

Proceeding Paper

Sulfur-Containing Homo- and Methanofullerenes: Synthesis and Study of Tribological Properties [†]

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Abstract: The data obtained by the authors in the field of carbon cluster chemistry, namely the catalytic cycloaddition of sulfur-containing diazo compounds to C₆₀-fullerene under the action of complex Pd catalysts, are summarized. Cycloaddition reactions of diazoalkanes, diazoketones, and diazothioates with C₆₀-fullerene, catalyzed by Pd(acac)₂-PPh₃-Et₃Al, with the selective formation of new sulfur-containing methano-, homo-, and pyrazolinofullerenes, are promising as modern nanosized additives in oils for highly loaded mechanisms.

Keywords: fullerenes; diazo compounds; methanofullerenes; homofullerenes; metal complex catalysis; tribology; additives



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1. Introduction

Since the discovery of fullerenes, a new form of carbon existence, the chemistry of carbon clusters has become an independent branch of the organization of chemistry. Along with the study of the chemical properties of fullerenes, much attention is paid to determining possible areas of their application.

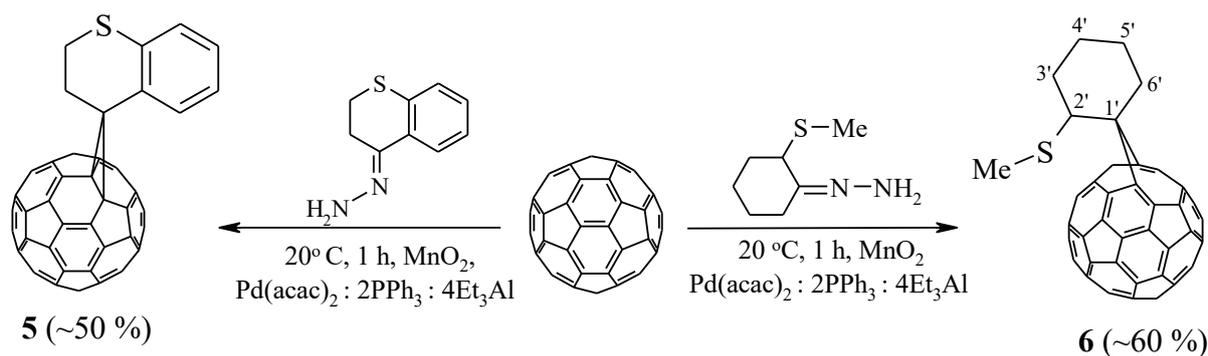
The interest in sulfur-containing fullerenes is due to the possibility of their application in medicine [1–4] and electronics and nonlinear optics [5], as well as solar energy photoconverters [6,7] and supramolecular dyes [8,9]. We assume that the spherical structure of the molecules of the simplest C₆₀- and C₇₀-fullerenes will play the role of nanobearings, which will allow them to be used as oil additives.

By the time we started our research, in the world literature, methods for the synthesis of sulfur-containing derivatives were described, focusing on C₆₀-fullerene, with the most attractive synthetic point of view being a method based on the thermal interaction of carbon clusters with diazo compounds [10,11]. However, the main disadvantage of the specified method is the low selectivity of the reaction. Meanwhile, it has recently been shown [12] that the introduction of methods such as metal complex catalysis in the reaction of fullerenes with diazo compounds allows one to achieve selective homo- or methanofullerenes.

In this regard, the use of metal complex catalysts in the reactions of sulfur-containing diazo compounds with fullerenes, as we assume, will allow us to develop highly selective and efficient catalytic methods of synthesis for sulfur-containing homo-, methane-, or pyrazolinofullerenes of a given structure, which will allow us to create, on their basis, promising nanocomponent additives for lubricating oils and highly loaded mechanisms.

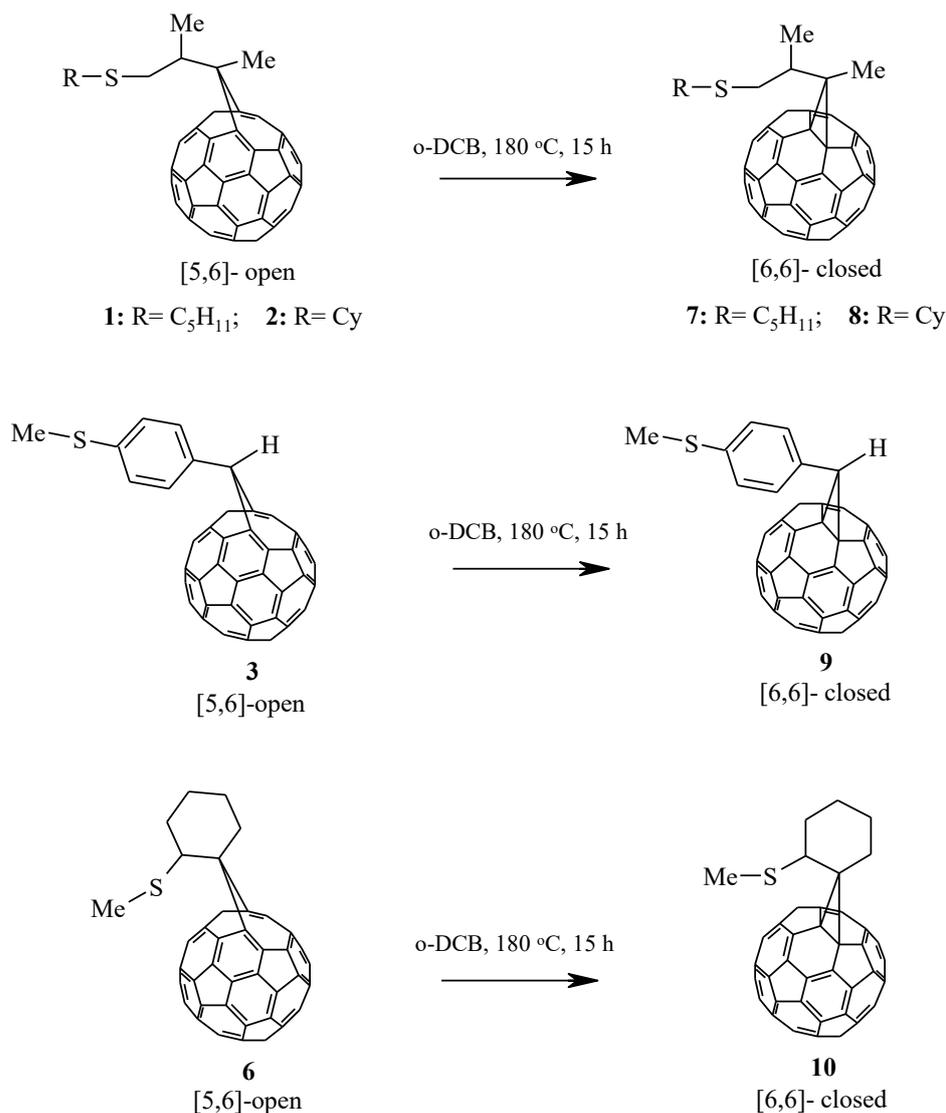
2. Results and Discussion

As a follow-up to the ongoing work in our group [13–20] related to the selective functionalization of C₆₀-fullerene with diazo compounds, we studied the catalytic cycloaddition reaction of sulfur-containing diazoalkanes generated in situ by the oxidation of hydrazones of the corresponding ketosulfides with MnO₂ to C₆₀. Of the tested catalysts based on salts



Scheme 3. Formation of spiro-methane and spiro-homofullerenes.

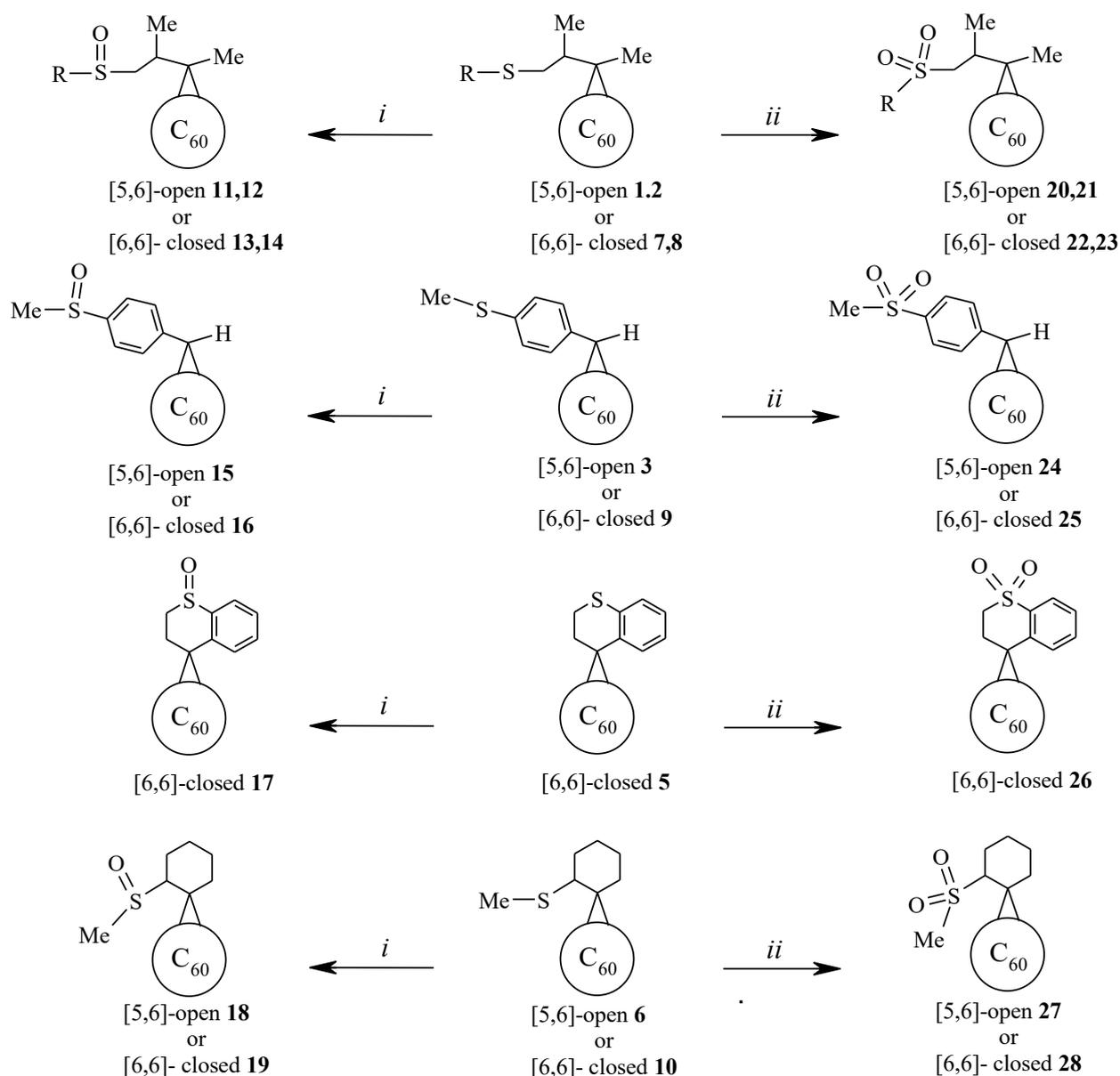
According to the literature [23], substituted homofullerenes can be quite easily isomerized into the corresponding methanofullerenes. In this regard, and also in order to obtain previously undescribed sulfur-containing methanofullerenes, we carried out the thermal isomerization of the synthesized [5,6]-open cycloadducts **1–3**, **6**. As a result of refluxing the indicated homofullerenes in 1,2-dichlorobenzene (o-DCB) for 15 h, individual [6,6]-closed isomers **7–10** were obtained in high yields of ~100% (Scheme 4).



Scheme 4. Thermal isomerization of [5,6]-open cycloadducts.

In the UV spectrum of individual methanofullerenes 7–10, a narrow, low-intensity absorption band is observed in the region of 427–430 nm, which is a fairly simple and reliable characteristic of the formation of [6,6]-closed cycloadducts.

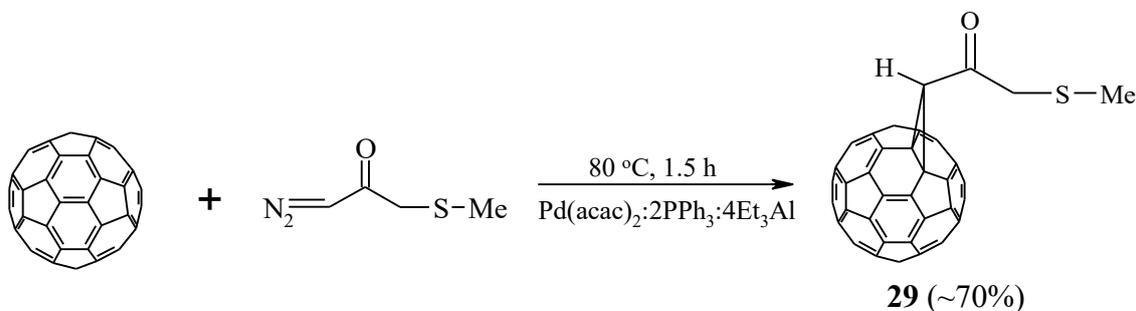
In order to obtain C_{60} adducts containing sulfoxide or sulfone groups, we oxidized the cycloadducts 1–3, 5–10, synthesized by us, which contain sulfide sulfur. It has been shown that the treatment of sulfides with 1–3, 5–10 equimolar amounts of *m*-CPBA leads to the formation of the corresponding individual sulfoxides 11–19 in quantitative yields (controlled by HPLC and 1H NMR). An increase in the amount of *m*-CPBA relative to the initial sulfide 1–3, 5–10 to 3:1 leads to the formation of individual sulfones 20–28, which are characterized by an even longer retention time (Scheme 5).



The reaction conditions: *i* - *m*-CPBA (1 equiv.), toluene, 20 °C, 1 h
ii - *m*-CPBA (3 equiv.), toluene, 20 °C, 1 h

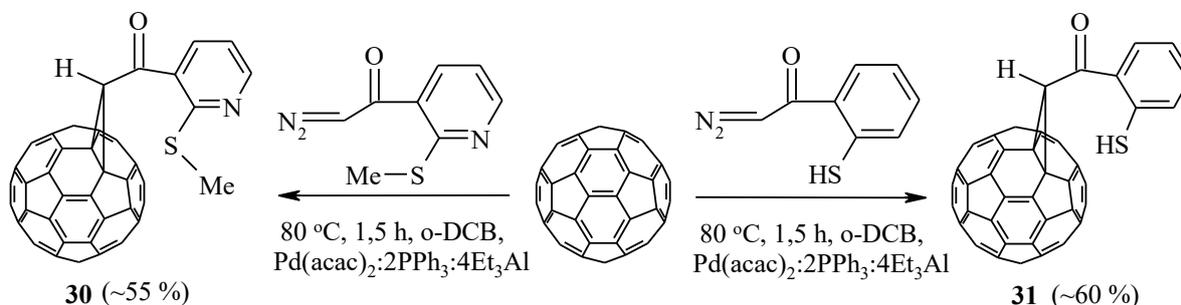
Scheme 5. Oxidation of C_{60} adducts containing sulfide sulfur to sulfoxide or sulfonic.

In order to develop our research, we carried out the catalytic cycloaddition of sulfur-containing diazoketones to C_{60} under these conditions ($\sim 80^\circ\text{C}$, 1.5 h, chlorobenzene or 1,2 dichlorobenzene) and only methanofullerene **29** was formed, with a yield of $\sim 70\%$. An increase in the reaction time to 2 h leads to the formation of dicycloadducts. Homofullerene and fullerodihydrofuran, which are usually formed under the conditions of the thermal reaction of C_{60} with diazoketones, were not found in our experiments (Scheme 6).



Scheme 6. Catalytic cycloaddition of sulfur-containing diazoketones to C_{60} -fullerene.

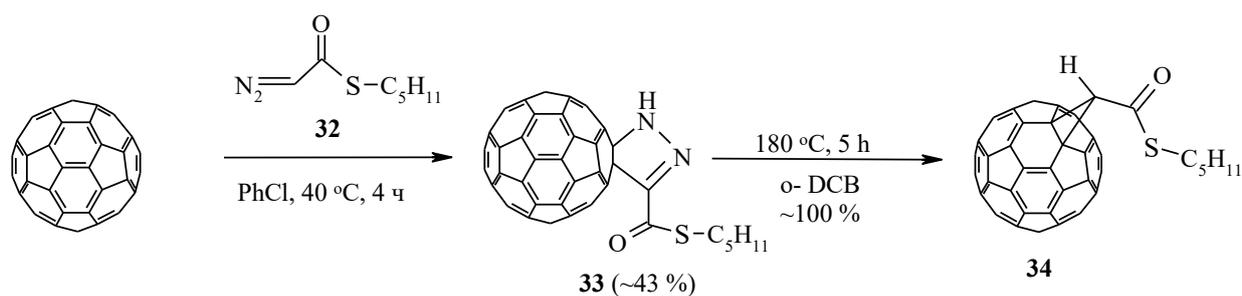
In order to study the effect of the structure of the starting diazoketone on the course and direction of the reaction under discussion, we studied the cycloaddition of diazoketones containing methylthiopyridyl and mercaptoaryl substituents to C_{60} . It has been shown that under the previously developed conditions (80°C , 1.5 h, *o*-dichlorobenzene), these aromatic diazoketones react with C_{60} -fullerene in the presence of a three-component catalyst, $\text{Pd}(\text{acac})_2\text{-PPh}_3\text{-Et}_3\text{Al}$ (1:2:4), to give the corresponding methanofullerenes **30** and **31** with a yield of ~ 55 and 60% , respectively (Scheme 7).



Scheme 7. Catalytic cycloaddition of sulfur-containing diazoketones to C_{60} -fullerene.

In order to develop effective methods for the synthesis of functionally substituted sulfur-containing C_{60} -carbon clusters, we, for the first time, carried out the interaction of C_{60} with diazothioates under the conditions of thermal and catalytic reactions [24]. Diazo compounds synthesized on the basis of α -amino acids (glycine, alanine, leucine, and methionine) and alkyl mercaptans were chosen as initial diazothioates.

It was found that diazothioate **32** quite easily reacted with C_{60} (20°C , 7 h, solvent chlorobenzene) to form pyrazolinofullerene **33** in a $\sim 28\%$ yield. An increase in the reaction temperature to 40°C leads to the target [3+2]-cycloadduct **33** in the same yield in 2 h. An increase in the reaction time at 40°C to 4 h makes it possible to synthesize pyrazolinofullerene **33** in a $\sim 43\%$ yield (Scheme 8).

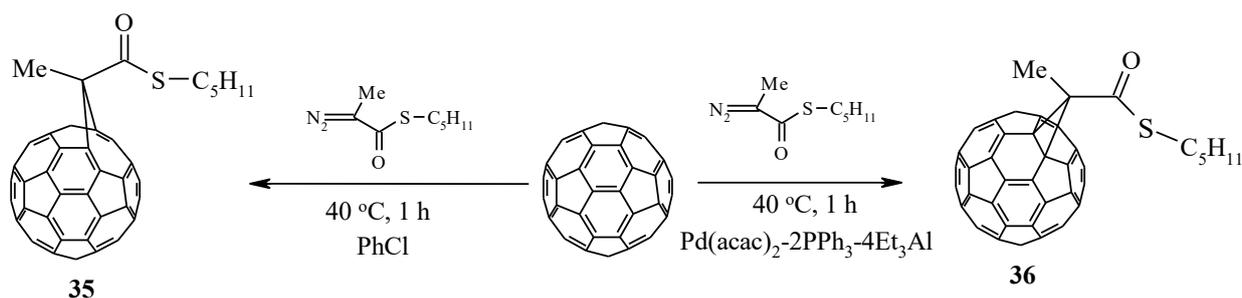


Scheme 8. Cycloaddition of diazothioates to C_{60} -fullerene.

Boiling pyrazolinofullerene **33** in 1,2-dichlorobenzene led to the extrusion of the N_2 molecule from the pyrazoline fragment and the quantitative formation of the corresponding methanofullerene **34**.

In order to study the influence of the structure of the initial diazothioate on the course and direction of the reaction, the cycloaddition of α -substituted diazothioates to C_{60} -fullerene was carried out.

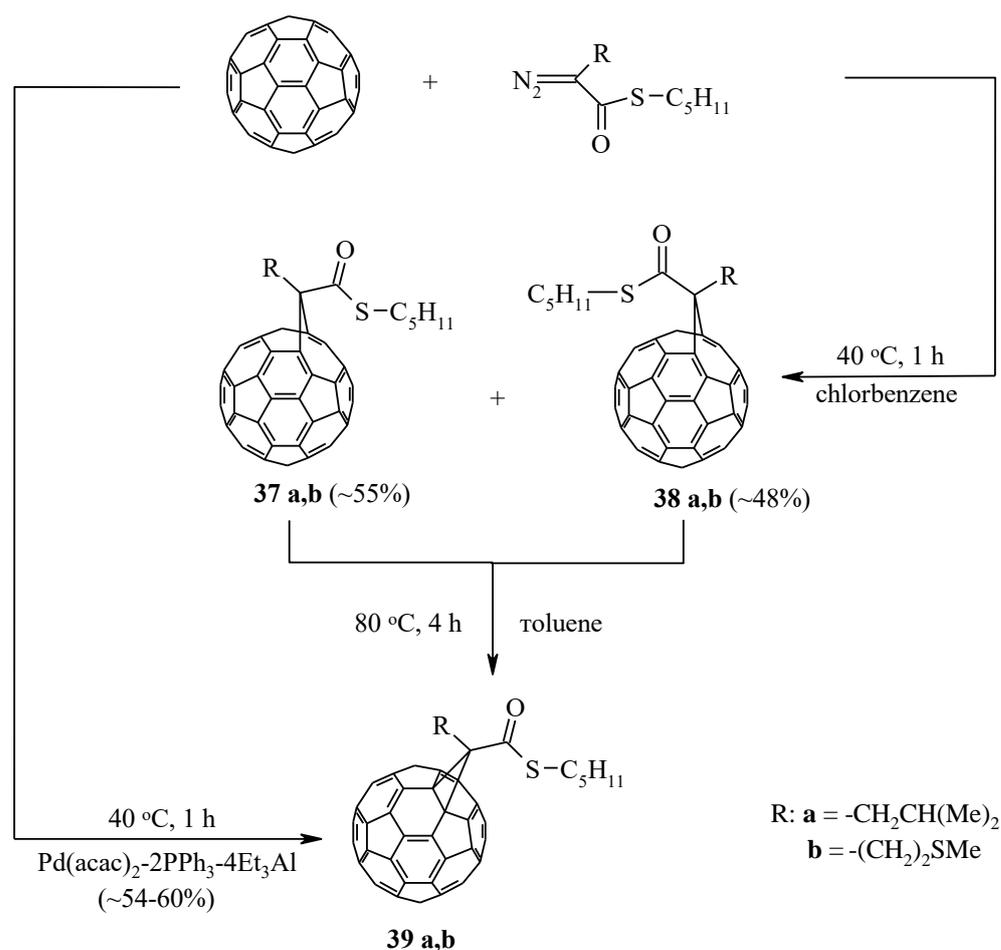
Thus, we found that, in contrast to the reaction of C_{60} -fullerene with unsubstituted diazothioates, the interaction of C_{60} with thiopentyl-2-methyl-2-diazothioate in chlorobenzene takes place at $40\text{ }^\circ\text{C}$ for 1 h, with the formation of an individual [5,6]-open fullerene adduct **35** with the arrangement methyl group at the bridging carbon atom above the plane of the five-membered fragment of the fullerene core (Scheme 9).



Scheme 9. Cycloaddition of α -substituted diazothioates to C_{60} -fullerene.

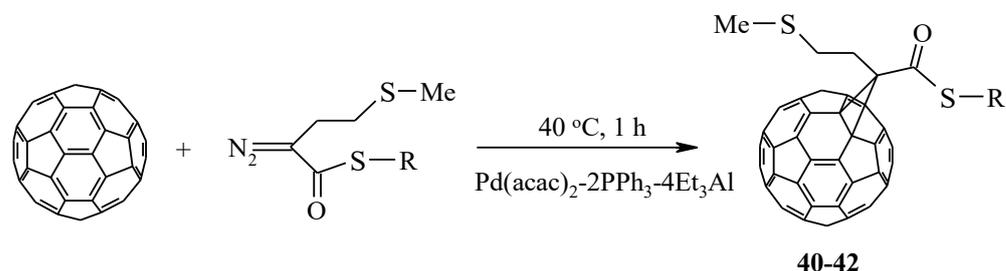
Subsequent experiments showed that the use of a 20 mol% three-component catalyst based on the Pd phosphine complex ($\text{Pd}(\text{acac})_2-\text{PPh}_3-\text{Et}_3\text{Al}$) with a component ratio of 1:2:4 in the reaction of C_{60} -fullerene with thiopentyl-2-methyl-2-diazothioate makes it possible to direct it towards the formation of an individual [6,6]-closed cycloadduct **36** with a yield of ~47%.

Later, we studied the effect of the size of the alkyl substituent in the α -position of the diazo compound on the yield and selectivity of the formation of C_{60} -fullerene cycloadducts, using the example of diazothioates synthesized from amyl mercaptan, leucine, and methionine. It was established that, under the developed conditions ($40\text{ }^\circ\text{C}$, 1 h) C_{60} reacts with the indicated diazo compounds (molar ratio 1:5) in the absence of a catalyst, forming a mixture of the corresponding stereoisomerichomofullerenes **37a,b** (55%) and **38a,b** (48%). Heating a mixture of homofullerenes **37a,b** and **38a,b** in toluene ($80\text{ }^\circ\text{C}$) for 4 h leads to the isomerization of [5,6]-open cycloadducts into [6,6]-closed **39a,b**, respectively (Scheme 10).



Scheme 10. Catalytic cycloaddition of α -substituted diazothioates to C_{60} -fullerene.

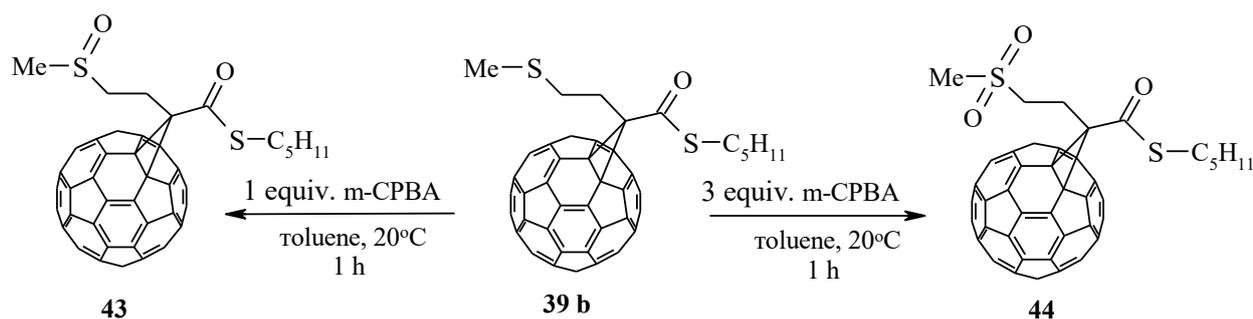
Carrying out the above reaction under catalytic conditions (40 °C, 1 h, 20 mol% $\text{Pd}(\text{acac})_2\text{-}2\text{PPh}_3\text{-}4\text{Et}_3\text{Al}$) leads to the production of exclusively methanofullerenes **39a,b** in 54–60% yields. Similar results were obtained using isopropyl, cyclohexyl, and benzyl diazothioates. In all experiments using the $\text{Pd}(\text{acac})_2\text{-}2\text{PPh}_3\text{-}4\text{Et}_3\text{Al}$ catalytic system, the corresponding methanofullerenes **40–42** are formed (Scheme 11).



40: R = *i*-Pr (~ 35%); **41:** R = Cy (~ 52%); **42:** R = Bn (~35%)

Scheme 11. Catalytic cycloaddition of isopropyl, cyclohexyl, benzyl diazothioates to C_{60} -fullerene.

Using the example of methanofullerene **39b**, we observed the possibility of the selective oxidation of sulfide sulfur to sulfoxide and the sulfone treatment of the starting compound with an equimolar amount or a three-fold excess of *m*-CPBA (Scheme 12).



Scheme 12. Selective oxidation of sulfide sulfur compound **39b** to sulfoxide and sulfonic.

Thus, for the first time, we performed the cycloaddition of diazothioates to C_{60} -fullerene under the conditions of thermal and catalytic reactions. We determined that the interaction of C_{60} with α -substituted diazothioates in the presence of a three-component catalyst based on Pd leads to the selective formation of the corresponding methanefullerenes, while, in the absence of a catalyst, only homofullerenes are formed.

Considering that the majority of additives currently used in industry are sulfur-containing compounds, it can be assumed that oil-soluble sulfur-containing fullerenes are promising as new functional nanomaterials to improve the lubricating and antifriction properties of additives, as well as materials with significantly improved extreme pressure and anti-wear properties.

In this regard, within the framework of this work, we studied the anti-wear and extreme pressure properties of oils containing the synthesized C_{60} derivatives, the structure of which contains sulfur atoms of various nature, as well as various functional groups [25]. The following compounds were chosen as model sulfur-containing C_{60} adducts (Figure 1):

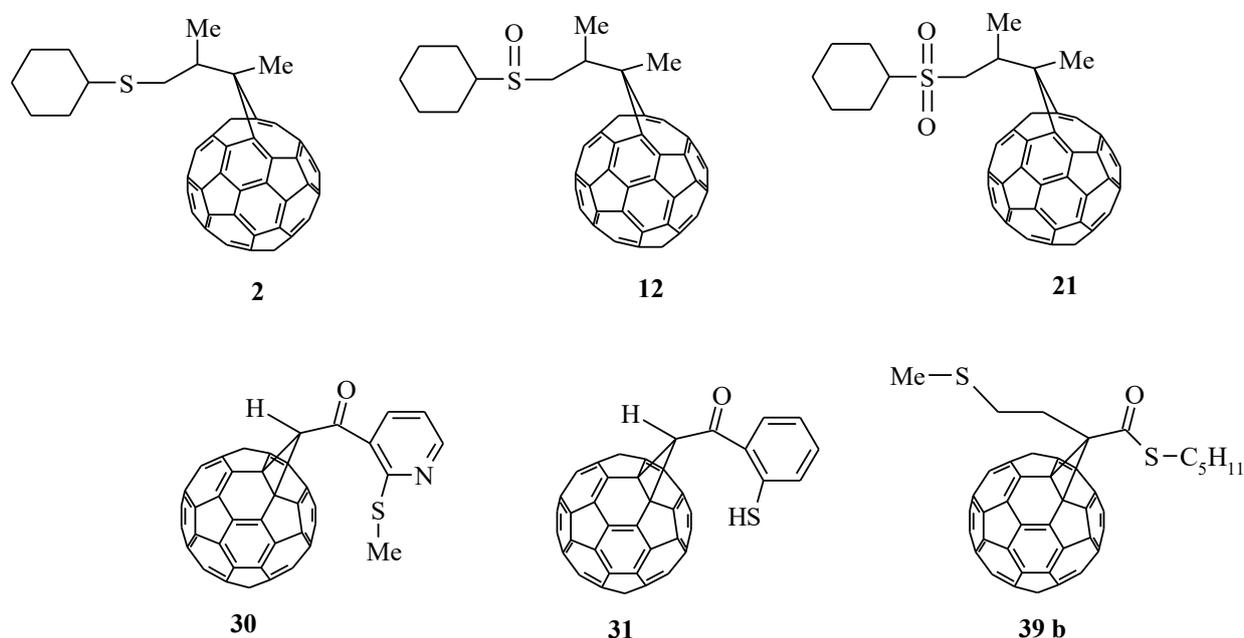
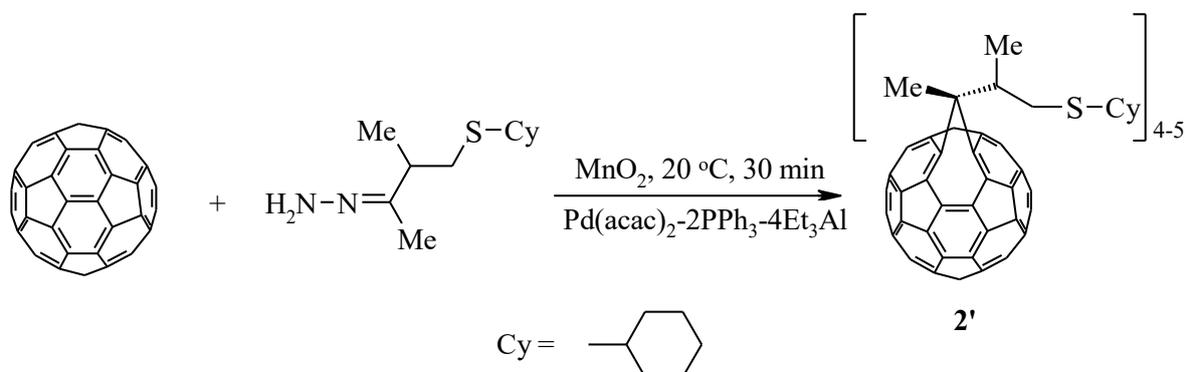


Figure 1. Selected C_{60} -fullerene adducts for the study of antiwear and extreme pressure properties of oils.

Compound **2** is practically insoluble in industrial oils, as well as in known sulfur-containing additives, as a result of which we attempted to carry out the polyaddition of the corresponding diazoalkane generated in situ by the oxidation of hydrazone (cyclohexylthiomethyl)-2-butanone with MnO_2 , to C_{60} , taken in a ratio of 50:1, respectively, in the presence of 20 mol% $Pd(acac)_2-2PPh_3-4Et_3Al$ catalyst, hoping to obtain polycycloadducts with good solubility (Scheme 13). Under these conditions, a mixture of

regioisomeric cycloadducts **2'** is formed, which are built from one C₆₀-fullerene molecule and five molecules of residues of the initial sulfur-containing diazoalkane. The fullerene C₆₀ conversion in this experiment is ~100%.



Scheme 13. Obtaining a sulfur-containing polycycloadduct of fullerene C₆₀.

The regioisomeric mixture of cycloadducts **2'** synthesized by us, as well as monoadducts **12**, **21** and **30**, did not dissolve in I-20A industrial oil, so we attempted to dissolve them in a well-known PRP additive, which is a sulfided propylene tetramer. The additive compositions obtained in this way were easily dissolved in industrial oil I-20A in an amount of 5 wt% with vigorous stirring under the given conditions (4 h, 60 °C), which made it possible to compare the effectiveness of the prepared additives with known samples.

The study of the obtained additives for extreme pressure properties was carried out on a four-ball friction machine, ChMT-1 (State Standard 9490-75). When tested on the ChMT, balls were used according to State Standard 3722-81, made of steel, with a diameter of 12.7 mm, and with a degree of accuracy of 20. We evaluated the welding load (P_w), which characterizes the maximum performance of the lubricant under test conditions, and the critical load (P_{cr}), as well as the wear diameter (d_{ws}), which determines the ability of the lubricant to prevent the occurrence of scuffing of rubbing surfaces and to provide anti-wear properties. The results of the tests carried out are presented in Table 1.

Table 1. Testing oils containing C₆₀-fullerene cycloadducts **2'**, **12**, **21**, **30**.

N ^o	Test Samples	P_{cr} , kgf	P_w , kgf	d_{ws} , mm
1	Industrial oil + 5 wt% STP * + 0.005 wt% of compound 2'	71	596	0.73
2	Industrial oil + 5 wt% STP + 0.005 mac.% of compound 12	75	>1000	0.76
3	Industrial oil + 5 wt% STP + 0.005 mac.% of compound 21	71	>1000	0.74
4	Industrial oil + 5 wt% STP + 0.005 mac.% of compound 30	71	>1000	0.51
5	Industrial oil + 5 wt% of sulfidized tetramers of propylene (STP) (Control sample)	79	398	0.93
6	Industrial oil + 40 wt% of sulfidized tetramers of propylene (STP) (Control sample)	100	596	0.75

* STP—sulfidized tetramers of propylene.

As can be seen from the data in Table 1, the obtained new compositions of additives, in comparison with the original (STP), have better anti-wear and extreme pressure properties and good compatibility with industrial oils, which makes it possible to reduce the consumption of the sulfur-containing extreme-pressure and anti-wear additives currently used and produced by the industry by eight times. They can be used as additives for highly loaded machines and mechanisms, while maintaining their efficiency, as well as to expand the range of new domestic multifunctional additives. It should be noted that C₆₀ adducts containing sulfoxide, sulfone, or sulfide and carbonyl groups have better

solubility in the STP additive, in contrast to monocycloadducts containing only a sulfide group. Methanofullerene **31** does not dissolve in oil and STP additive, as a result of which the tribological properties of this compound could not be studied.

When preparing composite oils for the study of the tribological properties, we found that monoadduct **39b**, in contrast to the compounds **2'**, **12**, **21**, **30** used above, dissolves well directly in industrial oil I–20A, as a result of which the addition of STP, in this case, was not carried out.

As a result of the research, it was shown that the industrial oil I–20 A, containing 0.005 wt% adduct C₆₀ with a thioate group, significantly exceeds the weldability load of oils containing 40 wt% STP ($P_w > 1000$ kgf); however, it has a low P_{cr} index (45 kgf).

The low critical load is likely due to the low sulfur content of the test samples, as we abandoned the use of 5 wt% STP. In this regard, we assumed that an increase in the number of fragments attached to the fullerene molecule would lead to an increase in the critical load index. To confirm our idea, we synthesized a model polyadduct **39b'**, which is an analogue of monoadduct **39b** and contains three to five attached cyclopropane fragments.

The test of the prepared composition consisting of industrial oil I–20 A and 0.005 wt% compound **39b'** showed that, indeed, an increase in the number of attached fragments contributes to an increase in the critical load (P_{cr}) from 45 to 63 kgf, while the welding load (P_w) slightly decreases to 942 kgf.

Using an electron microscope, as well as using atomic force microscopy (AFM), it was established that the introduction of sulfur-containing C₆₀-fullerene derivatives into industrial oil I–20A leads to the smoothing of the steel ball surface at the wear spot after tribocontact.

3. Conclusions

Thus, for the first time, we have developed effective methods for the synthesis of fullerene derivatives containing sulfur atoms of various nature by the cycloaddition of sulfur-containing diazo compounds to C₆₀-fullerene in the presence of the Pd(acac)₂–PPh₃–Et₃Al three-component catalytic system, which provides a fairly simple and effective method for the synthesis of homo- and methanofullerenes—effective additives to oils for highly loaded machines and mechanisms.

Author Contributions: Conceptualization, U.M.D., A.R.T. and A.A.K.; methodology, validation, and execution of chemistry experiments, A.A.K.; manuscript preparation, A.A.K. and A.R.T. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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