,6,7 tetrahydro-s-indacene-1,5-dione*



Polyphosphoric acid (500 g, a large excess) and **D** (19.17 g, 0.053 mol) were placed in a round-bottomed flask (1L) fitted with a mechanical stirrer and a nitrogen inlet. The mixture was stirred vigorously under nitrogen at 80 °C for 5 h. It was then poured into a solution of 500 g of ice in 2L of H_2O. The resulting bright yellow precipitate was filtered, washed with water and dried affording 14.37 g of crude **E**. Yield 83%, which was then recrystallized in hexane.

m.p. 113 °C; ^{1}H NMR: ($CDCl_3$): δ 0.92 (t, 6H, CH_3 (a), $^3J_{ab}$ = 7.1 Hz); 1.38–1.50 (m, 12H, CH_2 (b,c,d)); 2.59 (s, 6H, CH_3 in 4,8); 1.94 (dd, 2H, 50% of 4H, CH_2 (3,7)); 2.64 (m, 2H, CH (2,6); 3.19 (dd, 2H, 50% of 4H, CH_2 (3,7); ^2J = 17.6 Hz, ^{3}J = 8.6 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 12.8 (CH_3 (a), 13.9 (CH_3 in 4,8)); 22.7, 29.5 (CH_2 (b,c)); 31.3 (CH_2 (d)); 30.6 (CH_2 (3,7)); 48.4 (CH (2,6)); 132.7, 137.2, 152.5 (C_{IVAr}); 210.5 (CO). IR ($CDCl_3$, cm^{-1}) ν 1708 (C═O). *Anal.* Calc. for $C_{22}H_{30}O_2$: C, 80.94; H, 9.26. Found: C, 80.88; H, 9.15%.

*2.1.6. Preparation of **F**: 2,6-dibutyl-4.8-dimethyl-1,2,3,5,6,7,-hexahydro-s-indacene-1,5-diol*

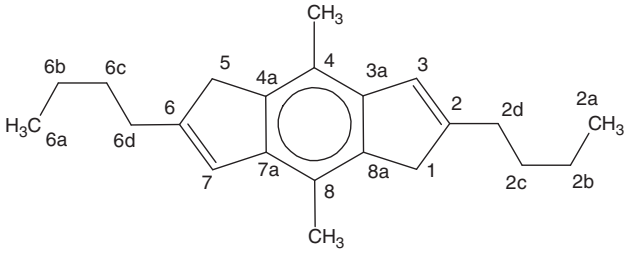


To $LiAlH_4$ (0.71 g, 18.7 mmol) in 25 mL of diethylether placed in a round-bottomed flask (250 mL), **E** (3.72 g, 11.4 mmol) in 25 mL of diethyl ether was added slowly with stirring at room temperature. After 3 h stirring at reflux, the mixture was cooled to 0 °C and a solution of HCl 18% was added slowly. After extraction with diethylether, drying with Na_2SO_4 and concentration of the solvent in vacuo, the residue of 3.52 g was identified as crude **F**: Yield 93%.

The **F** formed here is never pure because of partial dehydration [3] leading to **Ic**. Therefore, the crude compound **F** was immediately transformed into **Ic** with no further spectroscopic characterization.

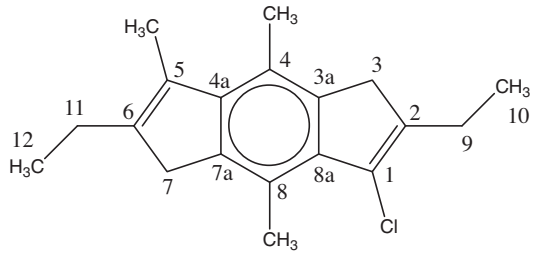
In order to characterize the transient diol the same preparation was repeated but performing the hydrolysis with water instead of HCl. to limit dehydration. The compound obtained was identified as crude **F**. (m.p. 143–150 °C) under two major isomeric forms in relative proportions 60/40%. ^{1}H NMR: ($CDCl_3$): δ 0.96 (t, 6H, CH_3 (a), $^3J_{ab}$ = 7.2 Hz); 1.30–1.80 (m, 14H, CH_2 (b,c,d) and CH (2,6)); 2.28 (s, 60%); 2.29 (s, 40%), 6H, CH_3 in 4,8); 2.25(m) and 2.58(m) 60% of 4H, in 3, 7); 2.90 (d,d) and 3.10 (d,d) (40% of 4H in 3,7, ^2J = 16 Hz, ^{3}J = 7.6 Hz); 4.89 (m, 40% of 2H in 1, 5); 5.06 (d, 60% of 2H in 1,5,^{3}J CHCH = 5.6 Hz). IR (KBr, cm^{-1}) ν 3355 (OH).

*2.1.7. Preparation of **Ic**: 2,6-dibutyl-4,8-dimethyl-1,5-dihydro-s-indacene*

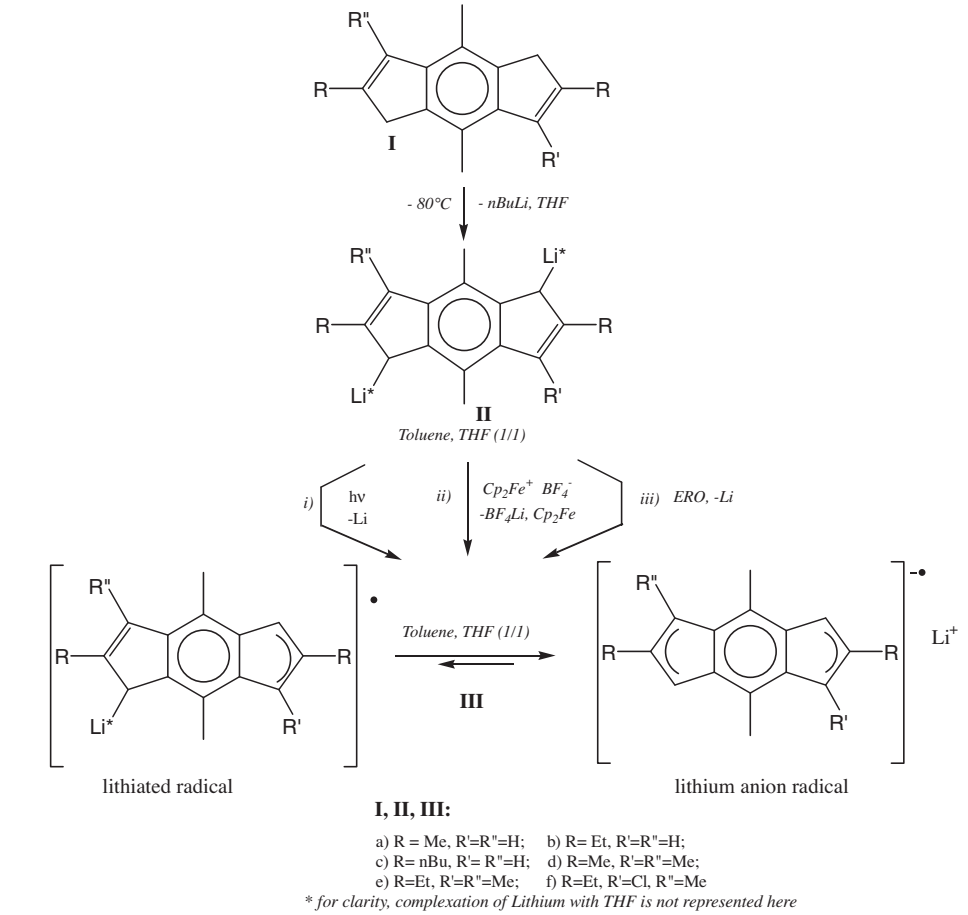


In a round-bottomed flask (250 mL) were mixed 3.53 g of crude **F** (10.68 mmol) and 0.25 g of paratoluenesulfonic acid in 100 mL of C_6H_6.The mixture was heated 2 h at 60 °C. The solution was then cooled to 0 °C and filtered. The liquid phase was washed with water. The organic phase was dried over $MgSO_4$ for 24 h. After evaporation of solvent in vacuo, the crude **Ic** was crystallized in pentane yielding 2.46 g. Yield 78%; m.p. 142 °C; ^{1}H NMR ($CDCl_3$): δ 0.97 (t, 6H, CH_3 (2a, 6a), $^3J_{ab}$ = 7.5 Hz); 1.41 (sext, 4H, CH_2 (2b, 6b); $^3J_{ab}$ = $^3J_{bc}$ = 7.5 Hz); 1.63 (quint, 4H, CH_2 (2c, 6c); $^3J_{bc}$ = $^3J_{cd}$ = 7.5 Hz); 2.37 (s, 6H, CH_3 in 4,8); 2.52 (t, 4H, CH_2 (2d, 6d), $^3J_{cd}$ = 7.5 Hz); 3.23 (bs, 4H, CH_2 (1,5)); 6.63 (t, 2H, CH (3,7), $^4J_{1,3}$ = $^4J_{5,7=}$1.3 Hz). ^{13} C NMR ($CDCl_3$): δ 14.00 (CH_3(2a, 6a)); 15.04 (CH_3 in 4,8); 22.59 (CH_2 (2b, 6b)); 31.32 (CH_2 (2c,(6c)); 31.50 (CH_2 (2d, 6d)); 40.06 (CH_2 (1,5)); 124.72 (CH (3, 7)); 140.58, 140.68 ($C_{IV\ ar}$, 3a, 4a, 7a, 8a, 4, 8)). 148.69 (C (2,6)); IR ($CDCl_3$, cm^{-1}) ν 1601 (C═C). MS (Ei, *m*/*z* (%)): $M^{+\cdot}$ 294 (84); $M^{+\cdot}$ – Pr 251 (100); $M^{+\cdot}$ – 2Pr 208 (6) ; $M^{+\cdot}$ – (2Pr + 2 Me) 178 (3). *Anal.* Calc. for $C_{22}H_{30}$: C, 89.73; H, 10.27. Found: C, 89.59; H, 10.42%.

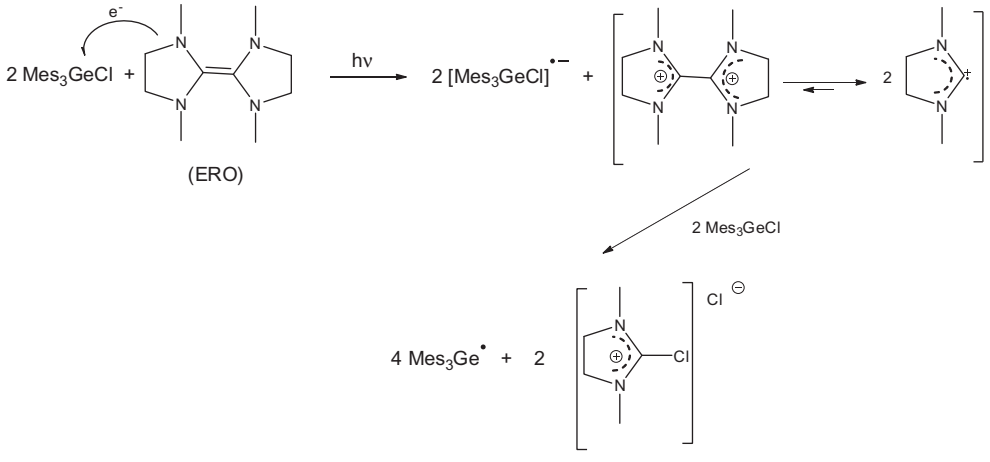
*2.2. Preparation of **If** (1-chloro-2,6-diethyl-4,5,8-trimethyl-3,7-dihydro-s-indacene)*



To a solution of 2,6-diethyl-4,8-dimethyl-2,3,6,7 tetrahydro-*s*-indacene-1,5-dione [3,20] (4.03 g, 14.05 mmol) in 100 ml of CH_2Cl_2 in a round-bottomed flask (500 mL) fitted with a nitrogen inlet and a reflux condenser was added at room temperature and with stirring PCl_5 (4.16 g, 20 mmol) in suspension in 80 mL of CH_2Cl_2. The mixture was stirred at reflux for 48 h and then cooled to 0 °C before water (100 mL) was added. After 2 extractions with 30 mL of CH_2Cl_2 and 30 mL of ether, the organic phase was treated with



Scheme 1.



Scheme 2.

50 mL of an aqueous solution of Na_2CO_3 (10%) and then was separated and dried over $MgSO_4$ for one night prior to removal of solvent on a rotary evaporator. The sticky residue (3.57 g) was analyzed by IR and GC/mass(EI), and identified as a mixture of initial diketone (GC/Mass, Ei, *m*/*z*: $M^{+\cdot}$ 270 (85%); $M^{+\cdot} - C_2H_4$ 242 (100%); IR (KBr): 1697 *v* C═O), compound intermediate **X** (Scheme 4) (GC/mass, Ei, *m*/*z*%: $M^{+\cdot}$ 324 (100%); $M^{+\cdot}$ – Cl 289 (63%)) and mainly compound **Y** (Scheme 4) (GC/mass, Ei, *m*/*z*%: $M^{+\cdot}$ 288 (100%); $M^{+\cdot} - C_2H_4$ 260 (83%). Since these compounds could not be easily separated, the whole mixture was dissolved in 50 mL of ether and treated with 10 mL of an aqueous solution of KOH (1%) to convert **X** to **Y**. The organic phase was dried over $MgSO_4$ for 48 h and then treated with an excess of methylmagnesium iodide (52.5 mmol, *i.e.* 35 mL of 1.5 M CH_3MgI in ether). The mixture was stirred and heated for 6 h at reflux, then cooled and hydrolyzed with HCl (37%) and extracted with 50 mL of ether. The organic

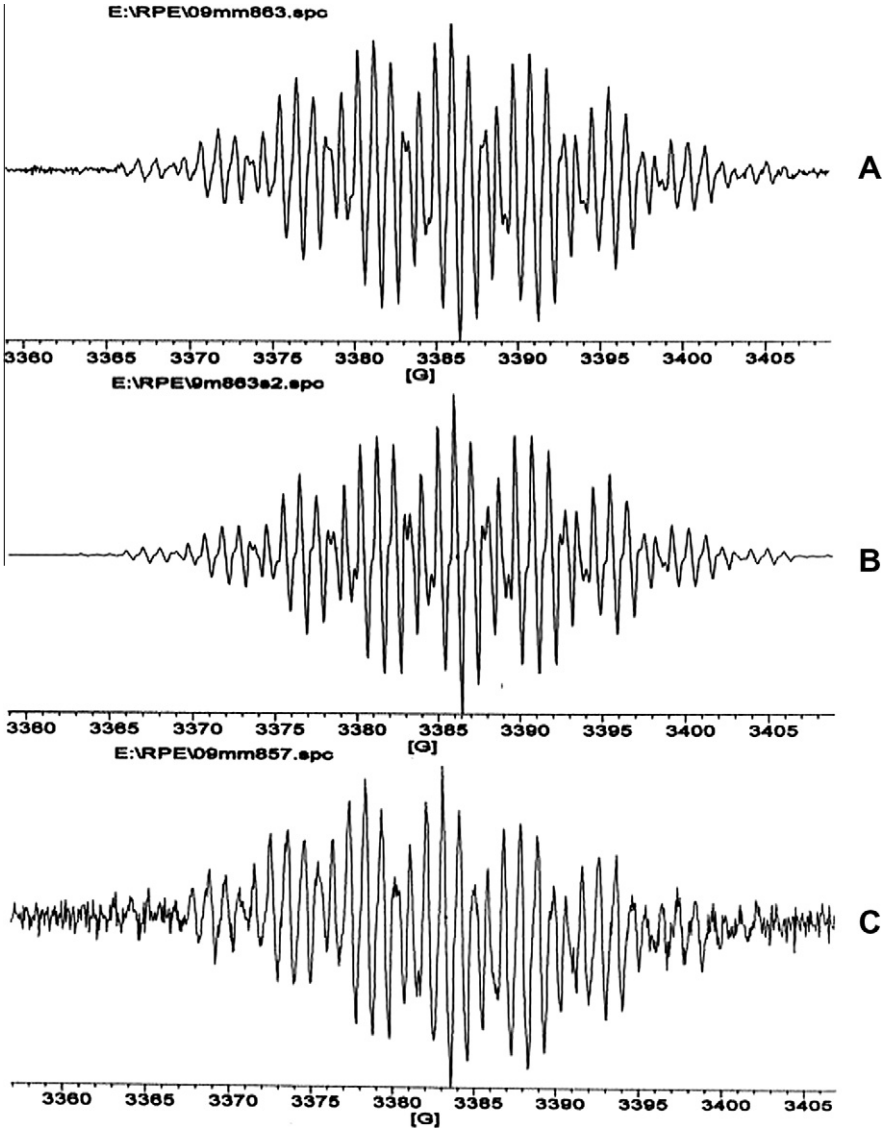


Fig. 1. ESR spectra of **IIIc**: (A) experimental spectrum obtained by reaction (iii) Scheme 1 (or 3a,b,d,e Scheme 3); (B) simulated spectrum L/G = 0.5, IW: 0.15; (C) experimental spectrum obtained by reaction (3f) Scheme 3.

phase was dried over $MgSO_4$ for one night prior to the removal of the solvent on a rotary evaporator. The residue was dissolved in 25 mL of hexane and stored in a deep freezer. After a few days, yellow brown large needles (0.73 g) were isolated by filtration. Yield 17%. A GC/mass analysis of a benzene solution of these needles shows that they are formed from a cocrystalization of two compounds: about 80% of the dissymmetric **If** (R = Et, R′ = Cl, R″ = Me), GC/mass, Ei, *m*/*z*%: $M^{+\cdot}$ 286 (100%); $M^{+\cdot}$ – Cl 251 (77%) and 20% of the symmetric hexaalkyl-*s*-indacene (R = Et, R′ = R″ = Me), GC/mass, Ei, *m*/*z*%: $M^{+\cdot}$ 266 [3]. These two compounds were separated by preparative HPLC on a column of silicagel microspheres 12 μm (20 g, Merck), pressure 10 bar, eluent: 90% petroleum ether and 10% of (CH_2Cl_2: 75%, ethylacetate: 25%). Each compound was crystallized and identified. The predominant one was identified as **If**.mp: 176–178 °C; ^{1}H NMR ($CDCl_3$): δ 1.15 (t, 3H, CH_3 (12), $^3J_{11,12}$ = 7.6 Hz); 1.18 (t, 3H, CH_3 (10), $^3J_{9,10}$ = 7.6 Hz); 2.26 (s, 3H, CH_3 on 5); 2.48 (q, 2H, CH_2(11), $^3J_{11,12}$ = 7.6 Hz); 2.51 (s, 3H, CH_3 on 4); 2.57 (q, 2H, CH_2(9), $^3J_{9,10}$ = 7.6 Hz); 2.65 (s, 3H, CH_3 on 8); 3.19 (s, 2H, CH_2 (7)); 3.22 (s, 2H, CH_2(3)). ^{13} C NMR ($CDCl_3$): δ 13.22 (C(10)); 14.19 (*C*H_3 on 5); 14.30 (C (12)); 14.47 (*C*H_3 on 8); 14.95 (*C*H_3 on 4); 21.63 (CH_2 (9, 11)); 37.54 (CH_2 (3)); 38.84 (CH_2(7)); 122.95 (C (4, 8)); 123.0 (C (6)); 126.70 (C (1)); 133.24 (C (5)); 135.04 (C (8a)); 139.58 (C (3a)); 141.48 (C (4a)); 141.99 (C (7a)); 142.58 (C (2)); 144.10 (C (6)). IR ($CDCl_3$, cm^{-1}) ν 1605, 1622 (C=C); MS (Ei, *m*/*z* (%)): $M^{+\cdot}$286 (100), $M^{+\cdot}$ – Cl 251 (77); $M^{+\cdot}$ – Me 271 (83); $M^{+\cdot}$ – (Cl + Et) 22 (31). *Anal.* Calc. for $C_{19}H_{23}Cl$: C, 79.56; H, 8.08; Cl, 12.36. Found: C, 79.37; H, 8.17, Cl, 12.24%.

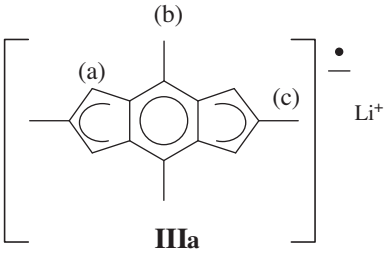
2.3. Preparation of ***IIa–f***

The dilithium derivatives of **Ia, b, d, e** [3], **Ic**, **If**, were prepared according to the general procedure described in reference [3].To the solution of **I** in THF was added at −80 °C and with stirring a solution of 2 M equivalents of BuLi (1.6 M in hexane). The solution was warmed to room temperature.

Monolithium derivative **IV** was prepared using the same procedure, from only 1 M equivalent of BuLi [3,6].

2.4. Preparation of III ***a–f*** and ***V***; ESR experiments

Each THF/pentane solution of dilithium derivatives **IIa–f** or monolithium derivative **IV** in approximately 0.04 M concentration was divided into three ESR quartz tubes (i), (ii) and (iii).



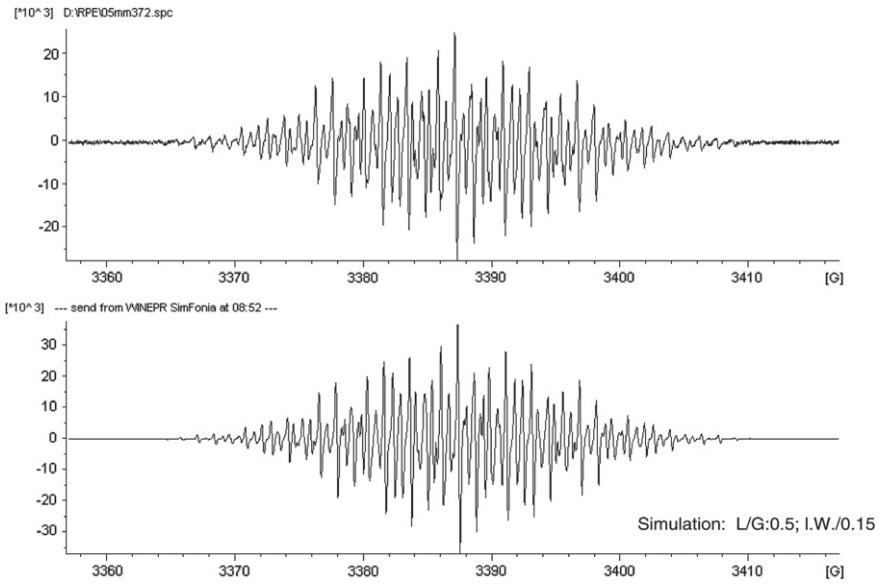
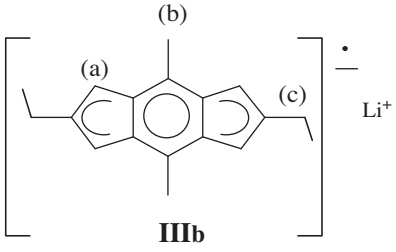


Fig. 2. ESR spectrum of **IIIa** and simulation.



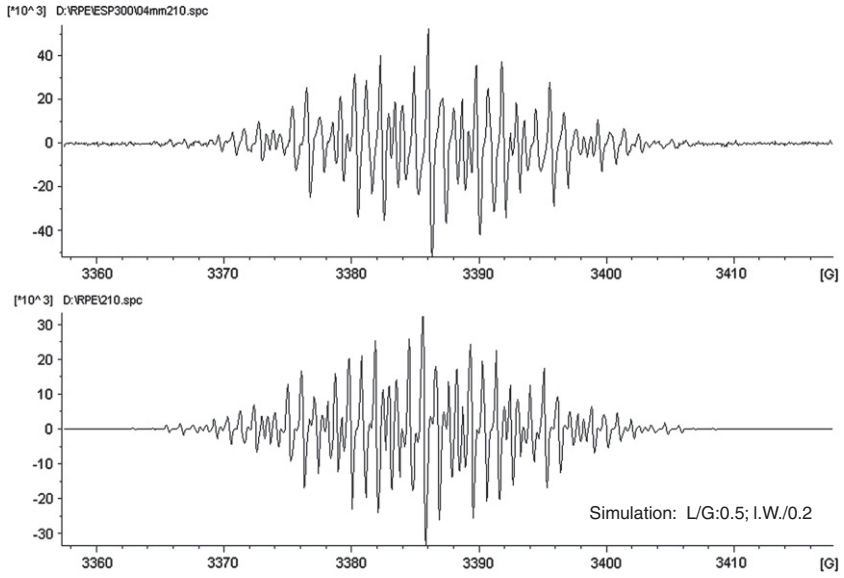


Fig. 3. ESR spectrum of **IIIb** and simulation.

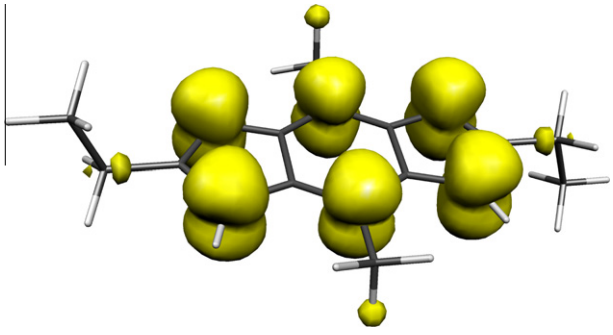


Fig. 4. Spin density localization for **IIIb**.

To (i) was added one volume of toluene and the sample was irradiated at 254 nm at 243 K in the ESR cavity.

To (ii) frozen in liquid nitrogen was added a solution of Cp_2Fe^+ BF_4^- in dichloromethane and the ESR spectrum was recorded at 243 K.

To (iii) frozen in liquid nitrogen was added a solution of the ERO in toluene and ESR spectra were recorded at 243 K (Figs. 1–5 and Table 1).

To a similar sample of **IIc** was added a solution of 1,3-dimethylimidazolidinium chloride[10] solubilized in THF/DMSO and at 243 K the ESR spectrum observed is the same as the spectrum of **IIIc** (Fig. 1). The remaining reaction mixture was then analyzed by GC/mass allowing the characterization of 1,1′,3,3′-tetramethyl bis-imidazolidine ($M^{+\cdot}$ = 198 amu).

3. Results and discussion

All radical anions presented here were prepared from the corresponding dimetallated derivatives of various polyalkyl-1,5-

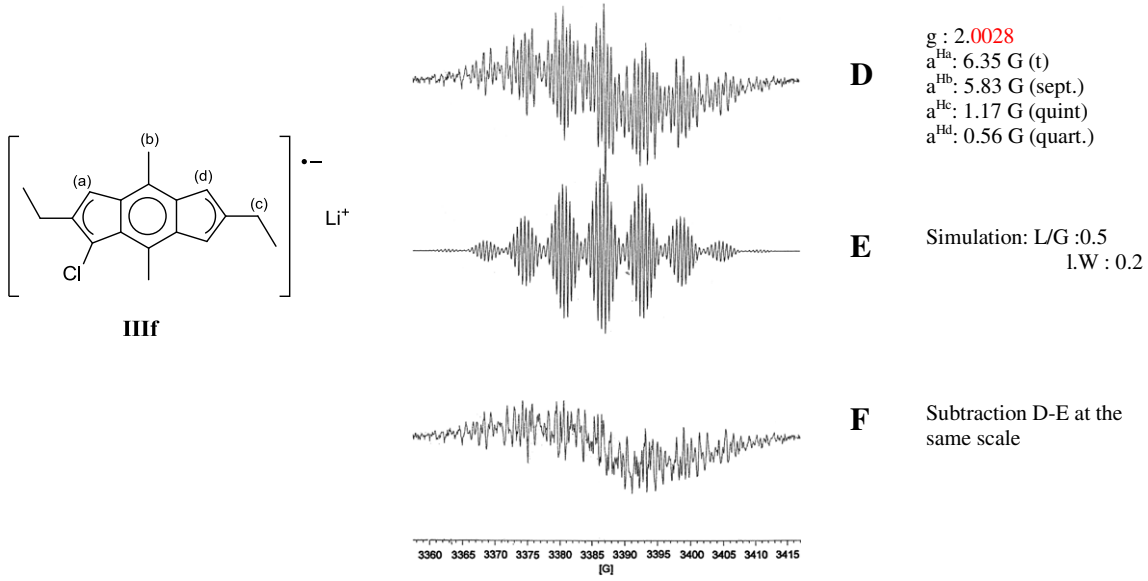
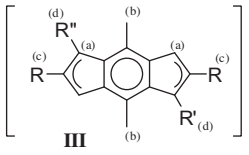


Fig. 5. ESR spectra of **IIIf**, (**D**) Experimental spectrum and ESR characteristics, (**E**) simulation, (**F**) subtraction (**D** and **E**) showing only background noise.

Table 1
ESR characteristics of **IIIa–e**.



IIIa: R = Me, R'=R"=H; **IIIb**: R= Et, R'=R"=H;
IIIc: R= nBu, R'= R"=H; **IIId**: R=Me, R'=R"=Me;
IIIe: R=Et, R'=R"=Me;

	g	a^{Ha}	a^{Hb}	a^{Hc}	a^{Hd}
IIIa	2.0029	5.75 (quint.)	3.75 (sept.)	1.30 (sept.)	–
III b	2.0028	5.76 (quint)	3.74 (sept.)	1.10 (quint.)	–
IIIc	2.0027	5.78 (quint.)	3.70 (sept.)	0.99 (quint.)	–
IIId	2.0028	8.93 (t)	5.70 (sept.)	1.33 (sept.)	3.25 (sept.)
IIIe	2.0028	10.06 (t)	4.85 (sept.)	1.00 (quint.)	2.70 (sept.)

dihydro-*s*-indacenes[3] or from chloropolyalkyl-1,5-dihydro-*s*-indacene using three different ways (Scheme 1).

The first method of preparation, (Scheme 1, i), has often been reported in the literature [21–25]. The second way, (Scheme 1, ii) occurs by a chemical oxidation of **II** using $[Cp_2Fe]^+$ $[BF_4]^-$. The third, a very simple and useful method (Scheme 1, iii) proceeds by a SET/retro – SET process (SET = Single Electron Transfer) initiated from the reaction between the dilithium derivative **II** and an electron rich olefin (ERO); it generates radical anions continuously in the middle and is detailed in Scheme 3.

The ERO has been used before to produce metal-centred radicals, by reduction of the metal in group 14 metal chlorides (MCl), followed by chlorine abstraction [24,26,27] (Scheme 2) and also to produce organic radicals [10] and anion radicals [28,29]. The initial SET processes were also established in the case of various compounds electron acceptors [10,28–30].

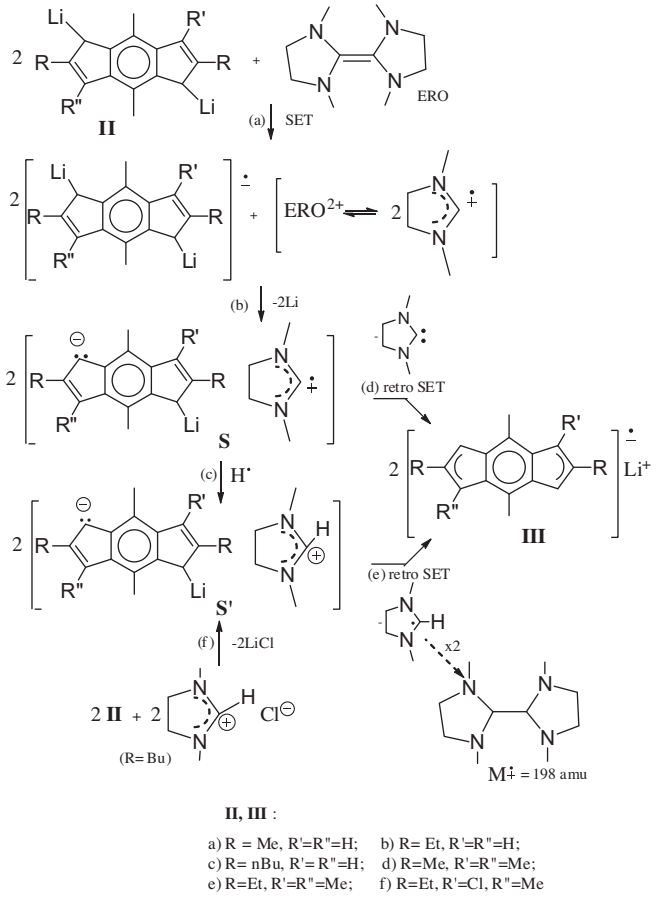
Scheme 3 details the reaction of ERO with polyalkyl-1,5-dilithio-*s*-indacenyl compounds.

In this monoelectronic reaction process (Scheme 3), the initial SET leads to the formation of the salt (**S**) which could directly decompose (reaction 3d) leading to the polysubstituted-*s*-indacene anion radical **III**. Although reaction 3d is expected, reaction 3e (Scheme 3) is probable as already stated [10] because of the great ability of the diazolidinium intermediate to pick an hydrogen from the reaction middle (reaction 3c).The same mechanism explains the formation of polyalkyl-hydro-*s*-indacenyl radicals from monolithiated analogs using the same method [10] and is supported by the fact that when the salt (**S′**) (Scheme 2) is generated in another way by addition of 1,3-dimethylimidazolidinium chloride on **II** (reaction 3f), it also decomposes with formation of the anion radical **III** (Fig. 1) and the corresponding dihydroERO ($M^{+\cdot}$ = 198 amu).

The ESR characteristics of the paramagnetic species **III a–f** were established and verified with the help of theoretical simulations of the spectra (Figs. 2 and 3 and Table 1). In each case, the observed spin distribution, verified by theoretical calculations, show that, in a 1/1 toluene/THF solution, the ESR spectra of **IIIa–e** (Figs. 2 and 3 and Table 1) are consistent with the structure of an anion radical [9,31], all of which present a very symmetrical distribution of spin (e.g. Fig. 4 for **IIIb**), also showing that the localization of the odd electron does not go farther than the methylene group of the R side chain as observed experimentally (Fig. 3 and Table 1). The g values are in the expected range for similar anion radicals [9,31].

In order to introduce a dissymmetry on the spin distribution, the dissymmetric indacene **If** (R = R″ = Me, R′ = Cl) was prepared (Scheme 4) by chlorination (PCl_5) and subsequent methylation (MeMgI) of the corresponding carbonyl groups of the 2,6-diethyl-4,8-dimethyl-2,3,6,7-tetrahydro-s-indacene-1,5-dione [3,20].

Chlorination of the carbonyl appeared selective and limited to one carbonyl group even in the presence of an excess of phosphorus pentachloride. One possible explanation is that the spontaneous elimination of HCl [32] (Scheme 4, ii) induces the protonation of the second carbonyl preventing its chlorination.



II, III :

a) R = Me, R'=R"=H; b) R= Et, R'=R"=H;
c) R= nBu, R'= R"=H; d) R=Me, R'=R"=Me;
e) R=Et, R'=R"=Me; f) R=Et, R'=Cl, R"=Me

Scheme 3.

The methylation of the chloroketone **Y** (Scheme 4, iii)) then gives the expected chloropolyalkyl-*s*-indacene **If** through dehydration of the transient alcohol in acidic medium. This compound was

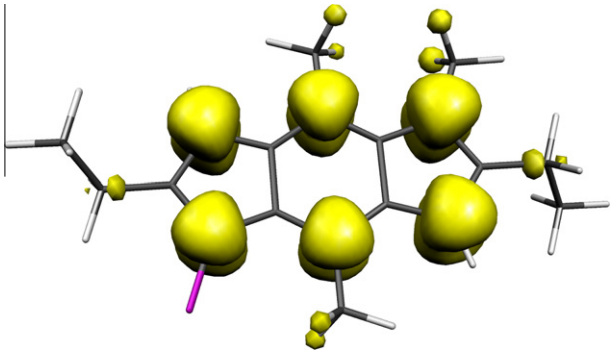


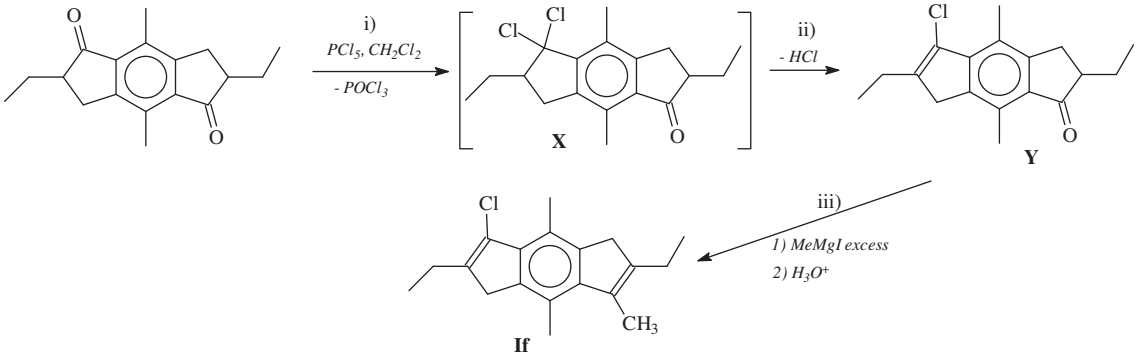
Fig. 6. Spin distribution for **IIIf**.

dilithiated according to Scheme 1 and converted to the anion radical **IIIf** (Fig. 5) following Scheme 1, iii. The anion radical **IIIf** appears homogeneously delocalized. The hyperfine coupling with chlorine is not observed which is consistent with the calculated spin distribution (Fig. 6).

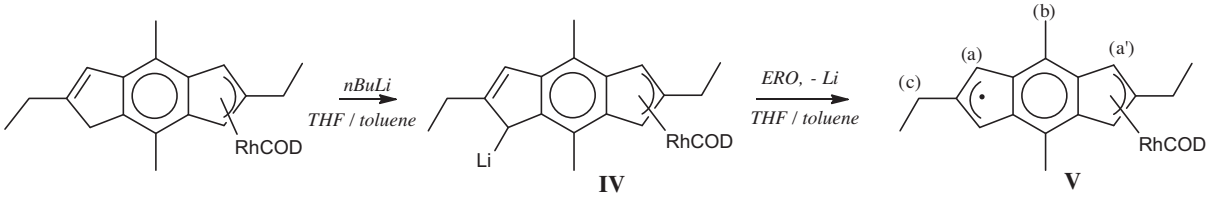
On the contrary, the metallated polyalkyl-*s*-indacenyl radical **V** (Scheme 5) [10] which cannot dissociate into the corresponding metallated anion radical presents an unsymmetrical spin distribution (Fig. 7) in accordance with the calculated spin distribution, the odd electron being mainly distributed on the cyclopentadienyl ring opposite to the Rhodium metal and also on the aromatic system.

4. Conclusion

It is now established within the indacenyl series that the SET/RetroSET reaction between the organolithium compounds studied and an electron rich olefin constitutes a general route to the corresponding radicals [10] and radical anions. In polyalkyl- and chloropolyalkyl-*s*-indacenyl anion radicals the donor effects of the alkyl substituents or of chlorine (mesomer donor) on the *s*-indacene



Scheme 4.



Scheme 5.

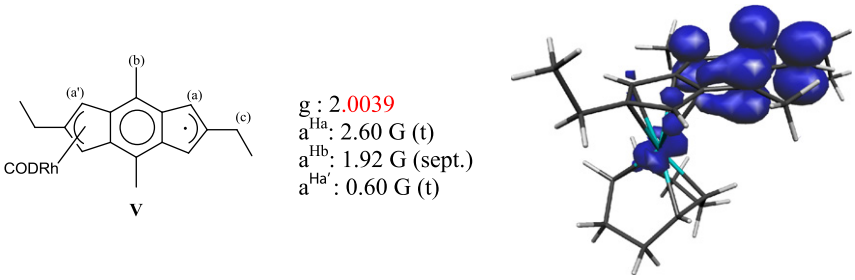


Fig. 7. ESR characteristics and spin distribution of **V**.

conjugated system, leads to a symmetric homogeneous spin localization which induces a coupling of the odd electron with the proton of the rings and the protons in alpha position on the side chains. On the contrary, in the case of Rhodium-COD polyalkyl-*s*-indacenyl radical **V**, the influence of the metal induces a non symmetric repartition of spin mainly located in the opposite Cp ring, regardless of the small contribution from rhodium atom compared to the Indacene ligand.

The easy formation of radicals and anion-radicals from metallated polyalkyl-*s*-indacene derivatives evidenced here opens the route to new anion-radicals from binuclear complexes of polyalkyl s-indacene; the study of which, now in progress, could be a help in the understanding of the catalytic activity of such complexes.

Acknowledgments

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