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Preliminary communication

(μ-DITHIO)BIS(TRICARBONYLIRON) AS AN ORGANIC DISULFIDE MIMIC: INSERTION OF LOW-VALENT METAL SPECIES INTO THE SULFUR—SULFUR BOND

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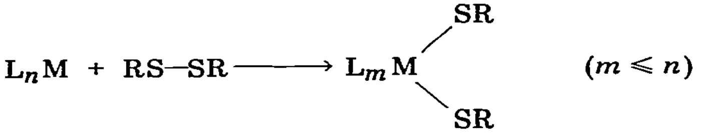
Summary

Low valent metal species: $(Ph_2PCH_2CH_2PPh_2)Ni^0$, $(Ph_3P)_2Pd^0$, $(Ph_3P)_2Pt^0$, η^5-$C_5H_5\,Co^I$ and $(CH_3)_2Sn^{II}$ insert into the S—S bond of $(\mu$-$S_2)Fe_2(CO)_6$ under mild conditions. Identical products were obtained by reactions of the dianion, $[(\mu$-$S_2)Fe_2(CO)_6]^{2-}$ with the corresponding metal chlorides.

The reactions of (μ-dithio)bis(tricarbonyliron) (I) [1] occur principally at the S—S bond and mimic those of organic disulfides. Thus, its reactions with sodium metal [2], potassium hydride [2] and lithium triethylborohydride [3] result in S—S bond cleavage and formation of the sulfur-centered dianion II. Organolithium reagents also cleave the S—S bond, alkylating or arylating one sulfur atom and forming the anion at the other [2]. Highly electrophilic acetylenes, such as hexafluoro-2-butyne and esters of acetylenedicarboxylic acid, upon UV irradiation insert into the S—S bond of I to produce bridging dithiolene complexes [4]. We report here another, apparently general, reaction of organic disulfides which occurs readily with $(\mu$-$S_2)Fe_2(CO)_6$.

The oxidative addition of the S—S linkage of acyclic [5] and cyclic [6] disulfides to low-valent transition metal species (i.e., the insertion of low-valent metal species into the S—S bond) (eq. 1) is a process which has been known since 1964. We have found that low valent metal intermediates insert into the S—S



$$L_nM + RS{-}SR \longrightarrow L_mM\begin{matrix}\diagup SR\\ \diagdown SR\end{matrix} \qquad (m \leqslant n) \tag{1}$$

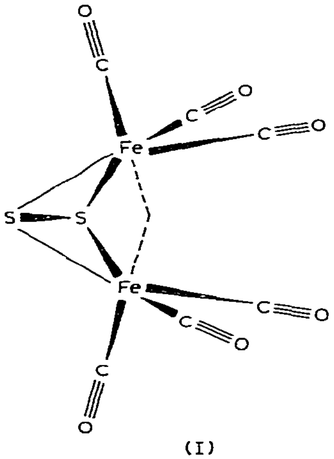
of (μ-dithio)bis(tricarbonyliron) and report concerning the following species.

[1,2-Bis(diphenylphosphino)ethylene]nickel(0). A solution of 2 mmol each of $(Ph_2PCH_2CH_2PPh_2)Ni(CO)_2$ and $(\mu$-$S_2)Fe_2(CO)_6$ in 40 ml of benzene was

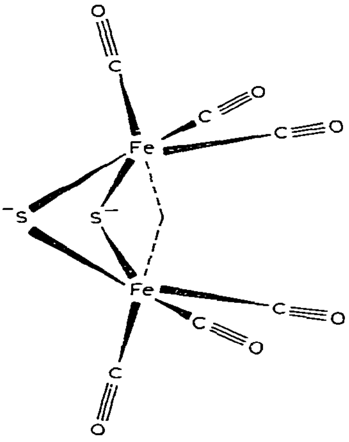
stirred under nitrogen for one day. Evaporation of solvent at reduced pressure, followed by column chromatography of the residue on silicic acid (pentane, followed by dichloromethane), gave a 77% yield of the brown-black, air-stable insertion product IIIa. This product was identical in all respects with IIIa which was prepared by the reaction of dianion II with $(Ph_2PCH_2CH_2PPh_2)NiCl_2$ [2].

Bis(triphenylphosphine)palladium(0). A suspension of 0.523 mmol of $(Ph_3P)_4Pd$ in benzene was purged with carbon monoxide for about 6 min. to form the soluble $(Ph_3P)_3PdCO$ [7]. Subsequently, 3 ml of iodomethane was added, then 1.45 mmol of $(\mu\text{-}S_2)Fe_2(CO)_6$ in CO-saturated benzene. After a reaction time of 2.5 h at room temperature, work-up as above gave the insertion product IIIb, a purple-brown, crystalline, air-stable solid, in 94% yield. A sample of IIIb prepared in 92% yield by the reaction of II with $(Ph_3P)_2PdCl_2$ was identical with this product. In particular, their IR spectra were superimposable.

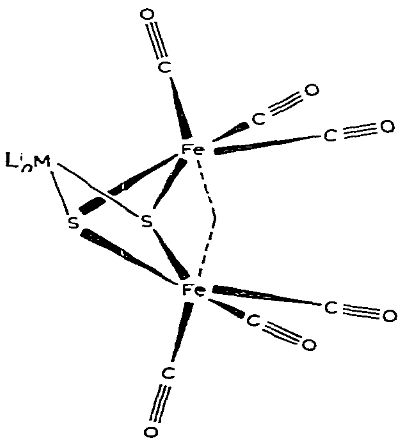
The iodomethane was added to the reaction mixture in order to convert the two molar equivalents of triphenylphosphine released in this reaction sequence into insoluble methyltriphenylphosphonium iodide. In the absence of iodomethane, free triphenylphosphine apparently reacted with starting material and/or product to displace CO, giving unresolvable mixtures.



(I)



(II)



(IIIa, L_nM = $(Ph_2PCH_2CH_2PPh_2)Ni$;
IIIb, L_nM = $(Ph_3P)_2Pd$;
IIIc, L_nM = $(Ph_3P)_2Pt$;
IIId, L_nM = $\eta^5\text{-}C_5H_5$;
IIIe, L_nM = $(CH_3)_2Sn$;
IIIf, L_nM = Cl_2Ge)

Bis(triphenylphosphine)platinum(0). The same procedure was used in the reaction of $(Ph_3P)_4Pt$ (0.39 mmol) with $(\mu\text{-}S_2)Fe_2(CO)_6$ (1 mmol), under nitrogen, in 50 ml of benzene containing 2.5 ml of iodomethane. An overnight reaction at room temperature, followed by the usual work-up, gave the insertion product, IIIc, in 99% yield as an orange-red, air-stable, crystalline solid, m.p. 200°C (dec). In this case also, this compound was prepared (80% yield) by the alternate dianion route from $(Ph_3P)_2PtCl_2$. The spectroscopic properties of the two samples of different origin were identical.

η^5-Cyclopentadienylcobalt(I). Irradiation (Rayonet Photoreactor, at 350 nm, quartz flask) was utilized to effect reaction between 2.9 mmol of $(\mu\text{-}S_2)Fe_2(CO)_6$ and 5.8 mmol of $\eta^5\text{-}C_5H_5Co(CO)_2$ in 75 ml of THF. Column chromatography gave the insertion product IIId in 54% yield as a black, air-stable solid, m.p. ~ 135°C (dec).

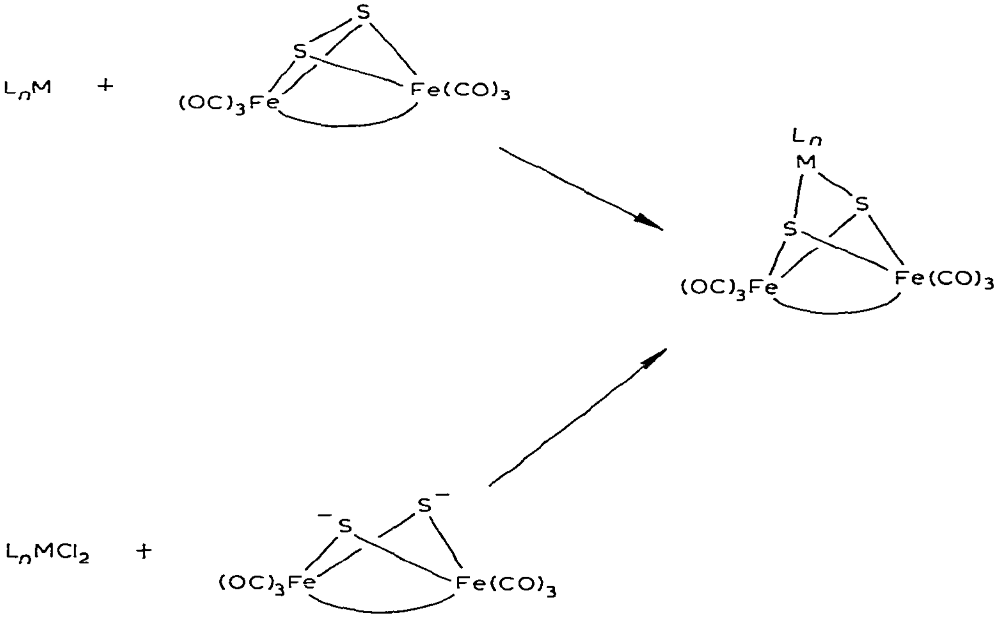
Dimethyltin(II). Irradiation of a solution of 2.9 mmol of $(\mu\text{-}S_2)Fe_2(CO)_6$ and 8.7 mmol of hexamethylditin in 50 ml of THF for 5 h as in the experiment above yielded, after column chromatographic purification, the known [1,2] $(\mu\text{-}Me_2SnS_2)Fe_2(CO)_6$ (IIIe), ruby-red, air-stable needles, in 85% yield.

The occurrence of this reaction implies a disproportionation of hexamethylditin as shown in eq. 2 under the conditions of the reaction. Such a redox disproportionation has been observed before in the reaction of hexamethylditin with dicobalt octacarbonyl [8] (eq. 3).

$$(CH_3)_3Sn{-}Sn(CH_3)_3 \rightarrow (CH_3)_2Sn + (CH_3)_4Sn \qquad (2)$$

$$(CH_3)_3Sn{-}Sn(CH_3)_3 + Co_2(CO)_8 \rightarrow (CH_3)_2Sn[Co(CO)_4]_2 + (CH_3)_4Sn \qquad (3)$$

These five examples involving four transition metal intermediates and one main group species indicate that the insertion of low-valent metal species into the S—S bond of (μ-dithio)bis(tricarbonyliron) is a general reaction type. In



(4)

addition the reaction of $HGeCl_3 \cdot Et_2O$ with $(\mu\text{-}S_2)Fe_2(CO)_6$, which gives IIIf [9], without doubt involves insertion of $GeCl_2$, a low-valent germanium species, into the S—S bond.

These reactions in general give the respective insertion product in high yield. The identity, in most cases (including the $GeCl_2$ insertion [2]) of the product of the insertion reaction and the dianion/metal dihalide reaction (eq. 4) provides what appears to be a reliable chemical proof of structure for the insertion products. All new products reported in this study were characterized by C/H analysis, IR spectroscopy, proton NMR spectroscopy and, in most cases, mass spectroscopy. Table 1 gives IR data.

Our studies of the chemistry of $(\mu\text{-}S_2)Fe_2(CO)_6$, $(\mu\text{-}Se_2)Fe_2(CO)_6$ [10] and related complexes are continuing.

TABLE 1

INFRARED SPECTRA IN THE CARBONYL REGION OF THE INSERTION PRODUCTS DERIVED FROM (μ-DITHIO)BIS(TRICARBONYLIRON)[a]

Complex		Absorption peaks (cm^{-1})
$(Ph_2PCH_2CH_2PPh_2)NiS_2Fe_2(CO)_6$	(IIIa)	2049s, 2080vs, 1970s, 1960sh
$(Ph_3P)_2PdS_2Fe_2(CO)_6$	(IIIb)	2049s, 2008vs, 1971s, 1959sh
$(Ph_3P)_2PtS_2Fe_2(CO)_6$	(IIIc)	2050s, 2009vs, 1972s, 1959s
$\eta^5\text{-}C_5H_5CoS_2Fe_2(CO)_6$	(IIId)	2068s, 2042vs, 1993s
$(CH_3)_2SnS_2Fe_2(CO)_6$	(IIIe)	2052m, 2009vs, 1973s, 1964s
$Cl_2GeS_2Fe_2(CO)_6$	(IIIf)	2089m, 2057vs, 2018s

[a] Infrared spectra were recorded on a Perkin—Elmer Model 457A grating infrared spectrophotometer. All complexes were examined as solutions in dichloromethane, except for IIIe, which was measured in acetone solution.

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