Letter

Easy access to unprecedented mixed functionalized dihydrofullerenes $C_{60}RH$ and $C_{60}RR'$: the $C_{60}{}^{2-}$ anion route

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Functionalized mixed dihydrofullerenes $C_{60}RH$ and $C_{60}RR'$ are easily obtained from reactions between $C_{60}{}^{2-}$ anion and halo derivatives RX and R′X. The key step consists in the selective reaction of the intermediate $[C_{60}R]^-$ ion, as soon as it is formed, with either CF_3CO_2H or R′X. This process is made possible thanks to the very fast single electron transfer (SET) reaction between $C_{60}{}^{2-}$ and RX. Functionalized dihydrofullerenes $C_{60}RH$ thus prepared are also shown to be very good starting compounds for obtaining various $C_{60}RR'$ derivatives.

The continuously expanding interest in the chemistry of C_{60},[1] since the production of this compound on the macroscopic scale,[2] arises in particular from the outstanding properties exhibited by C_{60} organoderivatives in various fields such as photovoltaïsm,[3] nonlinear optics,[4] artificial photosynthesis,[5] organic materials,[6] biology and medicine.[7]

In most cases so far, the functionalization of C_{60}, due to its electron-deficient polyolefinic character,[8] is achieved through two main pathways:[9] nucleophilic additions, as exemplified by the Bingel cyclopropanation reaction,[10] and cycloadditions among which [4 + 2] Diels–Alder and pyrrolidino[60]fullerene formation[11] processes are most often used. Recently the latter synthesis strategy was extended to the formation of isoxazolo[60]fullerenes[12a] and pyrazolino[60]fullerenes.[12b] On the other hand, as might be expected, reactions of organic electrophiles are rare and require very specific conditions.[13]

In this context, our interest was first focused on the reaction of $C_{60}{}^{2-}$ anion[14] with organic electrophiles, following first results reported by Kadish *et al.*[15] Recently we have shown that $C_{60}{}^{2-}$ anion can be easily and selectively generated in acetonitrile from reduction of C_{60} by means of excess sodium methanethiolate. Then, after addition of monoiodo- or diiodoalkanes, RI or $I(CH_2)_nI$ ($n = 3, 4$), into this medium the expected alkylation of $C_{60}{}^{2-}$ took place easily, leading to the corresponding adducts $C_{60}R_2$ or fused cycloadducts $C_{60}(CH_2)_n$ in very good yields.[16] Compared to the results of Kadish *et al.*, two points emerged from our work: the very simple chemical generation of $C_{60}{}^{2-}$ anion and the much higher regioselectivity observed in the formation of the adducts $C_{60}Me_2$, the 1,2-:1,4-isomer molar ratio being 9:1 instead of 1.4:1. We also extended our process to various halogenated derivatives possessing another functional group, thus giving rise to new functionalized C_{60} derivatives, such as the fused cyclopentanone $C_{60}(CH_2)_2CO$, which can be used as new building blocks in C_{60} chemistry.[17]

These results prompted us to study the following problem: would it be possible, starting from $C_{60}{}^{2-}$ anion, to obtain mixed adducts $C_{60}RR'$ in which the R and R′ groups may be different functional groups? So far, to our knowledge, only mixed alkylation of $C_{60}{}^{2-}$ has been reported in the literature.[18] It was shown in this work that $C_{60}({}^tBu)(CH_2Ph)$ and $C_{60}({}^tBu)(H)$ compounds can be isolated in a two-step process. In this case, in the first step the reaction between $C_{60}{}^{2-}$ anion and *tert*-butyl iodide (${}^tBuI$) stops when the $[C_{60}{}^tBu]^-$ ion is formed because of the bulkiness of the ${}^tBu$ group. Then the reaction is achieved upon addition of benzyl bromide ($PhCH_2Br$) or trifluoroacetic acid.

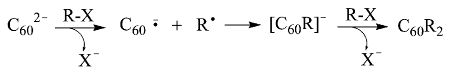
Despite its great interest, the latter process[18] does not appear to be entirely consistent with the synthesis of any $C_{60}RR'$ compound, owing to the needed bulky character of the first R group. More interestingly, the whole mechanism of the reaction leading to the $C_{60}R_2$ adduct as proposed in this paper[18] (Scheme 1) might provide another hypothesis, unexplored so far.

In this mechanism, the two R–X moieties are successively involved in two different pathways: the first one in a single electron transfer (SET) and the second one, after the formation of the $[C_{60}R]^-$ ion, in a nucleophilic substitution (S_N2). Moreover, if we wish to obtain a mixed $C_{60}RR'$ adduct, obviously it is necessary to stop the reaction after the formation of the $[C_{60}R]^-$ ion before a second R′X derivative is used.

This latter condition might be fulfilled if the rate of the SET step is higher than that of the S_N2 step, as it can be reasonably assumed.

We now wish to report that mixed functionalized dihydrofullerenes $C_{60}RH$ and $C_{60}RR'$ are easily obtained starting from $C_{60}{}^{2-}$ anion.

In order to check this hypothesis, we have prepared functionalized dihydrofullerenes $C_{60}RH$. For this purpose, trifluoroacetic acid was added into the reaction mixture when $[C_{60}R]^-$ ion is just formed in the reaction between $C_{60}{}^{2-}$ anion and an RX derivative, this moment being more or less precisely determined owing to the colour change in the medium (deep red at the beginning due to $C_{60}{}^{2-}$ ion, turning to dark greenish



Scheme 1 Reaction mechanism between $C_{60}{}^{2-}$ anion and a RX derivative.

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Table 1 Formation of functionalized dihydrofullerenes $C_{60}RH$ **4**–**6**

Starting compound RX	Reaction time with C_{60}^{2-}/min	$C_{60}RH$ (% yield)
1 (R = CH_2CO_2Me, X = Br)	2–3	**4** (35)
2 (R = CH_2CO_2Et, X = Br)	2–3	**5** (35)
3 [R = $CH_2P(O)(OEt)_2$, X = I]	2	**6** (10)
	5	**6** (33)
	10	**6** (24)

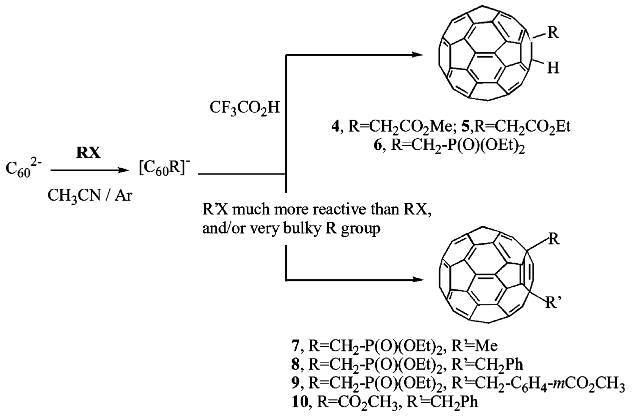
upon formation of $[C_{60}R]^-$ ion as already observed when R is an alkyl or alkynyl group[19]). On the other hand, in these experiments the halo derivatives were the bromoacetates $BrCH_2CO_2Me$, **1**, and $BrCH_2CO_2Et$, **2**, and diethyl iodomethylphosphonate, $ICH_2–P(O)(OEt)_2$, **3**.

The results are particularly striking (Table 1). $C_{60}(CH_2CO_2Me)(H)$, **4**, and $C_{60}(CH_2CO_2Et)(H)$, **5**, are formed in 35% yield when CF_3CO_2H is added after only a 2–3 min reaction time between C_{60}^{2-} anion and bromoacetates **1** or **2** at room temperature. For a slightly longer reaction time (*ca.* 4 min), a very small amount of adduct $C_{60}(CH_2CO_2R)_2$ (R = Me, Et) could be observed (column chromatography), suggesting that after 3 min $[C_{60}(CH_2CO_2R)]^-$ ion is progressively involved in the final nucleophilic substitution (Scheme 1), which may become the major process. By comparison, starting from ester **1** or **2** the reaction requires *ca.* 10 h, giving rise to a mixture of the 1,2- and 1,4-adducts $C_{60}(CH_2CO_2R)_2$ in *ca.* 20% yield.[20] Similar results are observed starting from $ICH_2P(O)(OEt)_2$, **3**. The best yield (33%) of $C_{60}[CH_2P(O)(OEt)_2](H)$, **6**, is obtained after 5 min reaction time, this yield being lower for either a shorter reaction time (2 min, 10%) or a longer one (10 min, 24%). However, in the latter case no adduct $C_{60}[CH_2P(O)(OEt)_2]_2$ could be clearly identified in the reaction products.

These results appear to be very interesting, since for the first time functionalized dihydrofullerenes $C_{60}RH$ are easily obtained in good yields through a simple process. Previously, the usual route to $C_{60}RH$ compounds proceeded from reaction between C_{60} and organometallic compounds RM (M = Li, MgBr),[19,21] which precludes the presence of functional groups such as esters in the structure of RM. On the other hand, the synthesis of $C_{60}RH$ derivatives in which the R group bears an ester functionality, as in $C_{60}(CO_2Me)(H)$[22] and $C_{60}(CH_2CO_2Et)(H)$, **5**,[23] requires very particular experimental conditions.

We also observed that reaction of phosphonate ester **3** with C_{60}^{2-} anion leads to hardly any adduct $C_{60}[CH_2P(O)(OEt)_2]_2$ at room temperature, even after a prolonged reaction time, probably because of the substantial steric effect of the $CH_2P(O)(OEt)_2$ group. This result prompted us to investigate one-pot processes in which, after reaction between C_{60}^{2-} and phosphonate **3**, a less hindered second halo derivative R′X was added to the reaction mixture when $\{C_{60}[CH_2P(O)(OEt)_2]\}^-$ ion is formed at maximum (thanks to the colour change from red to green, see above). As expected, we observed the formation of the new adducts $C_{60}[CH_2P(O)(OEt)_2]R'$, **7**–**9**, in moderate yields (10–20%) (Scheme 2). These compounds corresponded to a mixture of 1,2- and 1,4-adducts when R′ = Me (**7**) and pure 1,4-adducts when R′ = CH_2Ph (**8**) or $CH_2–C_6H_4–m\text{-}CO_2Me$ (**9**), as clearly established from ^1H NMR analysis.

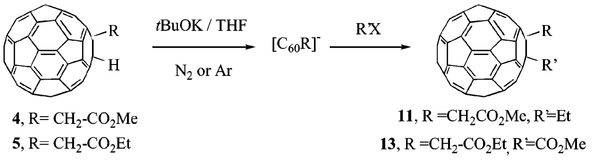
The nature of the halogen in the RX derivative may also be considered. Whereas benzyl bromide ($PhCH_2Br$) easily reacts at room temperature with C_{60}^{2-} anion in benzonitrile, thus giving rise to pure 1,4-adduct $C_{60}(CH_2Ph)_2$ in 60% yield,[15b] benzyl chloride ($PhCH_2Cl$) leads only to $[C_{60}CH_2Ph]^-$ anion after reaction with C_{60}^{2-} anion in THF upon heating at 50 °C for 3 h.[24] This latter result has been reproduced under our conditions; further addition into the reaction medium of a more reactive halo derivative such as methyl chloroformate ($ClCO_2Me$) leads to the expected pure 1,4-adduct $C_{60}(CH_2Ph)(CO_2Me)$, **10**, in 15% yield.



Scheme 2 Formation of dihydrofullerenes $C_{60}RH$ **4**–**6** and $C_{60}RR'$ **7**–**10** in one-pot processes.

All of these results show that in one-pot processes the yield of the final mixed adduct $C_{60}RR'$ is strongly dependent on the relative reactivities of both the RX and R′X derivatives. Accordingly, another route has also been explored, starting from functionalized dihydrofullerenes $C_{60}RH$ as previously obtained. In these experiments, $C_{60}(CH_2CO_2R'')(H)$, **4** (R″ = Me) or **5** (R″ = Et), was first transformed into the corresponding anion $[C_{60}(CH_2CO_2R'')]^-$ upon reaction with ^{t}BuOK in THF according to the method of Komatsu *et al.*[19b] Then this ion was further reacted with iodoethane (EtI), benzyl bromide ($PhCH_2Br$) or methyl chloroformate ($ClCO_2Me$). As might be expected, the corresponding pure 1,4-adducts $C_{60}(CH_2CO_2Et)(Et)$, **11**, $C_{60}(CH_2CO_2Et)(CH_2Ph)$, **12**, and $C_{60}(CH_2CO_2Me)(CO_2Me)$, **13**, were obtained in good yields (50–60%; Scheme 3).

The ^1H NMR spectra of 1,4-dihydrofullerenes $C_{60}[CH_2P(O)(OEt)_2](CH_2Ph)$, **8**, $C_{60}[CH_2P(O)(OEt)_2](CH_2–C_6H_4–m\text{-}CO_2CH_3)$, **9**, and $C_{60}(CH_2CO_2Et)(CH_2Ph)$, **12**, exhibit particular features. In these spectra, the two signals (AB system due to the diastereotopic hydrogens) arising from the methylene group bonded to both the C_{60} core and to the $P(O)(OEt)_2$ or the CO_2Et moieties are observed at an unexpectedly low chemical shift (mean values: $\delta = 2.5$ for **8**, 2.63 for **9** and 2.85 for **12**, see Fig. 1), whereas the same methylene group in other 1,4-dihydrofullerenes provides the AB pattern at $\delta = 3.56$ in $C_{60}[CH_2P(O)(OEt)_2](CH_3)$, **7**, 3.85 in $C_{60}(CH_2CO_2Et)(C_2H_5)$, **11** (Fig. 2), and 4.18 in $C_{60}(CH_2CO_2Me)(CO_2Me)$, **13** (Fig. 3), as can be normally expected. These results suggest a significant influence exerted by the CH_2Ph group. The shielding increase observed in compounds **8**, **9** and **12** might then be accounted for if we consider a possible magnetic anisotropy effect due to the phenyl group[25] from the CH_2Ph moiety towards this methylene group. CPK molecular models of a cyclohexane ring in a boat form substituted in the 1,4-positions by the same groups as in compounds **8**, **9** and **12** effectively showed that this methylene group can be very close to the phenyl group in a given conformation, thus lying in the shielding region of the phenyl ring.



Scheme 3 Formation of dihydrofullerenes $C_{60}RR'$ **11**–**13**.

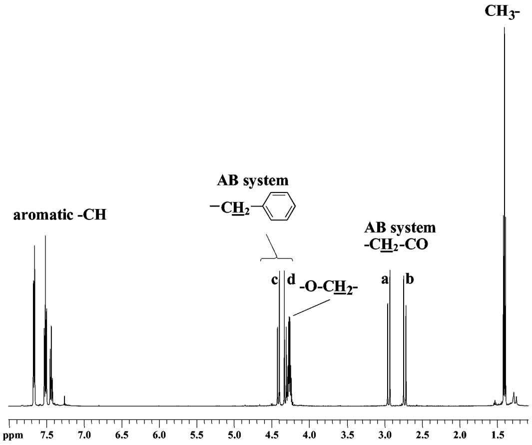


Fig. 1 ^{1}H NMR spectrum of compound **12** (solvent CS_2–$CDCl_3$).

In conclusion, we have demonstrated that C_{60}^{2-} anion is a starting moiety of choice for obtaining mixed functionalized $C_{60}RH$ and $C_{60}RR'$ derivatives from reactions with various RX and R′X compounds bearing a second functionality. In particular, we have shown that $[C_{60}R]^-$ anion can be selectively used as soon as it is formed from the reaction between C_{60}^{2-} and an RX compound. Accordingly, functionalized dihydrofullerenes $C_{60}RH$ can be obtained in good yields through a simple overall process, whereas the preparation of such dihydrofullerenes was rather difficult so far. Moreover, several routes have been explored for obtaining mixed functionalized $C_{60}RR'$ compounds from the intermediate $[C_{60}R]^-$ anion. In this latter case, the best results are observed when isolated $C_{60}RH$ derivatives are used as starting compounds. We are currently studying the scope and limitations of these different reactions in the search of new C_{60}-based covalent assemblies in the field of organic materials.

Experimental

General procedure for one-pot processes from C_{60}^{2-} anion

Reactions mentioned in this section were carried out in a glove box under argon.

A large excess (10–20 equiv) of sodium methanethiolate was added to a carefully deoxygenated suspension of C_{60} (150 mg, 0.21 mmol) in dry acetonitrile (125 mL). The flask was stoppered by a septum and the mixture was stirred. Progressively a deep red colour developed in the medium, due to the formation of C_{60}^{2-} anion, which was usually achieved within 24 h. The reaction mixture was filtered off, in order to eliminate unreacted C_{60} and most of the excess CH_3SNa. Then a large excess (*ca.* 20 equiv) of the halogenated derivative RX, either as a neat liquid or dissolved in dry acetonitrile when solid, was added to the resulting solution through a syringe and this mixture was stirred, the time and the temperature of this being dependent on the chosen process (see the text above). Then either trifluoroacetic acid or an excess of the R′X derivative was added through a syringe as above. In the first case, the formation of dihydrofullerenes $C_{60}RH$, **4**–**6**, was immediate, while in the second case the reaction mixture was stirred 24 h to give $C_{60}RR'$, **7**, 5 min for **8**, and 14 h for **9** and **10**.

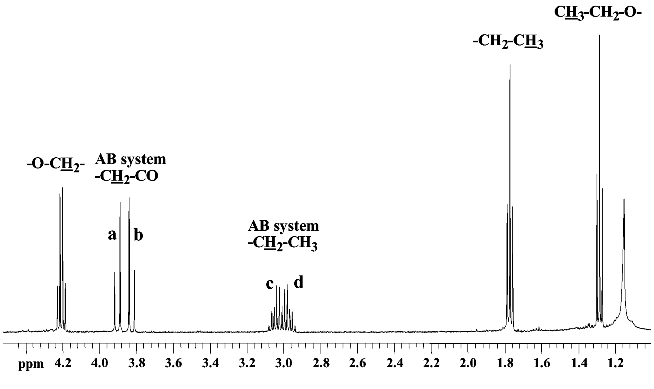


Fig. 2 ^{1}H NMR spectrum of compound **11** (solvent CS_2–C_6D_6).

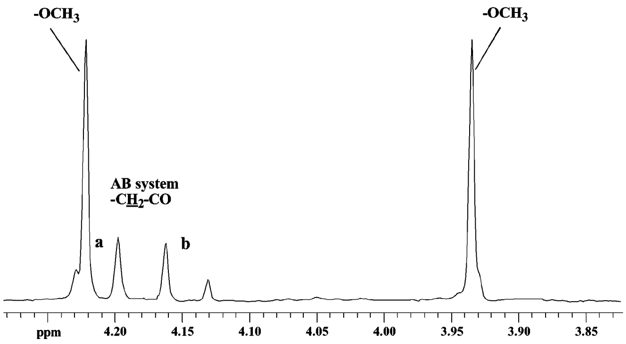


Fig. 3 ^{1}H NMR spectrum of compound **13** (solvent CS_2–$CDCl_3$).

After reaction, the obtained solid products were filltered off, washed with MeCN, isolated through column chromatography, and identified from MS and NMR analyses.

$C_{60}(CH_2CO_2CH_3)(H)$, 4. ^{1}H NMR (500 MHz, CS_2–$CDCl_3$) δ 4.09 (s, 3H), 4.47 (s, 2H), 6.80 (s, 1H); ^{13}C NMR (125.75 MHz) δ 49.20, 51.97, 59.09, 60.92, 136.23, 136.56, 140.01, 140.10, 141.45, 141.47, 141.77, 141.90, 142.01, 142.37, 142.41, 143.05, 144.32, 144.62, 145.16, 145.25, 145.41, 145.46, 145.63, 145.99, 146.02, 146.18, 146.24, 146.74, 147.08, 147.35, 153.16, 153.69, 170.07; MALDI-TOF-MS calcd. for $C_{63}H_6O_2$: 794, found 794 for $M^{-\bullet}$.

$C_{60}[CH_2P(O)(OEt)_2](H)$, 6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.52 (t, 6H, $^3J_{HH} = 7.0$ Hz, OCH_2–CH_3), 3.93 (d, 2H, $^2J_{HP} = 17.0$ Hz, CH_2P), 4.46 (m, 4H, OCH_2–CH_3), 7.12 (s, 1H, C_{60}–H); ^{13}C NMR (125.75 MHz) δ 16.66 (CH_3), 42.75 (d, $^1J_{CP} = 138.7$ Hz, CH_2P), 59.39 (sp^3 C_$_{60}$–H), 59.9 (d, $^2J_{CP} = 3.5$ Hz, sp3 C_$_{60}$–CH_2), 62.62 (d, $^2J_{CP} = 6.8$ Hz, OC_H$_2$–CH_3), 136.16, 136.23, 140,15, 140.31, 141.66, 141.68, 142.15, 142.34, 142.6, 142.64, 144.57, 144.90, 145.41, 145.43, 145.50, 145.62, 146.27, 146.28, 146.43, 147.08, 153.85 and 154.79 (the latter two signals, due to C_{60} sp^2 carbons, both correlated with H bonded to the C_{60} core); ES-MS calcd for $C_{65}H_{13}O_3P$: 872.0657, found 872.0602 for $M^{-\bullet}$; calcd for $C_{65}H_{12}O_3P$: 871.0506, found 871.0524 for $[M–H]^-$.[26]

$C_{60}[CH_2P(O)(OEt)_2](CH_3)$, 7. **7** was obtained as a mixture of inseparable 1,2- and 1,4-isomers, relative molar proportion was 30/70. ^{1}H NMR (500 MHz, $CDCl_3$) 1,2-isomer: δ 1.39 (t, 6H, $^3J_{HH} = 7.1$ Hz, OCH_2–CH_3), 3.45 (s, 3H, C_{60}–CH_3), 4.10 (d, 2H, $^2J_{HP} = 18.4$ Hz, C_{60}–CH_2), 4.30 (q, 4H, $^3J_{HH} \cong {}^3J_{HP} \cong 7$ Hz, OCH_2–CH_3); 1,4-isomer: 1.41 (t, 6H, $^3J_{HH} = 7.1$ 7.1 Hz, OCH_2–CH_3), 2.84 (s, 3H, C_{60}–CH_3), 3.52 (dd, 1H, $^2J_{HP} = 17.2$ Hz, $^2J_{HH} = 15.5$ Hz, C_{60}–CH_2), 3.62 (dd, 1H, $^2J_{HP} = 16.9$ Hz, $^2J_{HH} = 15.5$ Hz, C_{60}–CH_2), 4.35 (q, 4H, $^3J_{HH} \cong {}^3J_{HP} \cong 7$ Hz, O–CH_2–CH_3); MALDI-TOF-MS calcd. for $C_{66}H_{15}O_3P$: 886, found 886 for $M^{-\bullet}$.

$C_{60}[CH_2P(O)(OEt)_2](CH_2Ph)$, 8. Pure 1,4-isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36 and 1.37 (dt, 6H, $^3J_{HH} = 7.2$ Hz), 2.45 (dd, 1H, $^2J_{HP} = 28.1$ Hz, $^2J_{HH} = 15.5$ Hz, C_{60}–CH_2P), 2.49 (dd, 1H, $^2J_{HP} = 29.4$ Hz, $^2J_{HH} = 15.5$ Hz, C_{60}–CH_2P), 4.21 (q, 4H, $^3J_{HH} \cong {}^3J_{HP} \cong 7.2$ Hz, OCH_2–CH_3), 4.31 (d, 1H, $^2J_{HH} = 13.1$ Hz, CH_2Ph), 4.40 (d, 1H, $^2J_{HH} = 13.1$ Hz, CH_2Ph), 7.51 (t, 1H, *p*-Ph), 7.57 (t, 2H, *m*-Ph), 7.70 (d, 2H, *o*-Ph); ^{13}C NMR (125.75 MHz) δ 16.49 ($^3J_{CP} = 6.5$ Hz, CH_2–CH_3), 37.92 ($^1J_{CP} = 140.6$ Hz, CH_2–P), 48.97 (sp^3 C_{60}), 53.02 ($^2J_{CP} = 4.4$ Hz, sp^3 C_{60}), 60.56 (CH_2–Ph), 62.09 ($^2J_{CP} = 6.6$ Hz, OCH_2–CH_3), 128.00, 128.82, 131.17, 136.33, 137.75, 138.57, 139.06, 140.80, 141.52, 142.13, 142.24, 142.36, 142.57, 142.65, 142.99, 143.09, 143.19, 143.27, 143.29, 143.36, 143.54, 143.68, 143.86, 144.04, 144.07, 144.16, 144.31, 144.34, 144.36, 144.42, 144.49, 144.57, 144.63, 144.66, 144.79, 144.87, 145.08, 145.20, 145.41, 145.57, 145.59, 146.94, 146.97, 147.00, 147.05, 147.09, 147.24, 148.18, 148.21, 148.69, 148.72, 150.57, 157.76; MALDI-TOF-MS calcd. for $C_{72}H_{19}O_3P$: 962, found 962 for $M^{-\bullet}$.

$C_{60}[CH_2P(O)(OEt)_2](CH_2–C_6H_4–m\text{-}CO_2CH_3)$, 9. Pure 1,4-isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.37 and 1.38 (dt, 6H, OCH_2–CH_3), 2.56 (dd, 1H, $^2J_{HP} = 30.5$ Hz, $^2J_{HH} = 15.2$ 15.2 Hz, CH_2P) 2.70 (dd, 1H, $^2J_{HP} = 31.0$ Hz, $^2J_{HH} = 15.2$ Hz, CH_2P), 3.98 (s, 3H, OCH_3), 4.20 (m, 4H, OCH_2–CH_3), 4.38 (d, 1H, $^2J_{HH} = 13.1$ Hz, CH_2–Ph), 4.44 (d, 1H, $^2J_{HH} = 13.1$ Hz, CH_2–Ph), 7.63 (t, 1H, *m*-Ph), 7.90 (d, 1H, *p*-Ph), 8.15 (d, 1H, *o*-Ph), 8.34 (s, 1H, *o*-Ph); ^{13}C NMR (125.75 MHz) δ 16.45 ($^3J_{CP} = 6.3$ Hz, OCH_2–CH_3), 38.32 ($^1J_{CP} = 140.7$ Hz, CH_2P), 48.65 (sp^3 C_{60}), 52.20 (OCH_3), 52.96 ($^2J_{CP} = 3.9$ Hz, sp^3 C_{60}), 60.09 (CH_2–Ph), 62.17 ($^3J_{CP} = 7.5$ Hz, OCH_2–CH_3), 128.81, 129.19, 130.75, 131.94, 135.62, 136.73, 137.92, 138.58, 138.85, 139.00, 140.86, 141.58, 142.22, 142.33, 142.54, 142.65, 142.68, 143.03, 143.11, 143.31, 143.59; 143.77, 144.06, 144.31, 144.33, 144.46, 144.54, 144.59, 144.62, 144.86, 145.13, 145.23, 145.61, 145.62, 146.88, 146.96, 147.07, 147.25, 148.10, 148.18, 148.73, 150.22, 152.00, 152.08, 155.64, 157.05, 166.81 (C=O); MALDI-TOF-MS calcd for $C_{74}H_{21}O_5P$: 1020, found 1020 for $M^{-\bullet}$.

$C_{60}(CO_2CH_3)(CH_2Ph)$, 10. ^{1}H NMR (500 MHz, CS_2–$CDCl_3$) δ 4.18 (s, 3H, CH_3), 4.39 (d, 1H, $^2J_{HH} = 12.9$ Hz, CH_2–Ph), 4.5 (d, 1H, $^2J_{HH} = 12.9$ Hz, CH_2–Ph), 7.36 (t, 1H, *p*-Ph), 7.43 (t, 2H, *m*-Ph) 7.61 (d, 2H, *o*-Ph); MALDI-TOF-MS calcd for $C_{69}H_{10}O_2$: 870, found 870 for $M^{-\bullet}$.

Synthesis of compounds 11–13 from $C_{60}(CH_2CO_2Me)(H)$, 4, and $C_{60}(CH_2CO_2Et)(H)$, 5

^{t}BuOK (1 M) in THF (1.2 equiv) was added through a syringe under nitrogen (or argon) to a solution of 0.06 mmol dihydrofullerene **4** or **5** dissolved in 30 mL dry THF, and this medium was stirred for 1 h at room temperature. Then excess (*ca.* 20 equiv) deoxygenated halo derivative R′X was added to this medium, which was stirred for a further 24–48 h period, this time being dependent on the colour change in the solution from initial green (due to the anion $[C_{60}R]^-$) to brown. After evaporation of THF, acetonitrile was added to the residue and the solid reaction products were filtered off, washed with acetonitrile, isolated through column chromatography, and identified from MS and NMR analyses.

$C_{60}(CH_2CO_2Et)(C_2H_5)$, 11. ^{1}H NMR (500 MHz, CS_2–C_6D_6) δ 1.28 (t, 3H, $^3J_{HH} = 7.1$ Hz), 1.77 (t, 3H, $^3J_{HH} = 7.4$ Hz), 2.98 (m, 1H, $J = 13.4$ and 7.4 Hz), 3.03 (m, 1H, $J = 13.4$ and 7.4 Hz), 3.82 (d, 1H, $J = 14.6$ Hz), 3.90 (d, 1H, $J = 14.6$ Hz), 4.20 (q, 2H, $J = 7.1$ Hz); ^{13}C NMR (125.75 MHz) δ 12.21, 14.99, 36.81, 47.07, 55.00, 60.17, 61.35, 134.62, 136.45, 137.59, 138.62, 139.02, 139.42, 141.11, 142.00, 142.40, 142.57, 142.65, 142.92, 143.16, 143.37, 143.43, 143.50, 144.00, 144.06, 144.36, 144.46, 144.60, 145.00, 145.03, 145.06, 145.38, 145.51, 145.73, 145.76, 146.07, 147.09, 147.16, 147.21, 147.48, 147.62, 148.20, 148.62, 148.90, 149.38, 150.71, 150.77, 155.78, 168.30; ES-MS calcd for $C_{66}H_{12}O_2$: 836.08, found 835.83 for $M^{-\bullet}$.

$C_{60}(CH_2CO_2CH_2CH_3)(CH_2Ph)$, 12. ^{1}H NMR (500 MHz, CS_2–$CDCl_3$) δ 1.40 (t, 3H, $J = 7.1$ Hz), 2.73 (d, 1H, $J = 15.2$ Hz), 2.94 (d, 1H, $J = 15.2$ Hz), 4.24–4.30 (m, 2H), 4.32 (d, 1H, $J = 13.0$ Hz), 4.41 (d, 1H, $J = 13.0$ Hz), 7.44 (t, 1H, $J = 7.4$ Hz), 7.51 (t, 2H, $J = 7.5$ Hz), 7.67 (d, 2H, $J = 7.4$ Hz); ^{13}C NMR (125.75 MHz) δ 14.42, 45.11, 48.79, 54.50, 60.26, 60.57, 136.01, 137.42, 138.40, 138.60, 138.62, 140.49, 141.45, 141.78, 141.97, 142.01, 142.22, 142.35, 142.36, 142.39, 142.65, 142.76, 142.90, 142.91, 142.97, 143.26, 143.48, 143.55, 143.73, 143.79, 143.82, 143.96, 144.00, 144.01, 144.07, 144.15, 144.18, 144.36, 144.46, 144.53, 144.83, 144.84, 144.96, 145.05, 145.22, 145.24, 145.72, 146.54, 146.60, 146.65, 146.70, 146.82, 146.92, 146.94, 147.85, 148.06, 148.33, 148.38, 150.28, 151.26, 155.52, 157.43, 168.43; ES-MS calcd for $C_{71}H_{14}O_2$: 898.10, found 898.10 for $M^{-\bullet}$.

$C_{60}(CH_2CO_2CH_3)(CO_2CH_3)$, 13. ^{1}H NMR (500 MHz, CS_2–$CDCl_3$) δ 3.93 (s, 3H), 4.15 (d, 1H, $J = 15.8$ Hz), 4.21 (d, 1H, $J = 15.8$ Hz), 4.22 (s, 3H); ^{13}C NMR (125.75 MHz) δ 45.51, 52.30, 54.24, 55.02, 138.52, 138.57, 139.06, 139.26, 141.42, 141.96, 142.14, 142.65, 142.69, 143.16, 143.21, 143.30, 143.39, 143.48, 143.70, 143.90, 144.05, 144.21, 144.25, 144.37, 144.41, 144.55, 144.72, 144.80, 144.94, 145.24, 145.47, 145.63, 145.68, 145.73, 147.03, 147.09, 147.14, 147.36, 147.73, 148.07, 148.74, 148.80, 150.24, 151.48, 155.20, 168.87, 170.38; ES-MS calcd for $C_{65}H_8O_4$: 852.04, found 852.04 for $M^{-\bullet}$.

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26 Note that, in the case of compounds **5** and **6**, the analysis by mass spectrometry using an electrospray source as the ionization technique allows to observe not only the presence of a molecular ion $M^{\bullet -}$ but also the formation of a $[M–H]^-$ ion. Then, since the ions are generated by way of the well-known electrochemical step involved in such ionization processes, the loss of a hydrogen atom from the radical anion electrochemically generated in solution (at the tip of the ESI emitter) suggests an interesting behaviour for such a dihydrofullerene in the case of the electrochemical production of $C_{60}R^-$.