

(Cyclopentadienyl)chromiumtricarbonyl dimers as a source of metal-centered free-radicals to form stable η^2 -bonded spin-adducts with fullerenes

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Abstract

Spin-adducts (**I**, **IIb–c**) of C_{60} and C_{70} with metal-centered free radicals $CpCr(CO)_3$ (**I**, **IIa**) have been generated in toluene via interaction between fullerenes and the weakly metal–metal bonded dimeric complexes $[CpCr(CO)_3]_2$ ($Cp = \eta^5-C_5H_5$ (**I**); $Cp = \eta^5-C_5Me_5$ (**II**)). Their structures have been investigated using ESR spectroscopy and DFT-PBE calculations and η^2 -bonding to the C=C bond between two hexagons in C_{60} has been established. Calculations have been extended to investigate the nature of the intermediate η^2 -coordinated toluene chromium complexes (**I**, **IId**).

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1. Introduction

Fullerenes are known to readily add free radicals with the formation of spin-adducts, which are moderately stable in solution and amenable to study by ESR spectroscopy [1–3]. To date, the key atoms in such adducts directly attached to the fullerene core have been the non-metal atoms, namely, carbon, sulfur, phosphorus and boron, with platinum being the only metal involved. Valuable structural information can be obtained from the ESR spectra owing to the high sensitivity of hyperfine splitting patterns when *magnetic nuclei* are present in the key position such as ^{31}P , ^{10}B , and ^{11}B . The additional advantage of this approach consists of obtaining

two independent parameters (g -factor and hfc constant) instead of one (g -factor) that makes the assignment of ESR signals much easier. This methodology had been demonstrated in the characterization of fullereryl derivatives [4,5] when we have introduced P- and B-centered free radicals to form spin-adducts with the fullerenes. Similarly, the magnetic isotope ^{195}Pt ensured the observation of satellites in the ESR spectrum of the platinum–fullereryl radical adduct obtained from a σ -bonded platinum–mercury precursor complex [6].¹ Another suitable metal for such study seems to be chromium with

¹ One referee suggested to discuss the paper [7] in which the addition of the radicals $Re(CO)_5$ to C_{60} from photochemical decomposition of $Re_2(CO)_{10}$ had been reported. However, neither ESR spectroscopy nor quantum-chemical calculations were applied in that study, so, they just were unable to judge about possible paramagnetic intermediates. Correspondingly, there is no subject to discuss.

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magnetic isotope ^{53}Cr , nuclear spin $I = 3/2$ and natural abundance 9.54%. A good source of chromium-centered free radicals is the metal–metal bonded (cyclopentadienyl)chromium tricarbonyl dimer, in which facile and reversible homolytic cleavage of the weak Cr–Cr bond is well established [8–11]. Various aspects of the cyclopentadienylchromium chemistry has been reviewed recently [12].

In this paper, we describe the reactions of the title compounds with fullerenes C_{60} and C_{70} in toluene at room temperature and lower.²

2. General

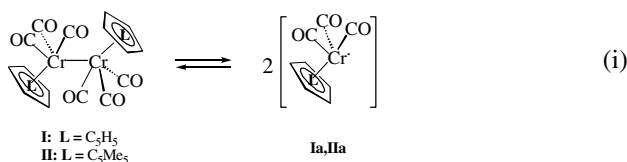
Fullerenes C_{60} (99.9% pure) and C_{70} (99.5% pure) were purchased from the Institute of Organometallic Chemistry (Nizhny-Novgorod, Russia), organochromium complexes **I–III** were prepared following [11,13].

3. Experimental part

Reagents were dissolved in toluene saturated with argon, then mixed and transferred into an ESR ampoule in the vacuum line, subjected to several “freeze–thaw” cycles and finally sealed under argon. ESR spectra were recorded on a Varian E-12A spectrometer. Temperature was controlled using a “Unipan” device. g -Factors were determined using the Varian standard with g -factor 2.0028. The TEMPO (“Aldrich”) ($[\text{TEMPO}] = 3 \times 10^{-3} \text{ mol L}^{-1}$) was applied as a reference standard for calculating concentrations of chromium fullereryl radicals.

4. Results and discussion

Dimers of (cyclopentadienyl)chromiumtricarbonyl (**I**) and pentamethyl-(cyclopentadienyl) analogue (**II**) undergo facile cleavage of the metal–metal bond to afford 17-electron monomers (**Ia**, **IIa**) (eq. i), which form long-lived spin-adducts with fullerenes (eq. ii).



² Presented in part at the 9th European Symposium on Organic Reactivity, Abstracts OR38, Oslo, Norway (2003).

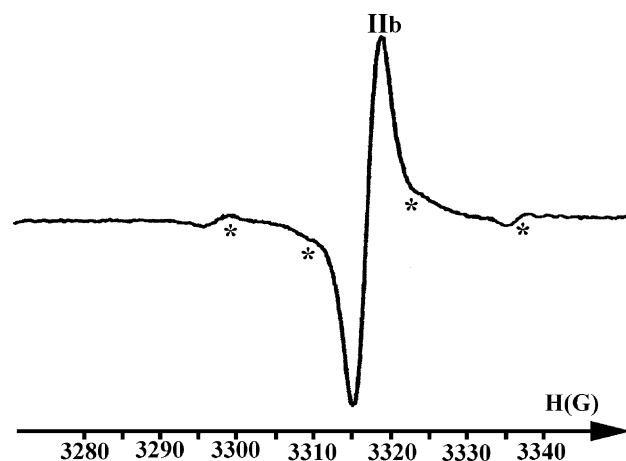
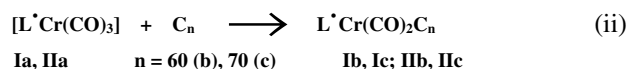


Fig. 1. ESR spectra of radicals $^*\text{Cp}^*\text{Cr}(\text{CO})_3$ and $^*\text{Cp}^*\text{Cr}(\text{CO})_2\text{C}_n$ obtained on interaction of $[\text{Cp}^*\text{Cr}(\text{CO})_3]_2$ with C_n ($n = 60, 70$) in toluene solution. $T = 243 \text{ }^\circ\text{K}$. The lines labelled * are due to ^{53}Cr in $^*\text{Cp}^*\text{Cr}(\text{CO})_2\text{C}_n$ radicals and ** are due to ^{53}Cr in $^*\text{Cp}^*\text{Cr}(\text{CO})_2(\text{C}_6\text{H}_5\text{CH}_3)$.



An ESR spectrum taken at 243 K (Fig. 1) of the resulting solution from the interaction of **Ia** or **IIa** with C_n ($n = 60, 70$) in toluene exhibit signals from free radicals both with coordinated toluene (ArH): $\text{Cp}^*\text{Cr}(\text{CO})_2(\text{ArH})$ (**Id**), $^*\text{Cp}^*\text{Cr}(\text{CO})_2(\text{ArH})$ (**IId**), and fullerenes: $\text{Cp}^*\text{Cr}(\text{CO})_2\text{C}_{60}$ (**Ib**, **Ic**), $^*\text{Cp}^*\text{Cr}(\text{CO})_2\text{C}_{70}$ (**IIb**, **IIc**), respectively (concentrations of radicals

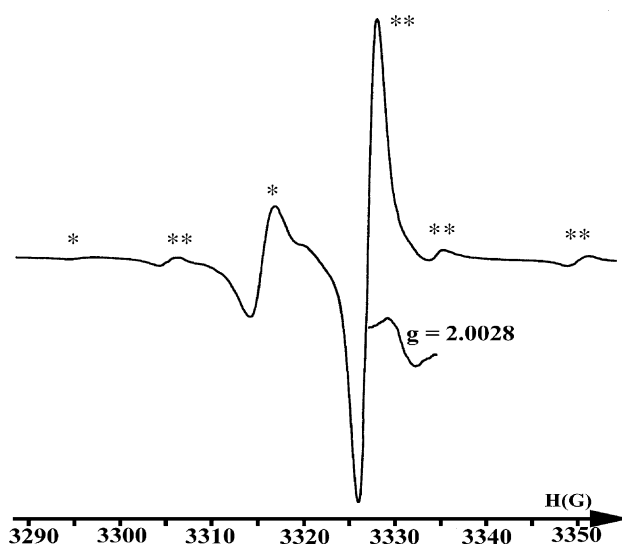


Fig. 2. ESR spectra of radical adducts $^*\text{Cp}^*\text{Cr}(\text{CO})_2\text{C}_n$ obtained on interaction of $[\text{Cp}^*\text{Cr}(\text{CO})_3]_2$ with C_n ($n = 60, 70$) in toluene solution. $T = 293 \text{ }^\circ\text{K}$. The lines labelled * are due to ^{53}Cr isotope in $^*\text{Cp}^*\text{Cr}(\text{CO})_2\text{C}_n$ radicals.

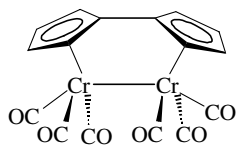
Table 1
Parameters of the radical spin-adducts obtained on interaction of **Ia** and **IIa** with fullerenes C_n ($n = 60, 70$) in toluene solution

X	CpCr(CO) ₂ X (I)			*CpCr(CO) ₂ X (II)		
	CO/solv	C ₆₀	C ₇₀	CO/solv	C ₆₀	C ₇₀
295 °K						
<i>g</i> -factor	2.0045 ^a	2.0134	2.0138	2.005	2.0127	2.0138
$a(^{53}\text{Cr})$	–	13.25	13.25	–	13.25	13.25
243 °K						
<i>g</i> -factor	2.0045	2.0120	2.0130	2.005	2.0120	2.0130
$a(^{53}\text{Cr})$	15.00	13.25	13.25	15.00	13.25	13.25

^a Reported previously [11].

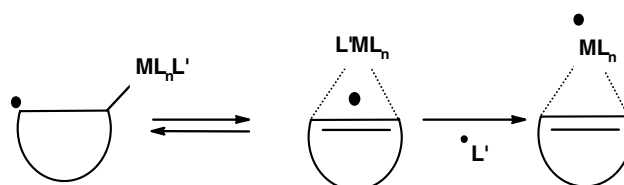
$\sim 10^{-5}$ mol L⁻¹). The intensity of signals for radicals **I**, **II(b, c)** increases while that for **Id** and **IIId** decreases with time. The latter signals are absent from the spectra taken at room temperature (Fig. 2). These results show that chromium centered free radicals **I**, **II(b, c)** coordinated with fullerenes are more stable than **I**, **IIId** radicals with coordinated toluene and that substitution of CO groups for the C_n molecule proceeds readily at room temperature. The ⁵³Cr satellites have been observed in ESR spectra for all spin-radicals studied. Signals of **Ib**, **Ic** or **IIb**, **IIc** radicals are more dominant with rise of temperature and progression of time. Intensities of them remain unchanged during several weeks in sealed ampoules. Positive shift of *g*-factor for these radicals in relation to *g*-factor of **Id** and **IIId** radicals apparently points to the transfer of electron density from metal on fullerene. Actually, the higher hyperfine coupling constants $a(^{53}\text{Cr})$ for **Id** and **IIId** radicals are somewhat larger than $a(^{53}\text{Cr})$ for **Ib**, **Ic** (**IIb**, **IIc**) radicals (see Table 1). Coordination of solvents to the chromium-centered free radicals has been observed previously [11] but the observation of ⁵³Cr satellites was not reported.

Fulvalene dichromium complex (**III**), in which the two cyclopentadienyl rings are linked by a carbon–carbon σ -bond, does not give any ESR signal under the same conditions.³



While atoms of non-transition elements such as phosphorus or boron can only have one possible bonding mode, namely, $\eta^1(\sigma)$ -bonding, transition met-

³ Rupture of the chromium–chromium bond in a phosphine derivative related to **III** had been reported [13] and assumed homolytic though without any ESR evidence.



Scheme 1.

als can also bind via η^2 -bonding. However, in this case, a possible equilibrium between both η^1 -bonded and η^2 -bonded species involving the elimination of a free radical cannot be excluded as shown on the Scheme 1.

The η^1 structure of a platinum spin-adduct had been previously proposed [6] from the observation of two different spin–spin ³¹P coupling constants in the ESR spectrum due to phosphorus nuclei in *cis* and *trans* positions. However, in the case of η^2 -bonding of the fullerene double bond to a metal, the same pattern of ESR spectrum would be observed. Hence these two possibilities cannot be distinguished, and a final conclusion can only be made on the basis of quantum-chemical calculations. We carried out such calculations for the case of C₆₀ fullerene.

5. Calculation procedure

Studies of the potential energy surfaces were performed for following compounds: (η^2 -C₆₀)CrCp(CO)₂ (**IIb**), some its neutral and charged fragments, dimer [CrCp(CO)₃]₂ (**I**), radicals *CrCp(CO)₃ (**Ia**), *CrCp(CO)₂ (**Ia'**), *CrCp(CO)₂(η^2 -C₆H₅CH₃) (**Id**) as well as toluene itself C₆H₅CH₃. Geometry of the species considered was optimized by the DFT using the Perdew–Burke–Ernzerhof exchange–correlation potential (DFT-PBE) [14]. The total energies were calculated both without and with inclusion of zero-point vibration energy correction. The basis sets employed were TZ for Cr atoms and DZ for the other atoms. The character of the stationary points was determined using the number of negative eigenvalues of the Hesse

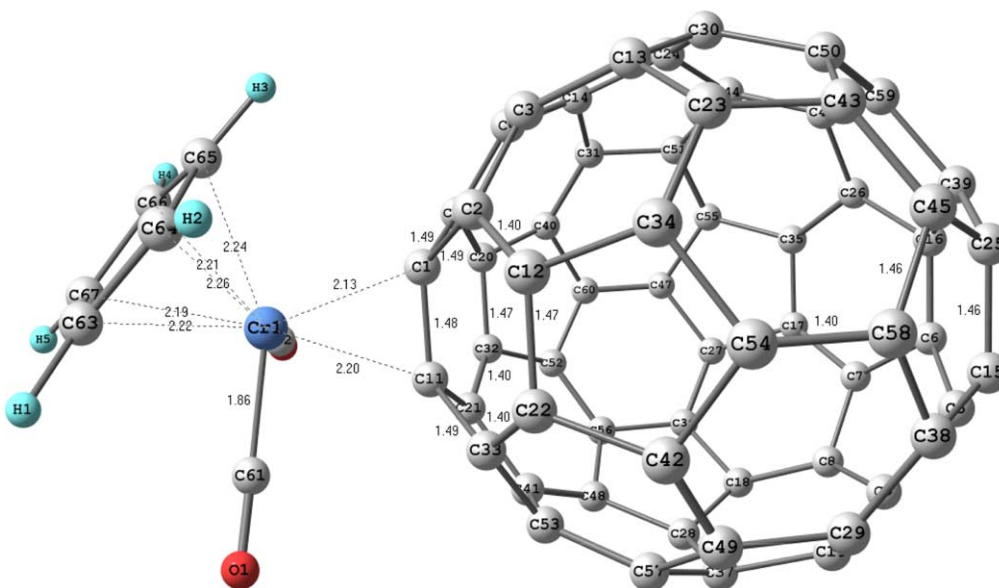


Fig. 3.

matrix. Calculations were carried out using the PRI-RODA program (Version 1.10) [15] which was preliminary tested taking the transition metal complexes with C_{60} as examples [16,17].

Only two local minima on the potential energy surfaces of complex $(\eta^2-C_{60})CrCp(CO)_2$ were found corresponding to the structures **Ib** and **Ib'** shown on Figs. 3 and 4. Energy of the first complex is less than energy of the second one by 12.4 kcal/mol. In the spin-adduct **Ib**, the chromium atom of radical **Ia** forms η^2 -bond with a 6/6 double bond of C_{60} , whereas in the spin-ad-

duct **Ib'**, the metal atom of radical **Ia** is coordinated also in η^2 -type with atoms of a 6/5-bond which is formally ordinary one. Lengths of Cr-C(C_{60})-bonds in **Ib** (**Ib'**) are equal to 2.134 and 2.198 Å (2.163 and 2.254 Å, respectively). That means the 6/6 double bond is preferential for coordination with metal in both electronically unpaired and paired [18] fullerene complexes.

It follows from Table 2 that energies of $\eta^2(\pi)$ -bonds in complexes **Ib** and **Ib'** are equal to 39.3 and 27.0 kcal/mol, respectively. Substitution reaction of CO

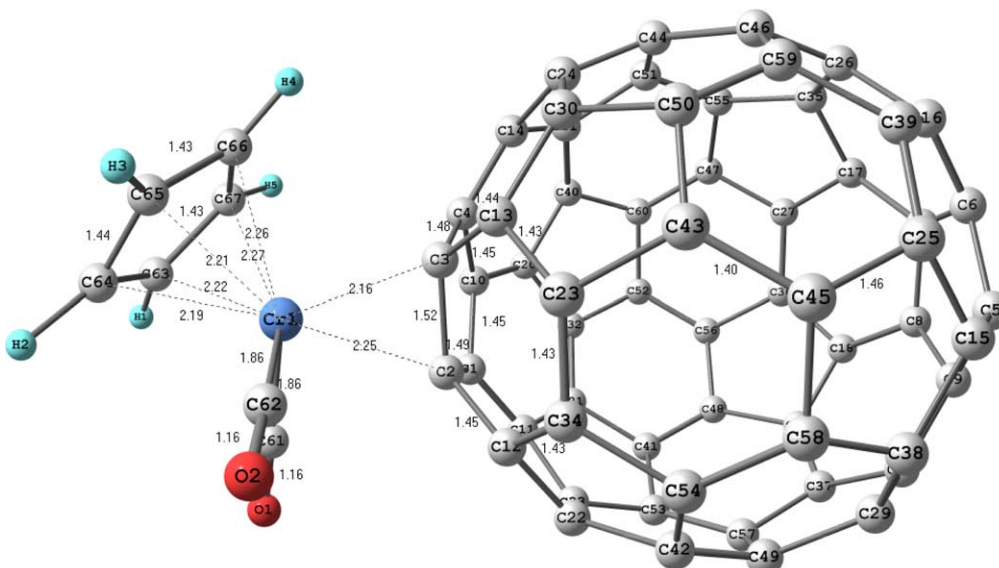


Fig. 4.

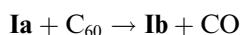
Table 2
Main results of DFT-PBE calculations of radicals **1b**, **1b'** and related species

Molecule/radical	<i>M</i>	<i>-E</i>	<i>-E</i> ₀	<i>q</i> (Cr)	<i>s</i> (Cr)
(η^2 -C ₆₀)CrCp(CO) ₂ (1b) [6:6] ^a	2	3747.7580	3747.2802	1.18	0.84
(η^2 -C ₆₀)CrCp(CO) ₂ (1b') [6:5] ^a	2	3747.7384	3747.2619	1.18	0.82
C ₆₀	1	2283.7138	2283.3368	–	–
[CrCp(CO) ₃] ₂ (I)	1	3154.4719	3154.2510	0.89	–
CrCp(CO) ₃ (1a)	2	1577.2178	1577.1087	0.87	0.72
CrCp(CO) ₂ (1a')	4	1463.9815	1463.8829	0.99	2.53
CrCp(CO) ₂ (η^2 -C ₆ H ₅ CH ₃) (1d)	2	1735.2054	1734.9785	0.94	0.81
C ₆ H ₅ CH ₃	1	271.1928	271.0670	–	–
CO	1	113.1540	113.1491	–	–

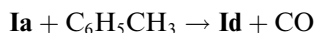
(*M* – multiplicity; *E* (*E*₀) – total energy without (with) inclusion of zero-point vibration energy (in a.u.), *q* – charge, *s* – spin density).

^a Bracketed are the fullereryl bonds engaged in η^2 -bonding to the metal atom.

group in CpCr(CO)₃ radical **1a** for fullerene C₆₀ is slightly endothermic, energy of 12.3 kcal/mol is necessary.



With inclusion of the zero-point vibration energy correction this value is decreased to 10.2 kcal/mol. Note for comparison that substitution of CO group in radical **1a** for toluene to give **1d** requires 32 kcal/mol (without zero-point vibration energy correction) and 30.2 kcal/mol (with zero-point vibration energy correction):



Spin density at Cr atom in radical (η^2 -C₆H₅CH₃)CrCp(CO)₂ (**1d**) is greater than in radical **1a**, but less than in radicals **1b** and **1b'** (see Table 2).

Note that no stable $\eta^1(\sigma)$ -bonded isomers of **I** were found.

6. Conclusions

Thus we have demonstrated the facile addition of chromium-centered organometallic free radicals to fullerenes C₆₀ and C₇₀ to form moderately stable spin-adducts observable by way of ESR spectroscopy. This approach can obviously be used for introducing unpaired electrons and metal atoms onto the fullerene materials. In these paramagnetic adducts, fullerenes are η^2 bonded to a chromium metal atom, this type was not known for the fullerene complexes with unpaired electrons. This kind of bonding may also exist in the fullerene odd-electron complexes with some other metals, like vanadium, for example.

List of species

Molecule/radical
 η^2 -C₆₀)CrCp(CO)₂ (**1b**) [6:6][&]
 η^2 -C₆₀)CrCp(CO)₂ (**1b'**) [6:5][&]
 [CrCp(CO)₃]₂ (**I**)
 [Cr*Cp(CO)₃]₂ (**II**)
 Cp*Cr(CO)₂C₆₀ (**IIb**)

*Cp*Cr(CO)₂C₆₀ (**IIb'**)
 Cp*Cr(CO)₂C₇₀ (**1c**)
 *Cp*Cr(CO)₂C₇₀ (**1c'**)
 {fulvalene[Cr(CO)₃]₂} (**III**)
 CrCp(CO)₃ (**1a**)
 CrCp(CO)₂ (**1a'**)
 CrCp(CO)₂(η^2 -C₆H₅CH₃) (**1d**)
 Cr*Cp(CO)₂(η^2 -C₆H₅CH₃) (**1d'**)

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