prediction. Furthermore, there is a marked similarity between the spectrum of $W(CO)_3(CH_3CN)_3$ and the spectra of many substituted hexacarbonyls of the type $(Ar)M(CO)_3$, where (Ar) is an aromatic group and M is Cr, Mo, or W.[17] Such π-bonded complexes must almost certainly contain symmetrically arranged carbonyl groups. Finally, one would expect symmetrical trisubstitution as the natural consequence of *cis*-disubstitution, as has been shown.

The last question involves the nature of the bonding between CH_3CN and the central metal atom. Orgel[18] mentions that alkyl cyanides can form complexes involving the donation of π-electrons to form T-shaped bonds. The other alternative would involve the donation of the lone pair from the nitrogen to the metal to form a linear coördinate covalent bond. The first mechanism could be expected to drastically lower the CN stretching frequency. Coördinate bonding, on the other hand, should raise the CN stretching frequency somewhat from the 2254[19] cm.$^{-1}$ found in the free acetonitrile molecule. Gerrard[20] has explained this effect in terms of mesomeric forms possible in a free nitrile which can lower the CN bond order from that of a pure CN triple bond; differences in hybridization make such mesomerism impossible in bonded RCN. Coerver and Curran[21] have reported the $C\equiv N$ stretching frequency for the addition complex $CH_3CN:BF_3$, which undoubtedly contains a nitrogen-to-boron coordinate bond, to be 2359 cm.$^{-1}$. If bonding is through the lone pair, we should expect that increased orbital mixing due to the influence of the negative charge on the metal to result in the successive lowering of the CN stretching frequencies from this value for the mono-, di-, and trisubstituted complexes. These frequencies are given in Table II, and exhibit such a trend.

TABLE II

THE CYANIDE STRETCHING REGION OF THE INFRARED FOR ACETONITRILE-SUBSTITUTED TUNGSTEN HEXACARBONYLS

Complex	Medium	Obsd. CN stretching freq.,[a] cm.$^{-1}$	Predicted CN stretching bands for linear $W-NCCH_3$ bonds
$W(CO)_5(CH_3CN)$	KBr	2347	1, (A_1)
$W(CO)_4(CH_3CN)_2$	KBr	2311 (s), 2282 (m)	2, (A_1, B_1)
$W(CO)_3(CH_3CN)_3$	Nujol	[2276 (sh)], 2255 (m), 2215 (s)	2, (A_1, E)

[a] Band intensities: s, strong; m, medium; sh, shoulder.

Evidence for the linearity of the metal–$NCCH_3$ bond, to be expected for bonding through the lone pair of the nitrogen, comes from a comparison of the number of CN stretching vibrations predicted for linear bonding and the number found experimentally in the three acetonitrile derivatives. Table II gives these data; the experimentally determined numbers of bands can be seen to correspond to the numbers predicted by theory (with the possible exception of a weak shoulder in $W(CO)_3(CH_3CN)_3$). Although evidence of this nature often is inconclusive because close-lying infrared bands often remain unresolved, agreement between the predicted and observed spectra in three cases constitutes a strong argument for metal–CN bond linearity, especially when considered in conjunction with the other evidence cited to support coördinate bonding.

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CONTRIBUTION FROM THE MELLON INSTITUTE,
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Organosulfur Derivatives of Metal Carbonyls. II.[1] The Reaction between Triiron Dodecacarbonyl and Certain Episulfide Derivatives

BY R. B. KING

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Triiron dodecacarbonyl reacts with cyclohexene sulfide in refluxing benzene to produce cyclohexene and purple-red diamagnetic volatile $Fe_3(CO)_9S_2$ (II). This carbonyl sulfide of iron is different from the $Fe_3(CO)_9S_2$ (I) obtained from $HFe(CO)_4^-$ and sulfite ion.[2] The new $Fe_3(CO)_9S_2$ (II) may also be synthesized from 3-chloropropylene sulfide and $Fe_3(CO)_{12}$ in about 50% yield.

Triiron dodecacarbonyl has been found to react with dialkyl sulfides, dialkyl disulfides, and mercaptans to give compounds of general formula $[Fe(CO)_3SR]_2$ (III),[2-4] with alkyl vinyl sulfides to give compounds of general formula $RSCH{=}CH_2\cdot Fe_2(CO)_6$ (IV),[5] and with thiophene to give the sulfur-free material $C_4H_4Fe_2(CO)_6$ (V).[6]

In a further study of reactions between triiron dodecacarbonyl and organic sulfur compounds it has been found that triiron dodecacarbonyl reacts with certain episulfide derivatives to give the purple-red diamag-

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[1] For part I of this series see R. B. King, *J. Am. Chem. Soc.*, **84**, 2460 (1962).

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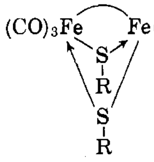
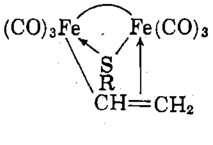
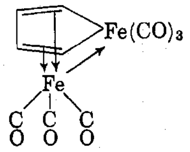
netic, crystalline, volatile compound $Fe_3(CO)_9S_2$ (II). This carbonyl sulfide of iron is different from the $Fe_3(CO)_9S_2$ (I) obtained from $HFe(CO)_4^-$ and sulfite ion.[7]



III



IV



V

Experimental

Infrared spectra were recorded in the metal carbonyl region on a Perkin-Elmer Model 112 machine with CaF_2 optics. Halocarbon oil mulls were used. The cyclohexene sulfide was purchased from Aldrich Chemical Co., Milwaukee, Wisconsin. The 3-chloropropylene sulfide was synthesized from epichlorohydrin and thiourea.[8]

Reactions between Cyclohexene Sulfide and Triiron Dodecacarbonyl.—A mixture of 10.8 g. (21.4 mmoles) of triiron dodecacarbonyl, 9.0 ml. (~80 mmoles) of cyclohexene sulfide, and 120 ml. of thiophene-free benzene was refluxed under nitrogen for 4 hr. The green color of the triiron dodecacarbonyl soon became purple. After the reaction period was over, the reaction mixture was allowed to cool to room temperature and then filtered, a purple filtrate being obtained. Removal of solvent from this filtrate at ~20 mm. left a purple crystalline residue. This was treated with 50 ml. of pentane and the product precipitated from the red-purple solution by cooling to −78°. The resulting purple crystals finally were purified by sublimation at 80–100° (0.1 mm.) to give 1.03 g. (10% yield) of dark red-purple crystals of $Fe_3(CO)_9S_2$ (II), m.p. 114°.

Anal. Calcd. for $C_9O_9S_2Fe_3$: C, 22.3; H, 0.0; O, 29.8; S, 13.2; Fe, 34.7; mol. wt., 484. Found: C, 22.1; H, 0.0; O, 29.6; S, 13.6; Fe, 34.3; mol. wt., 571 (vapor pressure osmometer in benzene solution).

Solvent recovered from this reaction mixture was shown to contain large quantities of cyclohexene by vapor phase chromatography.

Reaction between 3-Chloropropylene Sulfide and Triiron Dodecacarbonyl.—By a procedure similar to that described above a 55% yield of $Fe_3(CO)_9S_2$ was obtained from 3-chloropropylene sulfide and triiron dodecacarbonyl. This product was shown by a mixed melting point determination to be identical with the product obtained from cyclohexene sulfide and triiron dodecacarbonyl.

Anal. Calcd. for $C_9O_9S_2Fe_3$: C, 22.3; H, 0.0; S, 13.2; Fe, 34.7. Found: C, 22.4; H, 0.0; S, 13.2; Fe, 34.8.

An attempt to obtain $Fe_3(CO)_9S_2$ (II) from propylene sulfide and triiron dodecacarbonyl under similar conditions gave only sticky brown polymeric material.

Reaction between $HFe(CO)_4^-$ and Sulfite Ion to Give $Fe_3(CO)_9S_2$ (I) (Hieber–Gruber Reaction).[7]—The reaction between $HFe(CO)_4^-$ and sulfite ion was carried out essentially as described by Hieber and Gruber.[7] After acidifying the reaction mixture the product was isolated by filtration, washed with methanol and pentane, and sucked dry. It was purified by Soxhlet extraction with pentane. The resulting dark red extract was filtered from decomposition products. Solvent was removed from the filtrate at 30 mm. leaving a red-black residue of $Fe_3(CO)_9S_2$ (I) which was recrystallized from pentane.

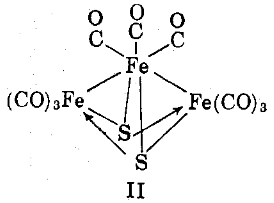
Anal. Calcd. for $C_9O_9S_2Fe_3$: C, 22.3; H, 0.0; S, 13.2; Fe, 34.7. Found: C, 21.8; H, 0.2; S, 12.4; Fe, 35.5.

On attempted sublimation of this material at 80° (0.1 mm.) only a very small yield of a red-black crystalline sublimate was obtained.

Discussion

In view of the isolation of a product of composition $Fe_3(CO)_9S_2$ from the reaction between $Fe_3(CO)_{12}$ and cyclohexene sulfide or 3-chloropropylene sulfide, it is of interest that several years ago an iron carbonyl sulfide of exactly the composition $Fe_3(CO)_9S_2$ was reported as being formed in the reaction between $HFe(CO)_4^-$ and sulfite ion.[2] This synthesis was successfully repeated and the properties of $Fe_3(CO)_9S_2$ (I) were compared with those of the new compound (II) obtained from $Fe_3(CO)_{12}$ and cyclohexene sulfide. The two compounds were found to be distinctly different materials. Thus the new $Fe_3(CO)_9S_2$ (II) is a readily sublimable red-purple solid which exhibits a definite melting point (114°) on heating. The known $Fe_3(CO)_9S_2$ (I), however, is a red-black solid which sublimes at 0.1 mm. only with extensive decomposition and which does not exhibit a definite melting point on heating. Moreover, the infrared bands in the carbonyl region (calcium fluoride optics, Perkin-Elmer Model 112 machine, halocarbon oil mull) of the two compounds are distinctly different: new $Fe_3(CO)_9S_2$ (II): 2058 (s), 2040 (s), 2016 (s), 1994 (s), 1992 (s), and 1976 (s) $cm.^{-1}$; known $Fe_3(CO)_9S_2$ (I): 2108 (m), 2066 (s), 2060 (s), 2040 (s), 2019 (sh), and 2012 (s) $cm.^{-1}$. Neither compound shows absorption in the bridging carbonyl region. A proton n.m.r. spectrum of a saturated solution of the new $Fe_3(CO)_9S_2$ (II) in toluene was identical with the proton n.m.r. spectrum of pure toluene. No broadening or significant chemical shifts were observed, indicating this compound to be diamagnetic.

In view of the similarity of the preparation of $Fe_3(CO)_9S_2$ (II) from triiron dodecacarbonyl and episulfide derivatives to the preparation of the compounds $[Fe(CO)_3SR]_2$ from triiron dodecacarbonyl and dialkyl sulfides, the structure of the new $Fe_3(CO)_9S_2$ is probably quite similar to that of the compounds $[Fe(CO)_3SR]_2$ (III). One possible structure (II) for $Fe_3(CO)_9S_2$ has iron–sulfur bonds from the third $Fe(CO)_3$ group replacing the carbon–sulfur bonds in III. It will be noted that in this structure (II) suggested for $Fe_3(CO)_9S_2$ each of the three iron atoms has an inert gas configuration accounting for the diamagnetism and that there are no bridging carbonyl groups, in accord with the observed infrared spectrum. It must be emphasized, however, that this structure suggested for $Fe_3(CO)_9S_2$ (II) must remain tentative until X-ray data become available on this compound or on closely related compounds.



II

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