# Organometallic Chemistry

## Radical steps in the reactions of organometallic compounds with 2-methyl-2-nitrosopropane: experimental evaluation of the validity of the nitroxyl method for investigations of homolytic reactions of organometallic compounds

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Radical adducts formed in the reactions of organometallic compounds of group II—V elements and of some organochromium and organoiron compounds with 2-methyl-2-nitrosopropane and phenyl(*tert*-butyl)nitrone were studied by ESR. Nitroso compounds and nitrones can be used as selective spin traps for investigations of homolytic reactions involving organometallic compounds.

**Key words:** radicals; spin traps; organometallic compounds; ESR.

The interest in reactions of organometallic compounds (OMC) with nitroso compounds is caused by the fact that the latter are traditionally used as spin traps. The method of spin traps is the most facile and accessible and provides much information in ESR investigations of radical reactions in the liquid phase.[1,2] It is based on the capture of a short-lived radical by a certain compound (a trap) to yield a stable adduct having a characteristic ESR spectrum:

$$R^{\bullet} + Str \longrightarrow R{-}Str^{\bullet} \qquad (1)$$

where Str is a spin trap.

A substantial drawback of this method is that the spin trap is an additional compound introduced into the system that can react with the compounds under study including OMC. In the present work we have analyzed the interaction of OMC derived from group II—V elements with 2-methyl-2-nitrosopropane (MNP) and phenyl(*tert*-butyl)nitrone (PBN) and have evaluated the application of the nitroxyl method (the method of spin traps) to the chemistry of organometallic compounds using reactions of the above-mentioned OMC with oxygen and organometallic peroxides as examples.

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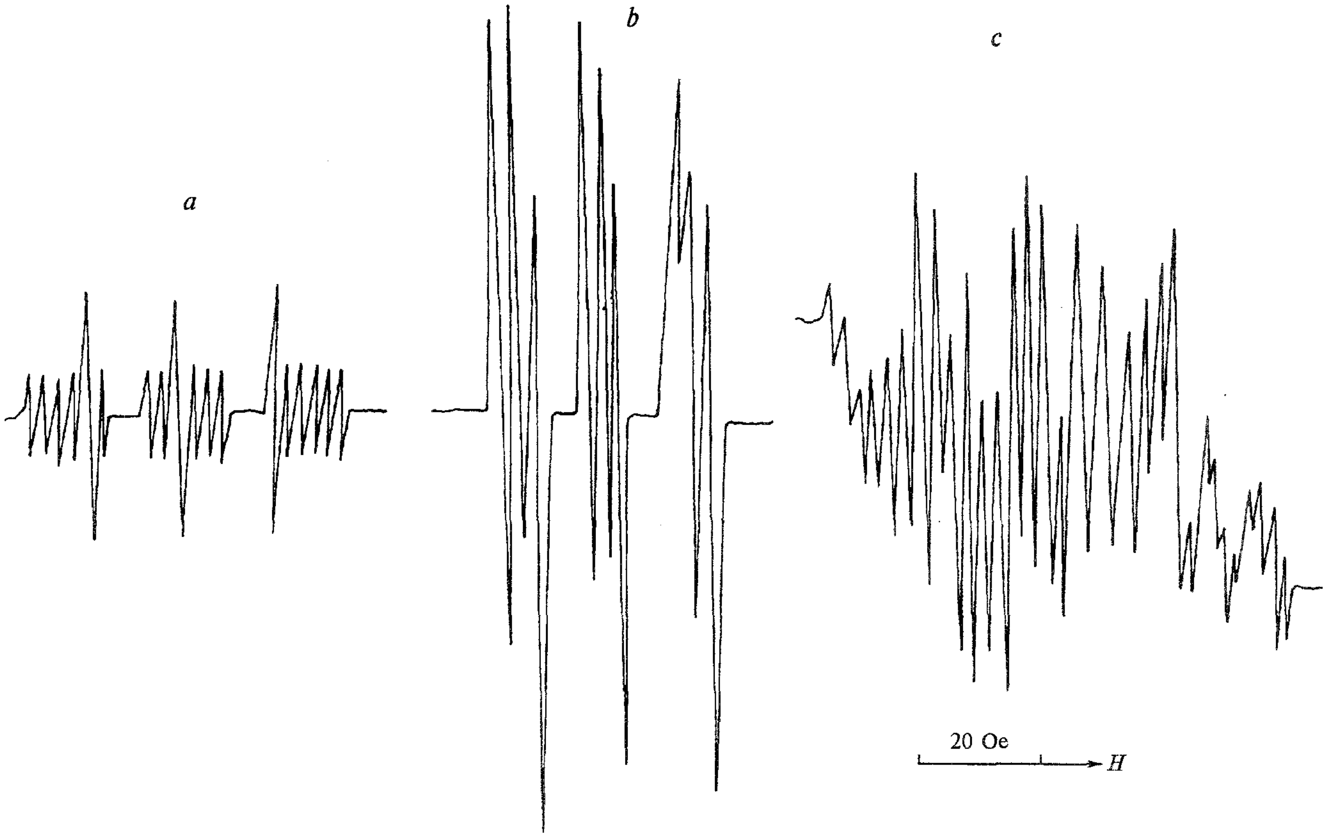


**Fig. 1.** The ESR spectrum of MNP—OMC systems at 293 K: trimethylaluminum (*a*); trimethylthallium (*b*); triethylaluminum (*c*).

## Experimental

ESR spectra were recorded at ~20 °C on EPA-2M and RE-1301 spectrometers. Samples for the analysis were prepared with exclusion of light by dosing solutions of reactants preliminarily freed from oxygen into special tubes followed by their evacuation to 1.3 Pa; concentrations of the reactants amounted to 0.05÷0.1 mol $L^{-1}$, that of the spin trap was 0.1 mole per mole of the reactant. Radical traps, peroxides, and OMC were prepared by standard procedures; their physicochemical constants correspond to the literature data.

## Results and Discussion

It has been found by ESR that the methyl derivatives of OMC of group II and III elements (Zn, Cd, Hg, B, Al, Ga, In, and Tl) do not form paramagnetic adducts when mixed with MNP in the dark. Trimethylaluminum and trimethylthallium react with MNP in the light to give radical complexes between the corresponding OMC and the product of photodecomposition of the spin trap, di(*tert*-butyl)nitroxyl (**1**) (Fig. 1).

$$(\mathrm{Bu^tNO})_2 \xrightarrow{h\nu} \dot{\mathrm{N}}\mathrm{O} + \underset{\mathbf{1}}{\mathrm{Bu^tN(\dot{O})Bu^t}} \longrightarrow$$

$$\xrightarrow[\mathbf{2}]{\mathrm{MMe_3}} \underset{\mathbf{3}}{\mathrm{Bu^t_2N \overset{\cdot}{-} O{:}\!\rightarrow MMe_3}} \qquad (2)$$

M = Al, Tl

The hyperfine splitting constants at the nitrogen and metal atom nuclei are the following: $a_N$ = 18.0 Oe, $a_{Al}$ = 1.5 Oe ($g$ = 2.0040); $a_N$ = 15.3 Oe, $a_{Tl}$ = 4.8 Oe ($g$ = 2.0020). Nitroxyl radicals form analogous complexes with group III metal halides as Lewis acids.[3,4] A multi-component signal associated with the splitting at Al, N, and H nuclei also appears in the ESR spectrum, when MNP is mixed with triethylaluminum (see Fig. 1, *c*).

Additions of pyridine suppress coordination of OMC by radical **1**, and the ESR spectrum exhibits a triplet corresponding to **1**. No other adducts, for example, methyl(*tert*-butyl)nitroxyl, which would attest to the occurrence of radical reactions between OMC and MNP, were observed even after prolonged (> 24 h) storage of the mixture of reactants. Similar data were obtained for PBN. This allows MNP and PBN to be used as spin traps for investigating radical reactions of methyl compounds of group II and III elements.

For example, in the reactions of these compounds with benzoyl peroxide, adducts of methyl radicals were detected ($a_N$ = 15.2 Oe, $a_H$ = 11.4 Oe), while in the case of *tert*-butyl peroxide and its organometallic analogs, the *tert*-butyl trimethylsilyl peroxide and *tert*-butyl triethylstannyl peroxide, along with methyl(*tert*-butyl)nitroxyl, the radical $Bu^tN(O)OR$ ($a_N$ = 27.3 Oe) was found. The validity of the data obtained is supported by

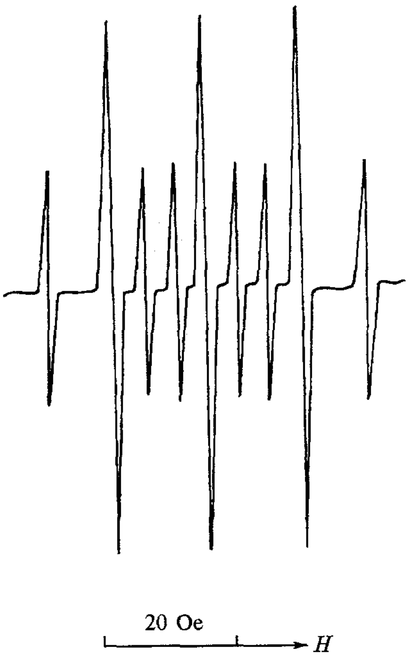


**Fig. 2.** The ESR spectrum of the MNP—tributylgallium system at 293 K.

the previously published information on the radical steps in the reactions of group II [5] and III [6,7] OMC with oxidants and on the analysis of the products of these reactions.[8]

In contrast to methyl derivatives, other alkyl derivatives of the above-mentioned metals react with nitroso compounds in the light to afford the corresponding adducts, which can be detected by ESR (Fig. 2).

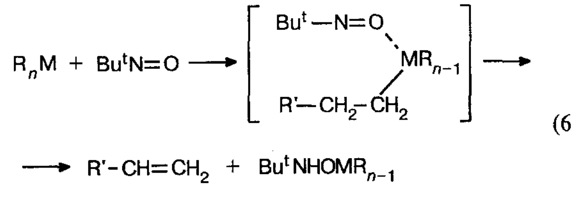
$$(\mathrm{Bu^tNO})_2 \xrightarrow{h\nu} \mathrm{Bu^tN(\dot{O})Bu^t} + \mathrm{\dot{N}O} \qquad (3)$$

$$\mathrm{Bu^t_2N\dot{-}O} + \mathrm{MR}_n \longrightarrow \mathrm{Bu^tNOMR}_{n-1} + \mathrm{R^{\cdot}} \qquad (4)$$

$$\mathrm{R^{\cdot}} + \mathrm{Bu^tNO} \longrightarrow \mathrm{RN(\dot{O})Bu^t} \qquad (5)$$

$\mathrm{R = Et, Bu, C_5H_{11}}$; $\mathrm{M = B, Al, Ga, In, Tl}$

Along with homolytic transformations, insertion of OMC at the —N=O bond occurs with the liberation of the alkene.



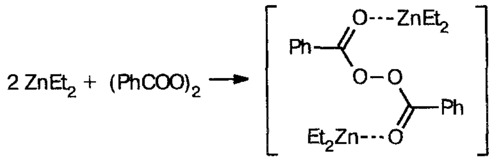
$$\mathrm{R}_n\mathrm{M} + \mathrm{Bu^tN{=}O} \longrightarrow \left[\begin{matrix}\mathrm{Bu^t{-}N{=}O} & \\ & \mathrm{MR}_{n-1} \\ \mathrm{R'{-}CH_2{-}CH_2} & \end{matrix}\right] \longrightarrow \mathrm{R'{-}CH{=}CH_2} + \mathrm{Bu^tNHOMR}_{n-1} \qquad (6)$$

In the condensates of the reactions of triethyl- and tributylgallium with MNP in benzene at 20 °C, ethylene and 1-butene in 28 % and 31 % yields, respectively, and trace amounts of ethane and butane were detected after 4 h. The previously studied similar reaction of diethylzinc with 2-bromo-2-nitrosopropane[9] occurs with a maximum yield of 70 %. Ethane, acetone, and acetoxime were found in the hydrolysis products. Tributylborane reacts with MNP at 25 °C to give 1-butene and *O*-butylborylhydroxylamine,[10] and this reaction occurs much more quickly than that described by Eq. (4).

The possibility of the occurrence of processes (3)—(6) impose some restrictions on the application of the method of spin traps for investigating radical reactions of the OMC in question, since a spin trap which has reacted with an OMC is removed from the reaction sphere and therefore cannot localize the radical sites. Moreover, the formation of radical adducts (see Eqs. (4) and (5)) hampers the interpretation of the data obtained.

The results of the study of radical reactions of OMC of group II and III elements with oxygen and organometallic peroxides indicate that the nitroxyl method may be advantageously used in the case of trialkylboranes[11,12] and organoaluminum compounds,[6,7] and may be used to a limited extent for organoindium, -gallium, and -thallium derivatives[11] and for alkylzinc and alkylcadmium compounds.[5] For example, it has been shown in a spin-trap study of reactions of organozinc compounds with peroxides that the appearance of the ESR spectrum depends considerably on the order in which the reactants are mixed. When benzoyl peroxide is introduced into a solution of 2-methyl-2-nitrosopropane and diethylzinc, the ESR spectrum exhibits a signal for the adduct $\mathrm{EtN(\dot{O})Bu^t}$ ($a_\mathrm{N}$ = 15.1 Oe, $a_\mathrm{H}$ = 10.2 Oe) and an intense triplet with the splitting constant $a_\mathrm{N}$ = 13.9 Oe ($g$ = 2.0039). This ESR signal is due to interaction of the trap with dialkylzinc and appears when they are mixed in the absence of peroxide. Analysis of the spectrum observed and the assignment of this signal to a particular radical are difficult (possibly $\mathrm{Bu^t_2N\dot{-}O{:}\rightarrow ZnEt_2}$ (**3a**)).

When diethylzinc is added to a mixture of peroxide and the trap, the intensity of the ESR signal caused by the assumed adduct **3a** is noticeably lower and the contribution of the ethyl(*tert*-butyl)nitroxyl radical is higher. If the spin trap is introduced into a preliminarily prepared mixture of dialkylzinc with peroxide, only the ESR signal for adduct $\mathrm{Bu^tN(\dot{O})Et}$ resulting from the radical reaction of diethylzinc with peroxide[8] is observed, *i.e.*, no adduct **3a** can be detected. When peroxide is mixed with an OMC, the formation of a donor-acceptor type complex, according to Eq. (7), obviously occurs, which prevents interaction between the OMC and the trap.



(7)

This complex decomposes to give ethyl radicals. No benzoyloxy radicals were detected in the solution. Notice that a similar procedure was used for investigating reactions of organoboron[12] and organoaluminum compounds[6] with peroxides.

Organometallic compounds of group IV elements are much more inert with respect to nitroso compounds and nitrones than OMC derived from group II and III elements. Alkyl and aryl derivatives of Si, Ge, Sn, and Pb do not react with MNP and PBN in solutions in hydrocarbons at 20 °C. This makes it possible to use the nitroxyl method successfully for investigating homolytic reactions of these compounds.

Similar results were obtained for organomercury compounds that do not react with MNP and PBN at 20 °C. In particular, ESR combined with the spin trap technique has been applied to the investigation of the reactions of diethyl- and diphenylmercury with peroxides,[5] the properties of diisopropylmercury as a co-initiator of radical polymerization,[14] and photolysis of dibenzyl-, dimethyl-, and diethylmercury.[15]

After mixing MNP with alkyl complexes of group V metals (trimethyl-, triethyl, and tributylantimony or -bismuth) in the dark, no paramagnetic adducts were detected by ESR. When the system was irradiated with light, di(*tert*-butyl)nitroxyl $Bu^tN(O)Bu^t$ ($a_N$ = 15.4 Oe) and the corresponding alkyl(*tert*-butyl)nitroxyls $Bu^tN(\dot{O})R$, where R = Et, Bu ($a_N$ = 15.2 Oe, $a_H$ = 10.2 Oe), and Me ($a_N$ = 14.9 Oe, $a_H$ = 11.3 Oe) were found. In analogy with OMC of group II and III elements, we may assume that these adducts are produced according to Eqs. (3)—(5) and that photodecomposition of organobismuth compounds unstable in the light plays a certain role in this process.[16] Therefore, to avoid photolysis of spin traps, radical reactions of OMC of group II, III, and V elements should be studied with protection from light, either using ampules of dark glass or under illumination with a low-power incandescent lamp (protected with a ZS-2 light filter).

The above-described procedure was successfully used for investigating reactions of antimony and bismuth alkyl derivatives with *tert*-butylperoxide, *tert*-butyl trimethylsilyl peroxide, di(*tert*-butyldioxy)triphenylantimony, and molecular oxygen. It was found that the reactions of organoantimony and organobismuth compounds with peroxides are homolytic. Adducts of the corresponding alkyl radicals were detected by ESR (Fig. 3); no alkoxy radicals were found. The integral intensity of the ESR signal for $Bu^tN(O)R$ adducts (R = Me, Et, Bu) resulting from the interaction of alkylbismuth and alkylantimony with peroxides varies in the following order: di(*tert*-butyldioxy)triphenylantimony > benzoyl peroxide > *tert*-butyl trimethylsilyl peroxide > *tert*-butyl peroxide, which is associated with the peculiarities of radical formation and the relative activities of these peroxides in the reactions with alkylboron derivatives in the presence of vinylic monomers.[12] The absence of ESR signals corresponding to adducts of RO radicals, together with the literature data on the structure and reactivity of organoantimony and organobismuth compounds,[16] make it possible to suggest that OMC derived from group V elements react with peroxides according to Eq. (8) *via* the intermediate formation of five-coordinate compounds.

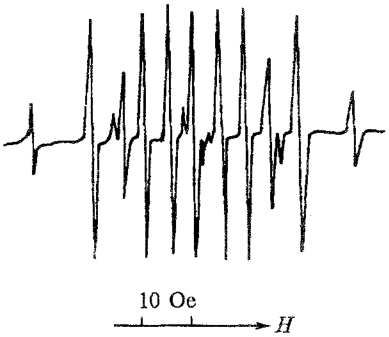


**Fig. 3.** The ESR spectrum of trimethylbismuth—di(*tert*-butyldioxy)triphenylantimony system at 293 K; MNP as the spin trap.

$$R_3Bi + R'OOR' \longrightarrow [R_3Bi(OR')_2] \longrightarrow 2R^{\cdot} + RBi(OR')_2 \quad (8)$$

Homolytic decomposition of five-coordinate bismuth complexes was established by ESR using the spin trap technique.[17]

Phenyl derivatives of antimony and bismuth do not react with the traps either in the dark or in the light. In the reaction of triphenylbismuth with benzoyl peroxide, the radical $PhN(O)Bu^t$ ($a_N$ = 12.4 Oe, $a_H$ = 1.9 Oe, $a_{H'}$ = 0.9 Oe) was detected by ESR. When the reaction was carried out in toluene, $Bu^tN(\dot{O})CH_2Ph$ ($a_N$ = 14.6 Oe, $a_H$ = 7.4 Oe) was found. 2,4,6-Tribromonitrosobenzene can also be used as a spin trap for investigating homolytic reactions of phenyl OMC derivatives. The nitroxyl method was successfully used in a study of radical polymerization of vinylic monomers in the presence of organobismuth compounds.[18]

It has been reported in the literature[19—21] that the method of spin traps has been used for investigating radical reactions of chromium, iron, and some other OMC. Many of these compounds and traps interact without forming radical adducts. However, the metal atom in these cases is undoubtedly coordinated by the nitroso group.

$$Bu^tN{=}O + MR_n \longrightarrow Bu^tN{=}O{:}{\rightarrow}MR_n \quad (9)$$

Analogous interaction is also possible when MNP and PBN are mixed with organic compounds of nontransition metals. The resulting complex differs from the starting OMC in its reactivity and this should be taken into account in interpreting data obtained by the method of spin traps. Therefore, it is worthwhile to verify the results by elemental analysis of the reaction products in combination with other methods.

Thus, the nitroxyl method is of limited utility in the investigation of homolytic reactions involving OMC. It can be successfully used if OMC are inert with respect to spin traps or if the rates of their reactions are lower than those of radical formation and of capturing the radicals by the trap in the system under study. The latter condition is often satisfied, since the rate constants of the capture of alkyl and alkoxyl radicals by nitroso compounds are relatively high ($10^5$—$10^6$ L mol$^{-1}$ s$^{-1}$). However, in each particular case, the application of the nitroxyl method to the chemistry of OMC requires the analysis of the interaction of the trap with the starting reactants.

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