Paramagnetic metal chelates of an *o*-quinone derivative of fullerene with Mn and Re carbonyls

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Reactions of the $^{\bullet}M(CO)_5$ radicals (M = Mn and Re) with an *o*-quinone derivative of fullerene C_{60} yield stable paramagnetic complexes (ESR data). Two carbonyl ligands in the resulting spin adducts were replaced by PPh_3.

Key words: fullerene, *o*-quinone, paramagnetic complex, ESR spectroscopy.

Homolytic reactions of fullerenes C_{60} and C_{70} are well studied. Carbon- and element-centered radicals have been reported to add to these fullerenes regioselectively.[1,2] The behavior of fullerene derivatives in radical processes remains much poorly understood.[3] All of the homolytic reactions studied yield fullerenyl radicals with an unpaired electron on the carbon polyhedron.

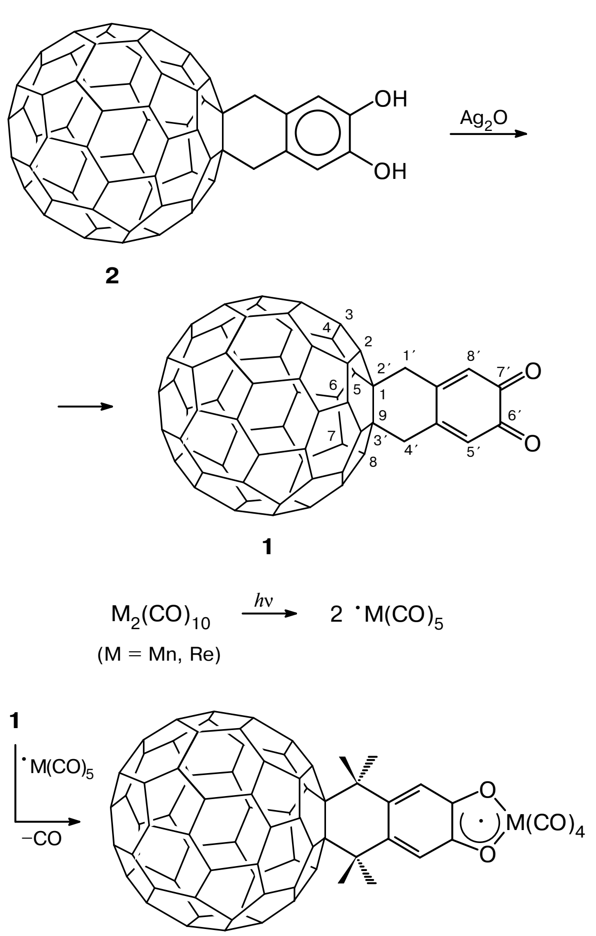
The discovery of ferromagnetism for a complex of fullerene C_{60} with tetra(diethylamino)ethylene, C_{60}(TDAE),[4] has aroused interest in fullerene derivatives whose unpaired electron is localized both on the fullerene framework and on the attached group of atoms. Thus, nitroxyl fullerenyl derivatives are reduced to give biradicals in which the fullerene-localized electron can interact with the unpaired electron of the nitroxyl part of the molecule.[5—7]

In the present work, the formation of paramagnetic metal chelates with fullerene was detected for the first time by ESR in the reactions of Mn- and Re-centered radicals with the previously unknown *o*-quinone derivative of fullerene C_{60}, namely, 6′,7′-dioxo-1,9,1′,4′,6′,7′-hexahydronaphtho[2′,3′:1,9]fullerene-C_{60} (**1**).

Results and Discussion

Compound **1** was prepared by oxidizing a solution of 6′,7′-dihydroxy-1,9,1′,4′-tetrahydronaphtho[2′,3′:1,9]fullerene-C_{60} (**2**)[8] in benzene with an excess of Ag_2O (monitoring by mass spectrometry and TLC). After $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$ in an equimolar amount was added, the reaction mixture was irradiated in a resonator of an ESR spectrometer.[9] As a result, the reaction of metal-centered radicals with compound **1** yields stable paramagnetic complexes **3** or **4** (Scheme 1).

Scheme 1



3: M = Mn; **4:** M = Re

The ESR spectrum of the reaction mixture shows a sextet of triplets (Fig. 1). Such a picture is attributed to an interaction of the unpaired electron with the ^{55}Mn or ^{185,187}Re nuclei ($I = 5/2$) and with two protons of the methylene groups that are axial to the plane of the aromatic ring (**3:** $a_{Mn} = 7.5$ G, $a_H = 6$ G, $g = 2.0034$;

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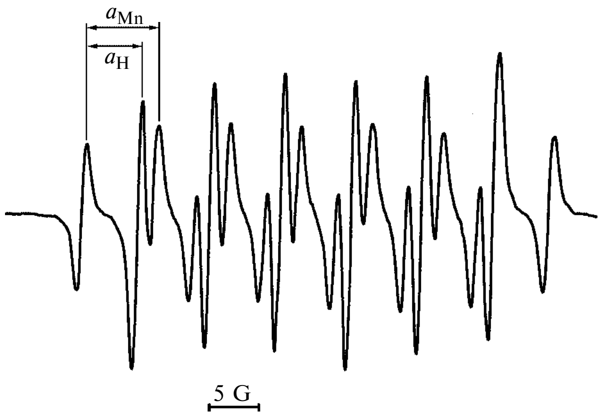

Fig. 1. ESR spectrum of paramagnetic complex **3** at ~20 °C.

4: a_{Re} = 30 G, a_H = 6 G, g = 2.0034). The presence of the fullerene framework causes the cyclohexane ring in these compounds to exist in a boat conformation.[8] Because of this, the methylene protons are magnetically nonequivalent, and the unpaired electron can interact with the axial protons.

When PPh_3 is added to compound **3**, the CO ligands in the metal coordination sphere are replaced[10] to give disubstituted complexes (ESR: a_H(2 H) = 5.5 G, a_P(2 P) = 16.5 G, a_{Mn} = 11 G).

Thus, the stable paramagnetic complexes based on the new *o*-quinone derivative of fullerene were synthesized for the first time.

Experimental

ESR spectra were recorded on a Varian E-12A spectrometer. Reaction mixtures were UV-irradiated with a DRSh-1000 lamp in a resonator of an ESR spectrometer. IR spectra were recorded on a Specord M-82 spectrometer. Mass spectra were obtained with the use of a Kratos MS-890A instrument. Benzene was distilled in an atmosphere of argon over Na immediately before use. Compound **2** was prepared as described in Ref. 8.

6′,7′-Dioxo-1,9,1′,4′,6′,7′-hexahydronaphtho[2′,3′:1,9]fullerene-C_{60} (1). A tenfold excess of Ag_2O was added to a 0.001 *M* solution of compound **2** in benzene. The reaction mixture was stirred for 40 min. The precipitate that formed was filtered off, and the filtrate was concentrated. Trituration of the residue with hexane gave compound **1** in 97% yield as a finely crystalline dark brown powder. TLC: R_f = 0.51 (Silufol, PhMe—AcOEt (4 : 1)). MS (EI, 70 eV), *m/z*: 854 $[M]^+$. IR, ν/cm^{-1}: 1665 (C=O).

Paramagnetic complex of 1 with $Mn(CO)_4$ (3). An equimolar amount of $Mn_2(CO)_{10}$ was added to a 0.001 *M* solution of compound **1** in benzene. The resulting solution was placed in a glass tube and irradiated in a resonator of the ESR spectrometer with the focused light of a mercury lamp with recording an ESR spectrum of product **3**. Compound **4** was obtained analogously.

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