

## DFT and ESR spectroscopic studies of new organoelement fullerene derivatives

Lopatin M.A., Ketkov S.Yu.\*, Markin G.V., Kuropatov V.A., Rychagova E.A., Kalakutskaya L.V., Domrachev G.A.

*G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,  
603950, Nizhny Novgorod, Russia*

*\*e-mail: sketkov@iomc.ras.ru*

The DFT calculations of recently synthesized fullerene polyadducts  $R_nC_{60}$  ( $R = Me_3Si$ ;  $n = 4, 6, 8, 10, 12$ ) and ESR study of new bis(toluene)tungsten fulleride have been performed. The natural charge distribution and NBO populations in the  $R_nC_{60}$  molecules were compared with those in the fullerene adducts with organic fragments ( $R = Me, t-Bu, CH_2Ph, CF_3$ ) as well as with the corresponding parameters in the  $R-CMe_3$  species. The  $Si(R)-C(C_{60})$  and  $Si(R)-C(C_{60})$  NBO population appears to be lower than the corresponding values for the  $Si(R)-C(CMe_3)$  and  $C(R)-C(CMe_3)$  bonds. The electron density distribution analyzed by the Bader's "Atom in molecules" approach also shows some  $\rho(r)$  decrease for the (3,-1) critical points of the R-C bonds on going from "classical" organics to the fullerene adducts. On the other hand, analysis of natural charges reveals increased polarization of the  $R-C_{60}$  ( $R = CH_2Ph, CMe_3, CF_3$ ) bond as compared to  $R-CMe_3$ . These findings are indicative of the higher lability of the  $R-C_{60}$  chemical bond. DFT calculations have been also carried out for the reduced and oxidized forms of  $R_nC_{60}$ . Both one-electron oxidation and reduction of 1,4- $R_2C_{60}$  results in an increase of the electron density on the C2-C12 and C3-C14 bonds and a decrease of  $\rho(r)$  on the C2-C3 bond of the  $C_{60}$  core. This agrees well with the HOMO and LUMO localization. Accordingly, the  $\rho(r)$  value in the (3,-1) critical point of the  $R-C_{60}$  bond changes stronger on going to the cation than to the anion. The formation of the  $(C_{60})^{\bullet-}$  fulleride anion has been studied in the reaction of fullerene with bis(toluene)tungsten.

$C_{60}$  reacts with  $(PhMe)_2W^0$  in PhMe at 293 K to form fulleride as black crystalline sediment (fulleride **I**). Fulleride **I** is insoluble in aliphatic solvents, soluble in PhCN and THF. Its ESR in THF at 290 K shows a line with typical hyperfine structure of  $(Arene)_2W^{\bullet+}$  and  $g = 1.9856$ ,  $a_H = 4.5G$ . The visible spectroscopy of fulleride **I** in THF at 291 K reveals a  $(C_{60})^{\bullet-}$  absorption band at  $\lambda = 1079$  nm. The EPR spectrum of crystalline  $[(PhMe)_2W^{\bullet+}][C_{60}^{\bullet-}]$  (**I**) at 290 K shows a single line with  $\Delta H = 111.2$  G and  $g = 1.9882$  which is intermediate between those characteristic for  $(Arene)_2W^{\bullet+}$  and  $(C_{60})^{\bullet-}$  because of strong exchange coupling between  $(PhMe)_2W^{\bullet+}$  and  $(C_{60})^{\bullet-}$ . On cooling **I** in the 260-200 K range the g-factor significantly shifts and the ESR spectrum of crystalline **I** at 120 K consists of a single line with  $\Delta H = 13.7$  G and  $g = 1.9849$  which is characteristic for non-interacting paramagnetic  $(PhMe)_2W^{\bullet+}$ .