Complexation of paramagnetic intermediates formed in the photolysis of 7,7-dimethyl-1,4,5,6-tetraphenyl-2,3-benzo-7-silanorbornadiene: a study by spin chemistry methods

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Complexation of paramagnetic intermediates formed in the photolysis of 7,7-dimethyl-1,4,5,6-tetraphenyl-2,3-benzo-7-silanorbornadiene with n-donors (PPh_3, O_2) was studied by spin chemistry methods.

Key worlds: triplet dimethylsilylene, biradicals, complexation, photochemistry, spin chemistry.

The chemistry of carbene analogs (silylenes, germylenes, stannylenes) is one of the most rapidly developing areas of modern chemistry of organoelement compounds. A great body of experimental data on generation and reactions of these highly reactive intermediates has been accumulated to date. However, data on detailed mechanisms of generation of carbene analogs and their successive transformations are still scarce.[1—5] The derivatives of 7-sila- and 7-germanorbornadienes occupy a particular place among convenient and often used sources of silylenes and germylenes. These compounds decompose with the formation of corresponding carbene analogs under conditions of liquid-phase thermolysis or photolysis.[6,7] Previously,[8—11] we studied the mechanism of their decomposition by the chemically induced dynamic nuclear polarization (CIDNP) technique and pulse laser photolysis. It was shown that the key stage of this process involves homolysis of one of the endocyclic C—E (E = Si, Ge) bonds resulting in a 1,5-biradical whose fragmentation gives a triply excited silylene (germylene). The first examples of reactions of dimethylsilylene (dimethylgermylene) in the triplet excited state were also reported.[10]

The aim of this work was to study complexation of paramagnetic intermediates (biradicals and the triplet dimethylsilylene) generated in the photolysis of 7,7-dimethyl-1,4,5,6-tetraphenyl-2,3-benzo-7-silanorbornadiene (**1**) with electron density donors (triphenylphosphine and oxygen) by spin chemistry methods (CIDNP and magnetic field effects (MFE)). Currently, it is spin chemistry that is one of the main sources of information on the structure and reactivity of paramagnetic intermediates formed in the reactions of silylenes and germylenes.[8—14]

Experimental

7,7-Dimethyl-1,4,5,6-tetraphenyl-2,3-benzo-7-silanorbornadiene (**1**) was synthesized following the known procedure[15] and triphenylphosphine (99%, Aldrich) was used without additional purification. The solvents (CCl_4, hexane) and deuterated cyclohexane, C_6D_6, and CD_2Cl_2 were dried following standard procedures. All experiments were carried out at ~20 °C and at atmospheric pressure. Samples were deoxygenated by Ar bubbling (15 min).

^1H NMR spectra were recorded on a JEOL JNM FX90Q spectrometer operated at 90 MHz and equipped with a photochemical accessory for sample irradiation by a DRSh-1000 high-pressure mercury lamp (1 kW) immediately in the probe of the NMR spectrometer. The concentration of **1** in the experiments was varied from 10^{-3} to 10^{-1} mol L^{-1}, triphenylphosphine was added in 2—5-fold excess with respect to **1**, and the concentration of CCl_4 was 3 mol L^{-1}.

Spectroscopic studies of complexation of dimethylsilylene with PPh_3 were carried out on a microsecond laser pulse installation using a XeCl eximer laser (λ = 308 nm). The standard concentrations of **1** and PPh_3 were $1 \cdot 10^{-3}$ and $2 \cdot 10^{-3}$ mol L^{-1}, respectively. The main product of the photolysis of **1**, 1,2,3,4-tetraphenylnaphthalene (TPN), was recorded by using changes in the optical density (ΔD) at λ 334 nm. The MFE that appeared in the course of the photolysis of **1** were measured in the external magnetic field produced immediately in the sample by a specially designed permanent Sm—Co magnet with varied distance between the poles. The MFE magnitude was calculated using the formula

$$\mathrm{MFE} = \frac{(\Delta D_0 - \Delta D_H)}{\Delta D_0} \cdot 100\%,$$

where ΔD_H and ΔD_0 are the TPN absorption for the reaction in the magnetic field of the magnet and in the earth magnetic field, respectively. The experiments on measuring the MFE were described in more detail in Ref. 11.

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Results and Discussion

Recently,[14] an attempt was made to carry out a CIDNP study of the reactions of Me_2Si with various halogen-containing compounds. 7,7-Dimethyl-1,4-diphenyl-2,3-cyclooctano-7-silanorbornadiene was used as a photochemical source of dimethylsilylene. The reaction of dimethylsilylene with CCl_4 resulted in C_2Cl_6, Cl_3CSiMe_2Cl, and Me_2SiCl_2 as the main products (all compounds were characterized by mass spectrometry and ^1H NMR spectroscopy). However, the attempt[14] to observe the CIDNP effects in this system using an NMR spectrometer (a Bruker AM 300 spectrometer operated at 300 MHz) failed despite the assumption that, by analogy with the previously studied similar reaction of dimethylgermylene,[12,13] in this case the reaction can also proceed by a radical mechanism.

Unlike the above-mentioned study,[14] we succeeded in detecting the CIDNP effects in this system (see Table 1) when studying the reaction of Me_2Si (generated in the photolysis of silanorbornadiene **1**) with CCl_4 in a weaker magnetic field (at 90 MHz). In fact, the recording of a polarized product of the Me_2Si insertion into the C—Cl bond of carbon tetrachloride ($ClMe_2SiCCl_3$) indicates that abstraction of a Cl atom from CCl_4 by dimethylsilylene results in a radical pair (RP) consisting of $^{\cdot}CCl_3$ and $ClMe_2Si^{\cdot}$ radicals (see Table 1).

As follows from the analysis of CIDNP effects on the insertion product ($ClMe_2SiCCl_3$) using the Kaptein rules[16] (the values of magnetic resonance parameters[17] are: the hyperfine interaction constant of methyl protons is positive, $g(ClMe_2Si^{\cdot}) = 2.0031$, $g(^{\cdot}CCl_3) = 2.0091$), this product is formed from the initially triplet RP (Scheme 1). This indicates that the triply excited Me_2Si enters into reaction with CCl_4. In turn, the emission on the $CHCl_3$ proton means that chloroform is also a cage product formed in the initial RP, likely as a result of abstraction by the $^{\cdot}CCl_3$ radical of a H atom from the methyl group in the $ClMe_2Si^{\cdot}$ radical (see Scheme 1). We failed in recording the other (labile) product of this reaction, methylchlorosilene, because silenes containing no bulky substituents are known to be short-lived molecules.[18]

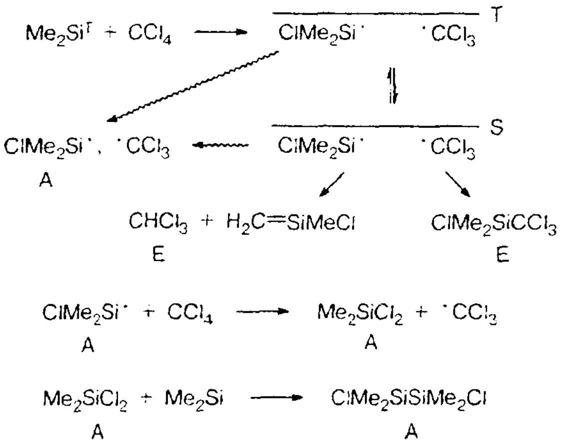
Table 1. ^1H CIDNP effects in the reaction of photodecomposition of **1** in the presence of trapping agents

Reaction product	δ	^1H CIDNP effects	
		1 + CCl_4	**1** + CCl_4 + PPh_3
$Cl(C\underline{H}_3)_2SiCCl_3$	0.70	E*	A*
$(C\underline{H}_3)_2SiCl_2$	0.72	—**	E
$Cl(C\underline{H}_3)_2SiSi(C\underline{H}_3)_2Cl$	0.66	A	—
$C\underline{H}Cl_3$	6.60	E	—

* E denotes emission and A denotes absorption.

** In the experiments carried out in the absence of triphenylphosphine, the CIDNP effect was observed only on tetramethyldichlorodisilane, the product of successive transformation of Me_2SiCl_2 (see Scheme 1).

Scheme 1



This reaction is the second example of chemical reaction of triply excited dimethylsilylene. The first example is the reported reaction of Me_2Si^T with thiacycloheptyne.[10]

The observation of CIDNP effects for a triplet RP indicates that the lifetime (τ) of triplet dimethylsilylene is longer than $1/k[CCl_4]$ in the process under study. No data on the rate constant for the reaction of Me_2Si with CCl_4 are available; however, the k value for Me_2Ge is known ($1.2 \cdot 10^7$ L mol^{-1} s^{-1}).[19] Hence, it can be expected that the lifetime of Me_2Si, which is more reactive than Me_2Ge,[20,21] is no longer than 10^{-7} s.

The introduction of triphenylphosphine in the reaction of Me_2Si with CCl_4 results in the sign change of CIDNP on the main products (see Table 1). Among these products, Me_2SiCl_2 is recorded instead of tetramethyldichlorodisilane (a product of Me_2Si insertion into the C—Cl bond of Me_2SiCl_2). By analogy with the previously studied complexation of PPh_3 with Me_2Ge,[22] it can be assumed that Me_2Si forms an unknown short-lived donor-acceptor complex with PPh_3 (see reviews[23,24] concerning stable complexes of carbene analogs with Lewis bases). It is known[25] that complexation results in significant changes in the spectral properties and reactivity of carbene analogs and, in some instances, in changes in the direction of chemical reactions. For this reason, the expected decrease in the reactivity of Me_2Si bound in a complex with PPh_3 is the most probable reason for the absence of subsequent transformations of Me_2SiCl_2. The experimental rate constant for the reaction of complex $Me_2Ge \cdot PPh_3$ with CCl_4 is $3.4 \cdot 10^6$ L mol^{-1} s^{-1}.[25]

The change in the CIDNP signs in the products of radical recombination in cage ($ClMe_2SiCCl_3$) and in the bulk solvent (Me_2SiCl_2), occurring in the presence of PPh_3, indicates the change in multiplicity of the reacting state of Me_2Si under the action of an n-donor agent. It is reasonable to assume that this is due to shortening of the lifetime of Me_2Si^T in the presence of PPh_3 as a result of weak interaction (complexation) between these molecules.

We tried to detect the $Me_2Si\cdot PPh_3$ complex using spectral methods (laser pulse photolysis). Previously,[8] we succeeded in using this method for detecting a complex of Me_2Si with $CHBr_3$. However, experiments on pulse photolysis of silanorbornadiene **1** in the presence of PPh_3 revealed no absorption bands of short-lived molecules in the wavelength range 320—600 nm. Thus, our attempt at direct detecting of a $Me_2Si\cdot PPh_3$ complex using a Xe laser with λ 308 nm as a photolyzing source failed. Possibly, it is the use of a Xe laser that can be the reason for the failure, since the maxima of the absorption bands of Me_2Si complexes with other phosphines (PBu_3, PCy_3) lie just in the λ region 306—310 nm.[26]

Despite the impossibility of direct spectroscopic detection of the $Me_2Si\cdot PPh_3$ complex in solution, we obtained indirect evidence of its existence from studying the effect of PPh_3 additives on the yield of TPN (the final stable product of the photolysis of silanorbornadiene **1**) in magnetic fields of different strength. It has been shown[11] that the yield of TPN is dependent on the strength of the constant external magnetic field. The detailed mechanism of the photolysis of silanorbornadiene **1** established on the basis of analysis of the MFE and ^1H CIDNP is presented in Scheme 2.

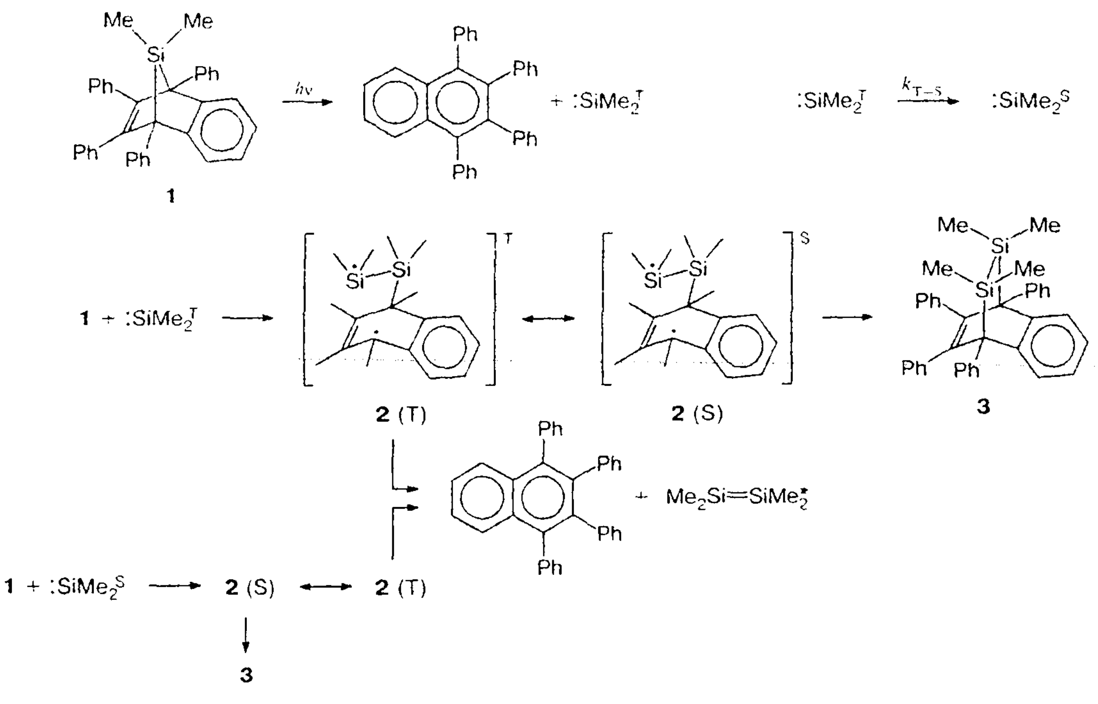
It was shown that the MFE is produced mainly in 1,6-biradicals **2** generated as a result of the reaction of both triplet and singlet dimethylsilylene with initial silanorbornadiene **1** in the bulk. The magnetic field dependences (MFE) recorded both in the presence and in the absence of PPh_3 are shown in Fig. 1. Their shape (the curves with extrema in the magnetic fields ~100—300 mT) is characteristic of the MFE produced in biradicals.[27] The sign of the MFE recorded in the absence of PPh_3 indicates that the biradical-precursor of TPN (Fig. 1, *a*) is initially in the triplet state, since only in this case does the minimum yield of TPN correspond to an extremum of the magnetic field dependence.

Based on the above-mentioned facts, it was suggested[11] that Me_2Si reacting with initial silanorbornadiene **1** is mostly in the triplet excited state. According to Scheme 2, this reaction results in a triplet 1,6-biradical. Hence the rate of T—S conversion in Me_2Si should be lower or comparable with that of its reaction with **1** ($k\cdot[\mathbf{1}] = 5.7\cdot 10^9\cdot 10^{-3} = 5.7\cdot 10^6\ s^{-1}$).[8] The reaction of **1** with the singlet dimethylsilylene proceeds much slower.

If, as was assumed above, the interaction of Me_2Si^T with PPh_3 shortens the lifetime of Me_2Si^T, it can be expected that the addition of PPh_3 will also affect the MFE observed in the course of the photolysis of **1**. In fact, virtually no MFE is observed in the presence of PPh_3 (Fig. 1, *b*). By analogy with the reactions of dimethylgermylene,[22] the absence of MFE in this case can be explained by the fact that the singlet dimethylsilylene bound in a complex with PPh_3 does not react with initial **1** and, hence, no 1,6-biradicals **2** are formed.

However, the observation of CIDNP effects on the protons of disilabicyclooctadiene **3** (a product of reac-

Scheme 2



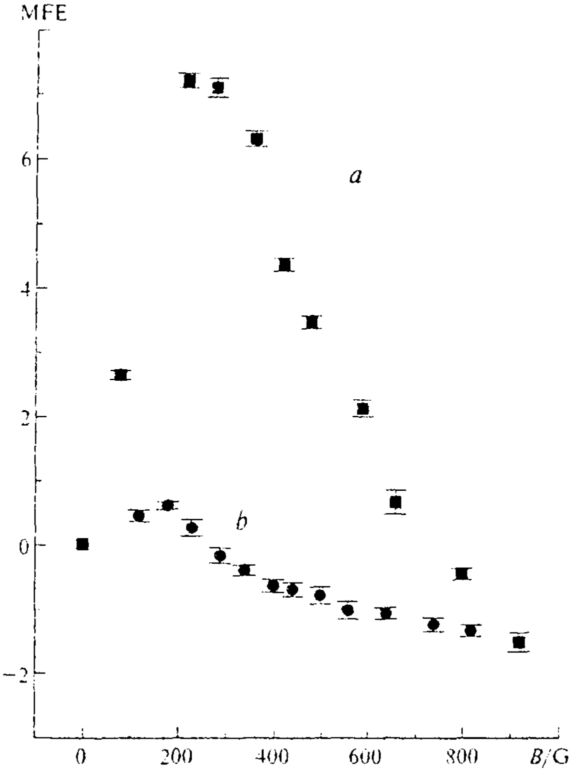


Fig. 1. Magnetic field dependences (MFE) recorded in the absence (*a*) and in the presence of PPh_3 (*b*).

tion between **1** and Me_2Si) in the reaction mixture in the presence of PPh_3 refutes the last assumption. The presence of CIDNP effects unambiguously indicates that, unlike dimethylgermylene, Me_2Si bound in a complex with PPh_3 does react with **1** to form biradical **2**. As follows from analysis of ^1H NMR spectra, only the ratio of the yields of **2** and TPN is changed in the presence of PPh_3, whereas the composition of the end reaction products remains unchanged.

Thus, the role of PPh_3 in photodecomposition of **1** can be represented by Scheme 3.

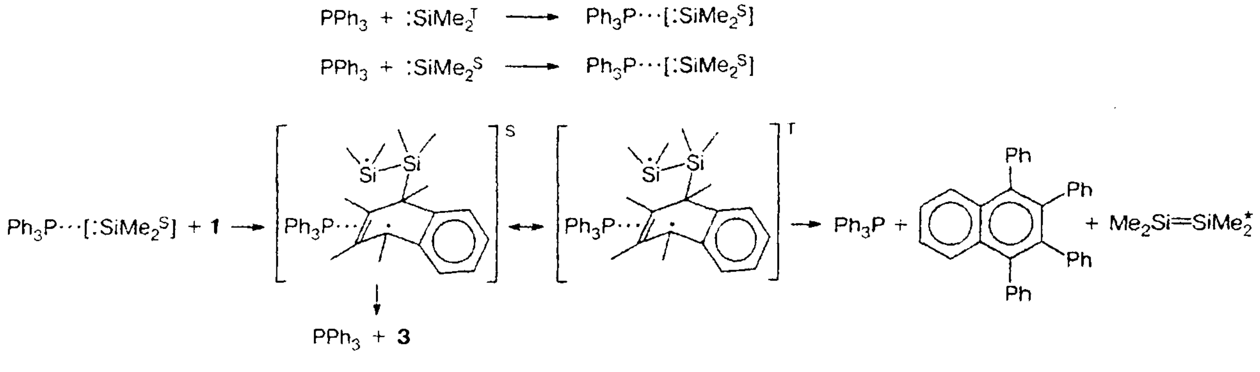
The reasons for the absence of MFE in the reaction of singlet dimethylsilylene bound in a complex with triphenylphosphine will be discussed below.

Dioxygen is another reagent affecting the magnitude of MFE observed in the course of the photolysis of **1**. In those cases where direct detection of short-lived biradicals is for any reason associated with considerable difficulties, valuable information on their lifetimes, multiplicity, structure, and reactivity can be obtained by studying their interaction with dioxygen[28] (in particular, by analyzing the composition of the products and the rates of their formation as functions of the O_2 concentration).

As is known, dioxygen is a multifunctional reagent. In the system under consideration, it can act as a highly efficient chemical trap of Me_2Si ($k = 2.25 \cdot 10^9$ L mol^{-1} s^{-1})[9] and as an active quencher of triplet states of the molecules (the rate constant k for quenching the triplet state of TPN by dioxygen is $2 \cdot 10^9$ L mol^{-1}s^{-1})[8]; finally, it can serve as a catalyst of singlet-to-triplet (S—T) conversion in paramagnetic intermediates, *e.g.*, biradicals.[27]

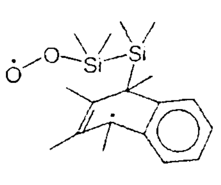
If photolysis of silanorbornadiene **1** in magnetic fields of various strength is carried out in the presence of dioxygen, the magnitude of the MFE observed increases by several times and the position of its maximum is shifted.[11] It has been shown[27] that, in accord with the nature of spin effects, their manifestation can be expected only in the processes involving the acts of S—T conversion. This indicates that dioxygen reacts immediately with biradical in the reaction under study. It is also known that the interactions resulting in manifestation of the MFE can be rather weak and that paramagnetic species, in which the S—T conversion occurs, are short-lived. On this basis, it can be suggested that complexation between O_2 and 1,6-biradicals **2** is reversible. Actually, the simultaneous effect of O_2 on the MFE magnitude and the position of extremum of the magnetic field dependence becomes understandable only in this case. In accord with this assumption, the MFE in the presence of O_2 is produced in another paramagnetic species, which is indicated by shifts of maxima of the magnetic field dependences.

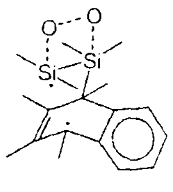
Scheme 3



The MFE of the opposite sign in the experiments with simultaneous participation of O_2 and PPh_3 (Fig. 2, *b*) indicates the interaction of O_2 with the singlet and triplet 1,6-biradicals **2**. Apparently, the singlet 1,6-biradicals **2** generated in the reaction of Me_2Si^S (bound in a complex with PPh_3) with initial silanorbornadiene **1** dominate in the bulk in this case. It is in this case that the MFE of the opposite sign (Fig. 2) should be expected.

A mirror shape of two magnetic field dependences recorded both in the presence and in the absence of dioxygen indicates that the MFE are produced in intermediates of identical chemical structure and differing only in their multiplicity. Most probably, these are complexes of 1,6-biradicals **2** with dioxygen:





Obviously, O_2 expels PPh_3 from its complex with biradical **2** (see Scheme 3), thus giving rise to the MFE (see Fig. 2, *b*).

The formation was reported[30] of reversible short-lived complexes of O_2 with biradicals, in which O_2 plays the role of catalyst of further transformations without generating new products. It is likely that this situation is similar to that studied in this work. Substitution of triphenylphosphine by dioxygen molecule in the complexes of triphenylphosphine with transition metals has also been reported.[31]

The absence of MFE in the photolysis of **1** in the presence of PPh_3 (but without dioxygen) (see Fig. 1, *b*) can be explained assuming that in the case where biradical **2** is bound in a complex with PPh_3 (see Scheme 3), this paramagnetic complex differs from the free biradical in properties, *e.g.*, by stronger exchange interaction. Thus, in accord with the laws of MFE production,[27] their interaction should manifest itself in much stronger magnetic fields that were not studied in this work.

High sensitivity of the MFE in the complexation reaction under study (*cf.* Figs. 1 and 2) means first of all that the lifetime of the complex of 1,6-biradical **2** with dioxygen is sufficient for the S→T conversion to occur, which is needed for producing the MFE. Calculations of the MFE produced in 1,6-biradicals **2** under the action of hyperfine and electron exchange interactions indicate that the lifetime of these complexes is of the order of microseconds.

The shift of maxima of the magnetic field dependences (MFE) toward stronger magnetic fields observed in the experiments with dioxygen indicates a strengthening of effective exchange interaction in the complexes of biradicals **2** with dioxygen compared with the exchange interactions in free biradicals **2**.

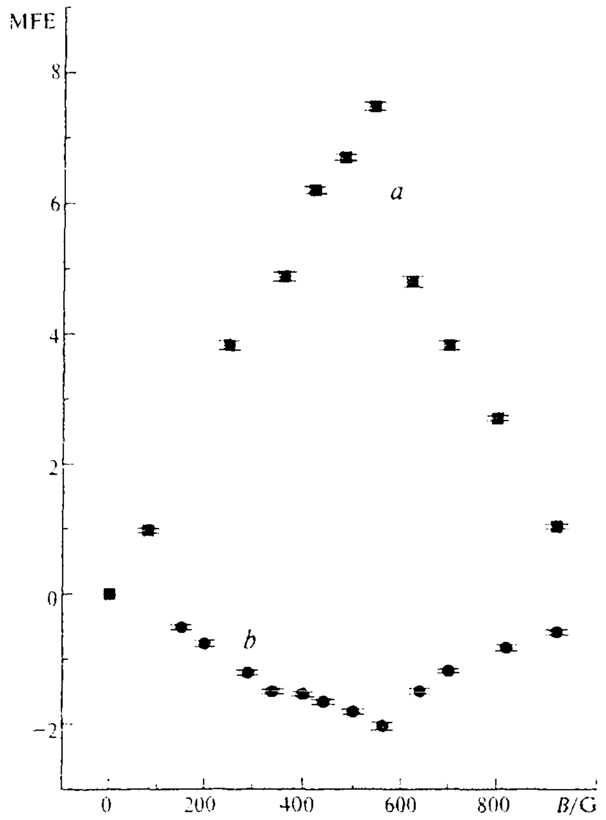


Fig. 2. Magnetic field dependences (MFE) recorded in the presence of O_2 (*a*) and in the presence of both O_2 and PPh_3 (*b*).

Our calculations of the MFE carried out taking into account the magnitudes of effective exchange interaction in the presence of O_2 do not reproduce the magnitude of the experimentally observed effect. Hence not only weak and exchange interactions in biradicals participate in the production of MFE. It can be assumed that appreciable increase in the magnitude of MFE in the presence of dioxygen is also due to acceleration of relaxation in a 1,6-biradical affected by paramagnetism of O_2. This phenomenon was called spin catalysis (see, *e.g.*, Refs. 32, 33).

Thus, our study has demonstrated high sensitivity of the spin chemistry methods for studying the complexation effects of short-lived paramagnetic intermediates. The uniqueness of such methods consists in providing the possibility of not only detecting the presence of weak interaction, but also making certain hypotheses concerning the structure and several physicochemical properties of the complexes studied.

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