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Chalcogen Derivatives of Iron Carbonyls. VIII. Reaction of $Fe_2(CO)_6(\mu X)_2$ (X = S, Se) with Nucleophiles: CO Substitution and Fe_3X_2 Cluster Formation

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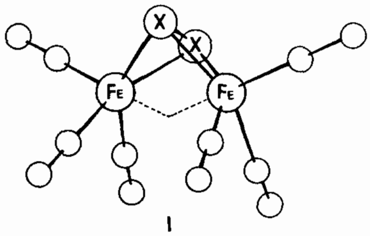
Phosphine ligands L react with $Fe_2(CO)_6(\mu X)_2$ (X = S, Se) complexes giving rise, together with the expected mono- and bi-substituted derivatives, $Fe_2(CO)_5LX_2$ and $Fe_2(CO)_4L_2X_2$, to more complex polynuclear clusters $Fe_3(CO)_{9-x}L_xX_2$ (x = 0, 1, 2). The yield of the different products is shown to depend on the ligand and the reaction conditions. A mechanism is proposed implying the initial formation of an 'adduct' $Fe_2(CO)_6LX_2$, which leads to the binuclear derivatives by loss of CO and to the trinuclear derivatives by coordination on the parent complex via the chalcogen atoms.

Introduction

A large number of structurally related diiron hexacarbonyl complexes of general formula $Fe_2(CO)_6(\mu X)_2$, in which X are organic sulfur, selenium or tellurium bridging groups, have been prepared and characterized [1]. Extensive investigations on the substitution chemistry of these complexes, by replacing one or two CO's with phosphine-type ligands [2], together with data on the mechanistic aspects of these reactions [3], have recently appeared. Among these complexes, unique structural feature is presented when X is simply a sulfur or a selenium atom (the tellurium compound is not known), *i.e.* a direct X–X bond, which maintains the diamagnetism of the species. The structure of the sulfur compound $Fe_2(CO)_6S_2$ (I) has been known from many years [4] and is similar to the general molecular structure of the $Fe_2(CO)_6X_2$ bridging dimers. The local coordination around each Fe atom can be described neglecting the Fe–Fe bent bond as a distorted tetragonal pyramid, with the S atoms at the two basal positions, the S–S bond causing an exceptionally low S–Fe–S angle. In contrast to the amount of information about the chemistry of $Fe_2(CO)_6X_2$ dimers, no data are reported on $Fe_2(CO)_6S_2$ and $Fe_2(CO)_6Se_2$, except for a brief note on the synthesis of the symmetrical disubstitution product $[P(C_6H_5)_3Fe(CO)_2]_2S_2$ by reaction of $Fe_2(CO)_6S_2$ with triphenylphosphine at room temperature [5]. The paucity of experimental data together with our interest in the chemistry of polynuclear chalcogen iron carbonyl complexes [6] prompted a general study of the reaction of $Fe_2(CO)_6X_2$ (X = S, Se) with ligands. This paper reports details on the isolation and characterization of the products of these reactions; another paper, at the moment in preparation, will be concerned with the kinetic and mechanistic data.



I

Results

The reactions of $Fe_2(CO)_6X_2$ (X = S, Se) complexes with ligand L give rise to quite different products, according in particular to the nature of both L and X.

When the ligand is a poor nucleophile such as $As(C_6H_5)_3$ or, with the more basic ligand $P(OC_6H_5)_3$, the less reactive Se complex has been used, the products are simply the monosubstituted $Fe_2(CO)_5LX_2$ and, to a lesser extent, the disubstituted $Fe_2(CO)_4L_2X_2$ complexes. The appearance of the second compound follows that of the first one and, qualitatively, depends on its concentration, suggesting the expected behaviour of two consecutive CO substitutions by the ligand:

$$Fe_2(CO)_6X_2 + L \longrightarrow Fe_2(CO)_5LX_2 + CO \quad (1)$$

$$Fe_2(CO)_5LX_2 + L \longrightarrow Fe_2(CO)_4L_2X_2 + CO \quad (2)$$

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No side products have been detected, nor other polysubstituted compounds. All the reaction products are air stable, well crystallized solids, quite soluble in the common organic solvents. The IR spectra of $Fe_2(CO)_5As(C_6H_5)_3S_2$ and of $Fe_2(CO)_5As(C_6H_5)_3Se_2$ in the CO stretching region show the typical pattern of the monosubstituted complexes, in which one CO *trans* to the M–M bent bonds is substituted [2].

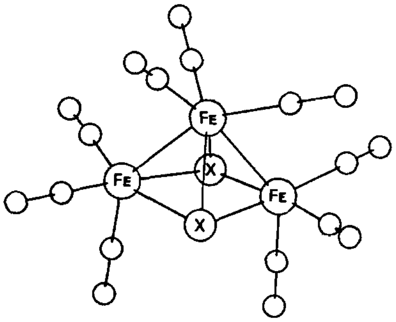
Three strong bands are observed in the spectrum of $Fe_2(CO)_4[As(C_6H_5)_3]_2Se_2$ and of $Fe_2(CO)_4[P(OC_6H_5)_3]_2Se_2$ and this is typical for a structure in which the two ligands are *trans* to the iron–iron bond, so maintaining a C_{2v} symmetry. However the appearance of the other three medium–weak peaks in the last spectrum can be explained in terms of the presence of another isomeric form in solution. Attempts to separate the two isomers were unsuccessful, as probably the equilibrium between them is established very rapidly.

The reaction between $Fe_2(CO)_6S_2$ and $P(C_6H_5)_3$ shows a different and more complicated behaviour. Only one compound is formed in a short time after mixing the reactants, but its full characterization has been impossible for it reacts further in the reaction mixture or decomposes rapidly when isolated, giving rise to the other reaction products.

The IR spectrum shows five strong bands in the CO stretching region (and probably a weak one) very close to those of $Fe_2(CO)_5P(C_6H_5)_3S_2$. This fact and its chemical behaviour suggest that the compound is an "adduct" between one molecule of both ligand and parent complex:

$$Fe_2(CO)_6X_2 + L \longrightarrow Fe_2(CO)_6X_2L \qquad (3)$$

The main products of the reaction are the substituted binuclear complexes $Fe_2(CO)_5P(C_6H_5)_3S_2$ and $Fe_2(CO)_4[P(C_6H_5)_3]_2S_2$ and the substituted derivatives of the trinuclear $Fe_3(CO)_9S_2$ complex (II), *i.e.* $Fe_3(CO)_8P(C_6H_5)_3S_2$ and $Fe_3(CO)_7[P(C_6H_5)_3]_2S_2$, together with traces of $Fe_3(CO)_9S_2$ itself.



II

$Fe_2(CO)_4[P(C_6H_5)_3]_2S_2$ was briefly reported as the only product of the reaction at room temperature between $Fe_2(CO)_6S_2$ and $P(C_6H_5)_3$ [5]. No infrared data have been given. Actually, the CO spectrum suggests a *trans–trans* disubstituted structure.

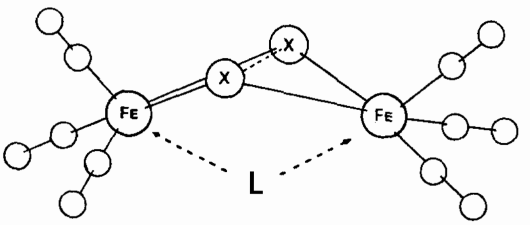
Similar behaviour has been shown by the reaction of $Fe_2(CO)_6S_2$ with $P(OC_6H_5)_3$. In this case, however, the "adduct" is not isolated, but the initial reaction product is the monosubstituted $Fe_2(CO)_5P(OC_6H_5)_3S_2$, which is very unstable and rapidly transforms into the other products. Its identification is based on the IR spectrum, which is very similar to those of analogous compounds. An interesting point is the isolation of a new compound, not yet completely identified, which appears at the beginning of the reaction. Its structure is probably quite complicated, as shown by the IR spectrum and the elemental analysis, and it cannot be ascribed to the known binuclear or trinuclear derivatives. It could be an addition product between $Fe_2(CO)_6S_2$ and $Fe_2(CO)_5P(OC_6H_5)_3S_2$ or $Fe_2(CO)_6S_2P(OC_6H_5)_3$, acting as reaction intermediate leading to trinuclear derivatives. Its subsequent decomposition gives rise to $Fe_2(CO)_4[P(OC_6H_5)_3]_2S_2$, $Fe_3(CO)_8P(OC_6H_5)_3S_2$ and $Fe_3(CO)_7[P(OC_6H_5)_3]_2S_2$ complexes. The two last compounds are the main products after long reaction times.

Finally, it is impossible to follow the formation of the products by reacting $Fe_2(CO)_6S_2$ with $P(nC_4H_9)_3$, as the reaction is nearly istantaneous at 0 °C. It is noteworthy that the yield of binuclear products is very poor: $Fe_2(CO)_5P(nC_4H_9)_3S_2$ is unstable, $Fe_2(CO)_4[P(nC_4H_9)_3]_2S_2$ has not been isolated. The main products are the trinuclear complexes, in particular $Fe_3(CO)_8P(nC_4H_9)_3S_2$ and $Fe_3(CO)_7[P(nC_4H_9)_3]_2S_2$. They are more likely obtained via addition intermediates than by CO substitution on $Fe_3(CO)_9S_2$ with tributylphosphine, as this rate is in effect much lower [7] than the rate by which they appear in the reaction.

Discussion

It is well known that $Fe_2(CO)_6S_2$ and $Fe_2(CO)_6Se_2$ are chemically and structurally related to the other $Fe_2(CO)_6(\mu X)_2$ complexes, in which the bridging X groups are alkyl- and aryl-sulphido or selenido groups; therefore their reactions with ligands show an interesting and important difference, in that the substituted binuclear complexes are not the only products, but a considerable yield of trinuclear complexes is obtained. Thus, equations (1) and (2) cannot represent as in the other cases the overall stoichiometry, but other mechanisms are implied, which account for the presence of the Fe_3S_2, or Fe_3Se_2 complexes. Another significant feature of this reaction is the noticeable effect of the nucleophilicity of L on the reaction rate and, in some way, on the nature of the reaction products. The largely different reactivity between, *e.g.*, $As(C_6H_5)_3$ and $P(nC_4H_9)_3$, indicates that a CO dissociation of the parent compounds is not probable, but that the initial reaction step is probably an attack of L on the substrate (eq. 3) [8].

The resulting 'adduct' $Fe_2(CO)_6X_2L$ is, as expected, generally too unstable to be isolated and characterized. Evidence for its formation has been obtained only in the reaction of $Fe_2(CO)_6S_2$ with triphenylphosphine. Instability makes it difficult to perform a detailed analysis, but it has been possible to record its IR spectrum in the CO stretching region, which shows the same typical pattern of the bands (number and relative intensities) of the $M_2(CO)_6(\mu X)_2$ complexes [9] suggesting that the structure of C_{2v} symmetry is maintained. On the other hand, the frequencies are shifted to longer wavelengths and are close to those of the well characterized monosubstituted derivative $Fe_2(CO)_5P(C_6H_5)_3S_2$, indicating the donor effect of one molecule of triphenylphosphine. We suggest for the 'adduct' the structure (III):



III

in which the ligand is formally coordinated to the two iron atoms on the metal–metal bond, giving a labile three-center donor–acceptor bond. Similar structures are not unusual with dinuclear iron chalcogen carbonyl complexes, as they are proposed for the adducts of $Fe_2(CO)_4L_2(SCH_3)_2$ with the proton [10] and mercuric dichloride [11] and for the ionic intermediates of the halogenation of several $[Fe(CO)LL'(SR)]_2$ complexes (L, L′ = CO, phosphines or phosphites) [12]. So the insertion of different groups in the iron–iron bond of $[Fe(CO)_3X]_2$ dimers seems to be a facile reaction.

Further proof is given by the oxidation of $[Fe(CO)_3SR]_2$ complexes by $(CF_3)C_2S_2$ or $NOPF_6$, whose main product is the $[Fe_2(SR)_3(CO)_6]^+$ species in which an SR group is inserted into the iron–iron bond [13], as shown by an X-ray diffraction study [14].

The monosubstituted product can be easily obtained from the adduct by a migration of the ligand on one Fe atom and simultaneous removal of a CO (4):

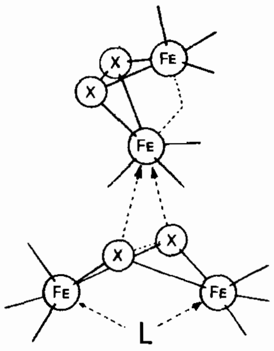
$$Fe_2(CO)_6LX_2 \longrightarrow Fe_2(CO)_5LX_2 + CO \qquad (4)$$

A subsequent attack of a second L on the other Fe atom gives rise to the disubstituted derivative.

The stability of the substitution products is clearly affected by the nature of the ligand. Relatively poor σ-donor and good π-acceptor ligands, such as triphenylphosphine or triphenylphosphite, give rise to stable, well characterized substituted binuclear derivatives, whereas the opposite is true with good σ-donor ligands, like tributylphosphine. Probably, the prevailing effect of the substitution of CO by good donor ligands on the Fe_2X_2 framework is the weakening of the iron–iron bond, owing to the increase of the electron density on the metal atoms and of the repulsion between them. This effect has been proposed to predominate in reactions of compounds containing an Fe–Fe bond [15].

The adduct could react by other mechanisms, probably implying the parent compound, yielding by means of successive transformations the various polyiron complexes. The observation that the yield of the triiron derivatives is large when the $Fe_2(CO)_6(\mu X)_2$ concentration is great with respect to that of L supports the previous suggestion. As the $[Fe_2(CO)_6(\mu X)_2][L]$ decreases, the probability of reactions like (1) and (2) becomes greater and the yield of the substituted binuclear derivatives increases. It is not easy to understand the correct mechanism by which the triiron complexes are obtained, owing to the practical impossibility of ascertaining even the overall stoichiometry of the reaction, because of the numerous reaction products and the partial decomposition to insoluble materials. Anyway, a close inspection of the well known structures of $Fe_3(CO)_9S_2$ [16] and $Fe_3(CO)_9Se_2$ [17] could offer some insight into this point. The $Fe_3(CO)_9X_2$ configuration ideally consists of a $Fe_2(CO)_6X_2$ moiety of C_{2v} symmetry bonded to an apical $Fe(CO)_3$ fragment by two Fe–Fe bonds and two Fe–X bonds. The cluster of heavy atoms represents a distorted square pyramid, in which the distortion is due to the movement of X atoms toward the apical Fe, the basal Fe_2X_2 framework being a puckered rhombus with two Fe–Fe and X–X non bonding distances and a dihedral angle along the X–X line. In other words, this structure may be regarded as arising from an insertion of an $Fe(CO)_3$ moiety into the metal–metal bond of $Fe_2(CO)_6X_2$. So the probable mechanism could be the following one.

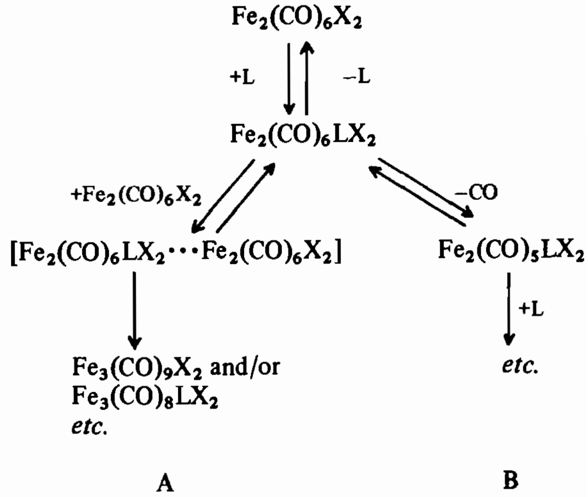
The addition of the ligand to the parent $Fe_2(CO)_6X_2$ molecule, forming the adduct, can give rise to a significant distortion from a 'quasi-tetrahedral' structure of the cluster Fe_2X_2 to a 'quasi-planar' one, by weakening the Fe–Fe bond and, consequently, the X–X bond. This effect can be ascribed to the steric bulkiness of the ligand or, more effecitvely, to its nucleophilic power. An MO calculation of $Fe_2(CO)_6(\mu X)_2$ type complexes [18] offers an indirect support to this suggestion, indicating that the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO) correspond closely to the bonding and antibonding counterpart of the metal–metal bond. If the initial attack of the ligand on the substrate occurs via the energetically most accessible empty orbital, *i.e.* LUMO, (which is probably also favoured by steric reasons), the increased electron density on this orbital by ligand donation can lower substantially the strength of the metal–metal bond, so favouring the distortion of the Fe_2X_2 core. It is so possible that a molecule of $Fe_2(CO)_6X_2$ begins to coordinate on the other side of the adduct's Fe_2X_2 framework, showing the incipient formation of the Fe_3X_2 core (IV):



IV

Subsequent rapid rearrangements will lead to the $Fe_3(CO)_9X_2$ and/or $Fe_3(CO)_8LX_2$ complexes by loss of L or CO, respectively. In this case the "adduct" can act as a ligand by means of the X donor atoms. Similar behaviour has been reported for complexes as $AsCo_3(CO)_9$ [19] and $SCo_2Fe(CO)_9$ [20], which exhibit character of Lewis bases with As or S as donor atoms, giving rise to complexes as $Fe(CO)_4$-$SCo_2Fe(CO)_9$ and $M(CO)_5AsCo_3(CO)_9$ (M = Cr, Mo, W), in which a CO of $Fe(CO)_5$ or $M(CO)_6$ is substituted by the 'ligands' $SCo_2Fe(CO)_9$ or $AsCo_3(CO)_9$. The behaviour of the 'adduct' $Fe_2(CO)_6LX_2$ as a ligand is due to the presence of L, which weakens substantially the X–X bond, as suggested before, and increases the electron density on the Fe_2X_2 cluster. Both effects could favour, for steric and electronic reasons, the donor character of the "adduct" molecule. Tributylphosphine, which is expected to have the greatest effect, gives rise to the highest yield of trinuclear derivatives.

This mechanism can explain why the $Fe_3(CO)_8$-LX_2 complexes appear at a rate much faster than that of the CO substitution on $Fe_3(CO)_9X_2$ [7]. On the other hand, these complexes are identical to those obtained by reacting $Fe_3(CO)_9X_2$ with L, where the ligand occupied only a coordination site on a basal Fe atom, as has been shown by ^{13}C n.m.r. techniques [21]. The appearance of the only basal isomer is a strong support to the proposed mechanism. Scheme 1 illustrates all the previous observations: path A is important when the ligand concentration is low and comparable to that of $Fe_2(CO)_6X_2$, otherwise path B is predominant. The scheme represents obviously an oversimplification and it should be regarded as tentative. Anyway, slightly more complex alternative paths like fragmentation of the adduct in $XFe(CO)_3$ and $XFe(CO)_3L$ radicals, formation of ionic intermediates *etc.* cannot be excluded with certainty.



Scheme 1

Experimental

The parent compounds have been obtained by the action of sulphite or selenite on aqueous alkaline carbonyl ferrate solution and subsequent acidification [22]. Both tri-iron $Fe_3(CO)_9X_2$ and di-iron $Fe_2(CO)_6X_2$ complexes are obtained, the yield of the latter being increased by increasing the ratio $[XO_3^=]/[Fe(CO)_4^=]$ in the reaction mixture. The separation is easily carried out by column chromatography (aluminium oxid 60 aktiv basisch. Type E; Merck) with petroleum ether as eluant: only $Fe_2(CO)_6X_2$ moves, whereas $Fe_3(CO)_9X_2$ remains on the top of the column and can be successively recovered by eluting with benzene.

The ligands were obtained commercially (Strem Chemicals) and purified by crystallization or vacuum distillation.

Trinuclear derivatives, $Fe_3(CO)_8LX_2$ and $Fe_3(CO)_7L_2X_2$, used for comparison purposes, were prepared as previously reported [23].

The IR spectra were recorded on a Beckman IR 12 grating spectrophotometer. The elemental analyses (C, H, S, Se, P) were performed by the Pascher Mikroanalytisches Laboratorium, Bonn, West Germany.

TABLE I. Experimental Details.

Complex	Ligand	Molar Ratio	Solvent	T, °C	Time
		Complex:Ligand			
$Fe_2(CO)_6S_2$	$As(C_6H_5)_3$	1:10	n-heptane	70°	200 hr
$Fe_2(CO)_6Se_2$	$P(OC_6H_5)_3$	1:5	n-heptane	60°	100 hr
$Fe_2(CO)_6S_2$	$P(C_6H_5)_3$	1:3	petroleum ether	20°	2 hr
$Fe_2(CO)_6S_2$	$P(OC_6H_5)_3$	1:4	petroleum ether	20°	90 min
$Fe_2(CO)_6S_2$	$P(nC_4H_9)_3$	1:4	petroleum ether	0°	instantaneous reaction
$Fe_2(CO)_6Se_2$	$As(C_6H_5)_3$	1:50	n-heptane	70°	2 weeks

TABLE II. Analytical and IR Data.

Complex	Colour	M.p.	Analysis: found (calcd)					IR (CCl_4)
			C	H	Fe	P	S	
$Fe_2(CO)_5As(C_6H_5)_3S_2$	red-brown	dec.	44.2 (44.40)	2.5 (2.43)	17.6 (17.95)		10.2 (10.30)	2059s 1997vs 1988m 1945 w
$Fe_2(CO)_5P(OC_6H_5)_3Se_2$	red-orange	135	38.4 (38.37)	2.1 (2.10)	15.4 (15.51)	4.1 (4.30)		2056s 2003s 1989m 1980m,sh 1957w
$Fe_2(CO)_4[P(OC_6H_5)_3]_2Se_2$	red-orange	84	47.8 (47.93)	3.1 (3.02)	11.4 (11.14)	6.2 (6.18)		2025vs 2018m, sh 1980m, br 1965s 1957m, sh 1940w
$Fe_2(CO)_6P(C_6H_5)_3S_2$	brown							2056s 2009s 1998s 1988m 1951w
$Fe_2(CO)_5P(C_6H_5)_3S_2$	orange	126	47.9 (47.78)	2.5 (2.61)	19.5 (19.31)	5.1 (5.36)	11.2 (11.09)	2055s 1996s 1986s 1975w,sh 1942w
$Fe_2(CO)_4[P(C_6H_5)_3]_2S_2$	yellow-orange	146	59.0 (59.13)	3.8 (3.72)	13.4 (13.75)	7.7 (7.63)	7.9 (7.89)	2006s 1958m 1943s
$Fe_2(CO)_4[P(OC_6H_5)_3]_2S_2$	yellow-orange	143	52.6 (52.88)	3.3 (3.32)	12.3 (12.29)	6.5 (6.82)	7.0 (7.06)	2032s 1985m 1972s
$Fe_2(CO)_5P(nC_4H_9)_3S_2$	orange	dec.	39.4 (39.40)	5.1 (5.25)	21.8 (21.55)	5.8 (5.98)	12.1 (12.37)	2054s 1993vs 1986s 1938m
$Fe_2(CO)_5As(C_6H_5)_3Se_2$	red-brown	118 dec.	38.7 (38.59)	2.2 (2.11)	15.4 (15.60)			2052s 1991s 1983s 1972w,sh 1933m
$Fe_2(CO)_4[As(C_6H_5)_3]_2Se_2$	brown	120 dec.	48.3 (48.33)	3.1 (3.04)	11.0 (11.23)			2003s 1955m 1941s

Iron was determined by an atomic absorption spectroscopic method using a Perkin-Elmer atomic absorption spectrophotometer mod. 303 with DCR 1.

The general method to prepare the derivatives consists in a solution reaction between the complex and the ligand at controlled temperature under nitrogen. The course of the reaction was monitored by removing small samples by syringe and analysing them by TLC. Purification was carried out by TLC (Kiesegel 60 $PF_{254+366\,\mathrm{I}}$Merck), eluting with petroleum ether or appropriate mixture of petroleum ether/ethyl ether. Further purification of the products by the same method is often necessary, followed, when possible, by crystallization. The yields have not been measured, but they are approximately 50–70% of the parent compound, referring to the iron carbonyl derivatives together. The yield of each product varies largely, depending on the reaction conditions. Anyway, it is noteworthy that the amount of triiron derivatives, if they are formed, is great and in some cases the prevailing one when the concentration of the ligand does not exceed 3–4 times that of the complex. When the ligand concentration is very large (20 times or more) practically only binuclear derivatives are obtained.

Full details on the experimental conditions are collected in Table I. Analytical and IR data of the complexes are reported in Table II.

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