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REACTIONS OF IRON CARBONYL COMPLEXES WITH DIMETHYLTHIOCARBAMOYL CHLORIDE

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Summary

The reactions of dimethylthiocarbamoyl chloride with a number of neutral and ionic iron carbonyl complexes in tetrahydrofuran are described. A variety of unusual products were obtained, viz. $Fe(CO)_2(S_2CNMe_2)_2$ from $Fe(CO)_5$; $Fe(CO)_2(S_2CNMe_2)(CSNMe_2)$ from $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, and $Fe(CO)_4{}^{2-}$; $[Fe(CO)_2(S_2CNMe_2)(CNMe_2)_2S]^+$ from $Fe(CO)_4{}^{2-}$, and $Fe_4(CO)_{12}S(CSNMe_2)(CNMe_2)$ from $Fe_2(CO)_8{}^{2-}$, as well as $Fe_2(CO)_6(CSSEt)_2$ from $Fe_2(CO)_9$ and ClCSSEt. The structures and behavior and some reactions of these complexes are described.

Introduction

In other papers we have described the reactions of dimethylthiocarbamoyl chloride ($ClCSNMe_2$) with carbonyl anions of manganese and molybdenum [1] and with $Ni(CO)_4$ [2]. In the former case the reaction proceeds by nucleophilic displacement of the chloride, followed by coordination of the sulfur atom; with $Ni(CO)_4$ the reaction appears to involve an oxidative addition mechanism. We have now extended this study to include reactions of $ClCSNMe_2$ with neutral and ionic carbonyl complexes of iron. A wide variety of unusual species were obtained, the production of many of which appears to involve transfer and insertion of sulfur atoms into metal—carbon bonds. Reactions of the similar compound ClCSSEt were also investigated.

Results and discussion

The reactions of dimethylthiocarbamoyl chloride with $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Na_2[Fe(CO)_4]$ and $NEt_4[Fe_2(CO)_8]$ were carried out, with the results described below. Spectroscopic data for all new compounds are presented in Tables 1 (NMR spectra) and 2 (infrared spectra).

It was surprising, in view of its high reactivity with $Ni(CO)_4$ and $Co_2(CO)_8$ [2]

TABLE 1

NMR SPECTRA [a]

II	6.79(3), 6.70(3) ($CDCl_3$)
III	6.26(3), 6.36(3), $CSNMe_2$; 6.64(3), 6.82(3), S_2CNMe_2 ($CDCl_3$)
IV-PF_6	6.05(3), 6.15(3), 6.65(3), 6.72(3), $CNMe_2$: 6.45(6), S_2CNMe_2 (acetone-d_6)
V	6.23(3), 6.30(3), 6.53(3), 6.73(3) ($CDCl_3$)
VI	6.02(6), 6.11(3), 6.16(3); 6.57(3), SMe (acetone-d_6)
VII	7.20(4tet, 2), CH_2; 8.80(3plet, 3), CH_3; $J(CH_2—CH_3)$ 7.2 Hz($CDCl_3$)
III(^{13}CO)	246.0, 208.4, $S_2\underline{C}NMe_2$ and $\underline{C}SNMe_2$: 214.4, $\underline{C}O$: 49.6, 47.5, $CSN(\underline{C}H_3)_2$; 39.1, $S_2C\underline{N}(CH_3)_2$ ($CDCl_3$)

[a] All peaks are $N—CH_3$ singlets unless otherwise indicated. Integrations are given in parentheses. Specific peak assignments are made only when unambiguous. Solvents are indicated. Proton NMR peaks are in τ vs. TMS; ^{13}CO peaks are in ppm downfield from TMS.

to find that dimethylthiocarbamoyl chloride (I) would not react with iron pentacarbonyl even in refluxing tetrahydrofuran. Only on ultraviolet irradiation of the solution did any reaction occur; this resulted largely in decomposition, with a 4% yield of $Fe(CO)_2(S_2CNMe_2)_2$ as the only isolated product. This compound was also prepared (in much better yield) by a "rational" synthesis from $Fe(CO)_4I_2$ and $NMe_2H_2(S_2CNMe_2)$. The infrared and NMR spectra of this complex clearly show that it has a *cis* geometry (II).

By contrast, I reacts readily with either $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$, giving as the only isolable product the complex $Fe(CO)_2(S_2CNMe_2)(CSNMe_2)$ (III).

An X-ray structure determination * has shown that this molecule contains

TABLE 2

INFRARED SPECTRA

	$\nu(C—O)$ (solvent) (cm^{-1})	Other peaks (KBr disc) (cm^{-1})
II	1980s, 1931s (heptane)	2920w, 1528s, 1392s, 1250m, 1145s, 1050w, 1020w, 985m, 800w, 620m, 570m, 510m, 430m, 358m
III	2013s, 1949s (heptane)	2920w, 2860vw, 1660w, 1570s, 1525s, 1442m, 1390s, 1245m, 1225m, 1155s, 1040m, 985s, 921s, 832s, 676w, 630s, 581s, 540s, 509m, 486m, 434m, 401m, 350m, 300w
IV-PF_6	2022s, 1996s (acetone)	2930w, 1570s, 1530s, 1438m, 1391s, 1250m, 1225m, 1147s, 1031w, 985w, 895m, 870m (sh), 835vs, 802m, 618m, 580m, 568m, 544s, 462w, 430w
V	2014s, 2048s, 2029s, 2022s, 1999m, 1993s, 2087m, 2082m, 2075w, 1966s, 1957m, 1948m (heptane)	2930w, 2865w, 1570s, 1500s, 1390s, 1230m, 1190w, 1150m, 1040w, 1012w, 921s, 849m, 740s, 580vs, 498m, 472w, 441m, 425w, 339m, 324w
VI	2040s, 2011s, 2004s, 1987s, 1955s, 1932m, 1919wsh (acetone)	2880w, 1545s, 1482m, 1375m, 1280w, 1215w, 1010—1145s (br), 911m, 840w, 735s, 590s (br)
VII	2078s, 2043s, 2006s (heptane)	2965m, 2920m, 2865w, 1510w, 1442m, 1418m, 1372m, 1261m, 1256m, 1058m, 1050m, 965w (sh), 952s, 875w, 848m, 825w, 761s, 715m, 653w, 646w, 615s, 670vs, 498m, 460w, 441w, 411w, 318w

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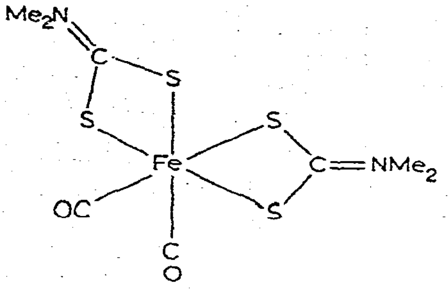
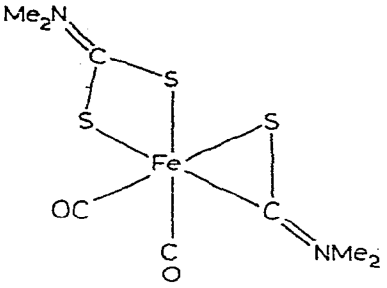
* The structures of these compounds have been determined by X-ray crystallography. Because the complexes possess features which are of intrinsic structural interest, the results of these studies will be published in full separately.



(II)



(III)

one chelating thiocarboxamido group such as have been found in several other complexes [1,3,4].

Some question arose during the characterization of this complex as to whether it might in fact be a complex of tetramethylthiuram monosulfide, $(Me_2NCS)_2S$. Interestingly enough, it can be made by the reaction of $(Me_2NCS)_2S$ with $Fe_2(CO)_9$; in this case a carbon—sulfur bond is broken to form the thiocarboxamido and dithiocarbamato ligands found in the product. Since a thiuram monosulfide complex, coordinated through all three sulfur atoms, would be rather severely strained, it is perhaps not surprising that this should occur.

The $Fe(CO)_2(S_2CNMe_2)(CSNMe_2)$ molecule is nonrigid, as shown by its NMR spectrum (Fig. 1). Two of the methyl groups exchange environments rapidly above room temperature, while the other two do not; at —25°C all motion is "frozen out". The exchanging methyl groups must be those of the dimethyldithio carbamate ligand; the methyl groups of the thiocarboxamido group cannot exchange environments except via rotation about the rigid C = N double bond. This would be expected to be a much higher temperature process, and in fact we have

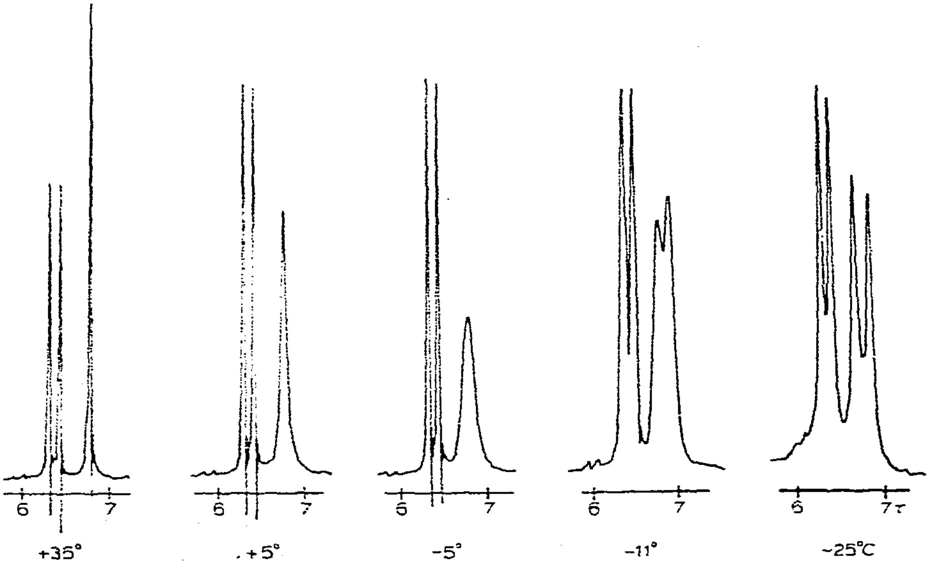


Fig. 1. Temperature-dependent proton NMR spectrum of $Fe(CO)_2(S_2CNMe_2)(CSNMe_2)$.

never observed such behavior for this ligand in any complex.

Neither is it likely that C = N bond rotation is responsible for exchange of methyl environments in the dithiocarbamate ligand; again, this is generally observed to be a high-temperature process, when observed at all [5]. Also, this motion would not in itself account for the apparent exchange of environments on the part of the carbonyl groups, as manifested by a rather broad singlet CO peak in the ^{13}C NMR spectrum at 35°C (Fig. 2). It is conceivable that both exchanges result from a dissociative process in which one sulfur atom becomes detached from the metal, followed by a rearrangement of ligands in the resulting five-coordinate complex and recoordination of the sulfur in such a way as to exchange the methyl group environments. However, this too seems rather unlikely in view of the fact that the NMR spectrum of $Fe(CO)_2(S_2CNMe_2)_2$ shows this molecule to be rigid at room temperature; it would be quite extraordinary if a dissociative rearrangement were seen in one and not the other of such similar molecules.

It is much more likely that the observed fluxional behavior results from a nondissociative intramolecular rearrangement. If the molecule is viewed as a six-coordinate, distorted octahedral complex, this process can be represented as a "trigonal twist" in which the three ligand sulfur atoms rotate by ca. 120° about a pseudo-threefold axis with respect to the other ligands. This motion is illustrated in Fig. 3 (top). Trigonal twists about the other pseudo-threefold axes of this complex either lead to other isomers or fail to achieve the interchange of sulfur atom environments (and thus of methyl group environments) in the dithiocarbamate ligand. It may be noted that this process also interchanges the environments of the carbonyl groups.

This complex may also be regarded as being five-coordinate, if the thiocarboxamido group is considered as a "monodentate" ligand. In this case the motion may be appropriately represented as a "Bailar twist", as shown in the lower half of Fig. 3. This is a normal Bailar twist mechanism with the additional requirement that the thiocarboxamido ligand rotates by 90° as shown, to preserve its relation to the other ligands.

It should be pointed out that these two diagrams do not in fact represent distinct motions; close inspection will reveal that in fact they portray exactly the

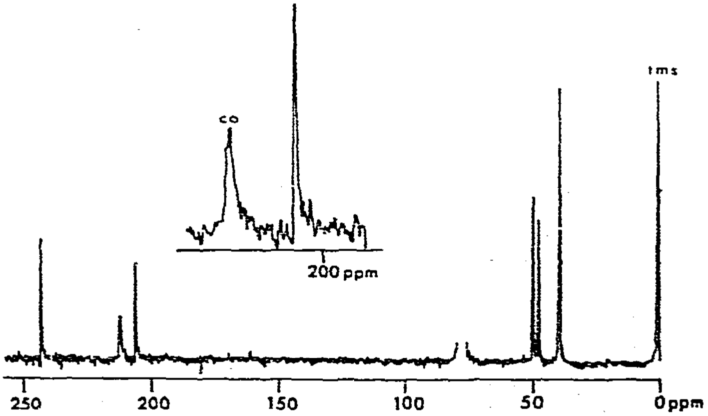


Fig. 2. ^{13}C NMR spectrum of $Fe(CO)_2(S_2CNMe_2)(CSNMe_2)$ (35°C). (Inset shows the broadness of the CO peak.)

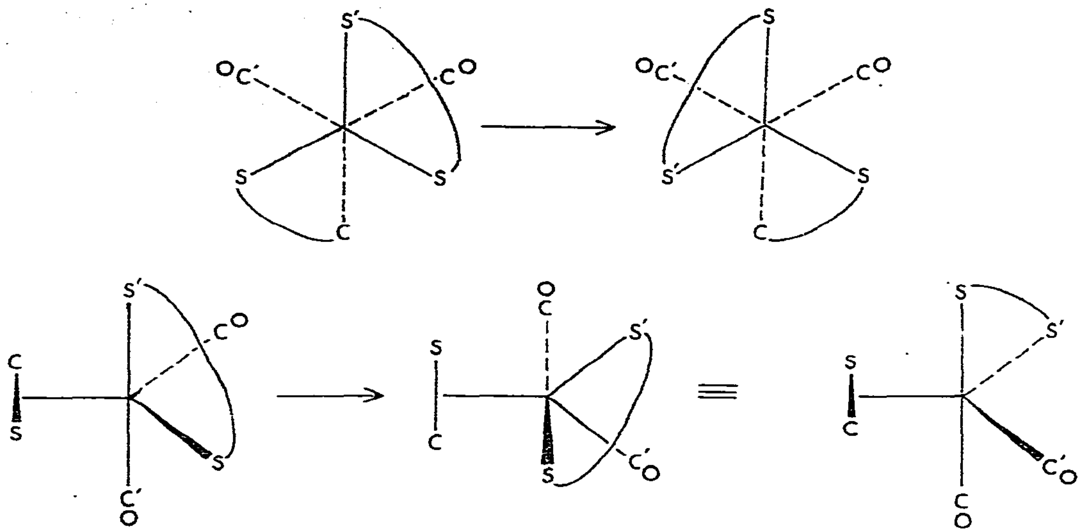
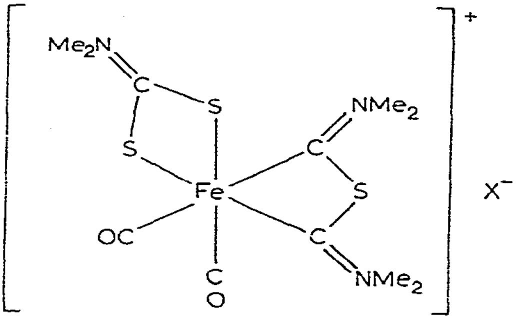


Fig. 3. Fluxional behavior of $Fe(CO)_2(S_2NMe_2)(CSNMe_2)$ represented as a trigonal twist (top) and as a cailar twist (bottom).

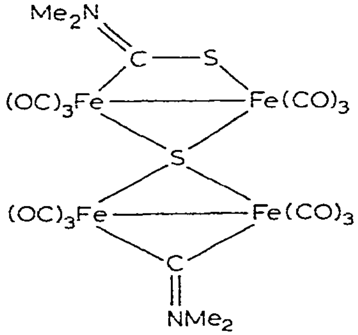
same motion from two extreme points of view, either of which might be considered valid for a complex of "intermediate" geometry such as this one. This complex is probably best regarded as octahedral, but highly distorted, due to the small chelating thiocarboxamido group, toward being five-coordinate. This distortion undoubtedly contributes to the fluxionality of this molecule by lifting it out of the deep potential well corresponding to octahedral coordination.

Compound III was also one of the products of the reaction of dimethylthiocarbamoyl chloride with $Fe(CO)_4{}^{2-}$. This reaction also yields an ionic product, which can be isolated as the hexafluorophosphate or tetraphenylborate salt of the $[Fe(CO)_2(S_2CNMe_2)(CNMe_2)_2S]^+$ ion, IV (see footnote p. 196).

The NMR spectrum of this complex (shown in Fig. 4) appears to suggest fluxional behavior, presumably via a motion similar to that suggested for III above, with the dithiocarbamate methyl groups being made equivalent by the motion. If this is in fact the case, the complex is very fluxional indeed; the NMR spectrum remains unchanged down to —75°C. There is no obvious reason why this complex should be so extraordinarily nonrigid; although it is distorted away



(IV) ($X^- = BPh_4{}^-$ or $PF_6{}^-$)



(V)

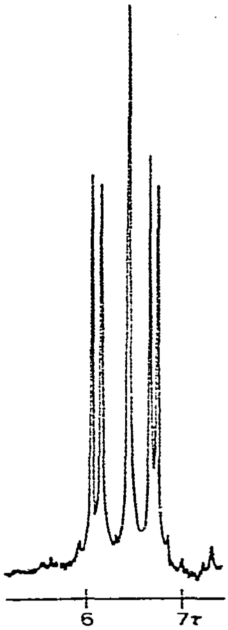
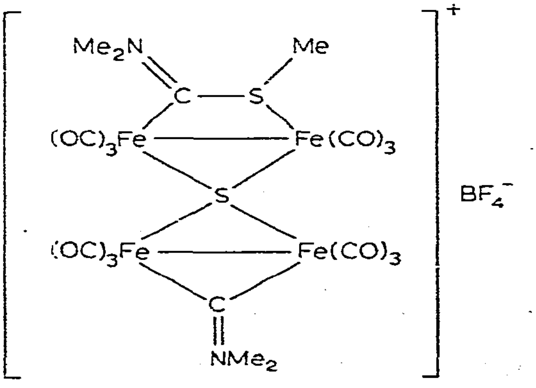


Fig. 4. Proton NMR spectrum of $[Fe(CO)_2(S_2CNMe_2)(CNMe_2)_2S]PF_6$ (35°C).

from octahedral geometry, it is less distorted than III, for which the motion is frozen out at a much higher temperature. It is also possible that two of the six methyl resonances are fortuitously degenerate, and no definite conclusion can be reached on the basis of the available data.

Quite a different product was obtained from the reaction of dimethylthiocarbamoyl chloride with $Fe_2(CO)_8^{2-}$. These reacted to give a compound formulated as $Fe_4(CO)_{12}S(CSNMe_2)$ (V) *. Here we find the thiocarboxamido group in a bridging position, a situation which has been observed in only one previous instance [6]. The other thiocarboxamido group has been cleaved to give a quadruply bridging sulfide and a bridging dimethyliminocarbene ligand.

Complex V, like some other thiocarboxamido complexes [1], can be methylated by $[Me_3O]BF_4$ to give an ionic product. The appearance of a new methyl resonance in the NMR spectrum of the methylated species (VI) at τ 6.57 ppm, somewhat up-field of the N—CH_3 resonances, is consistent with methylation at



(VI)

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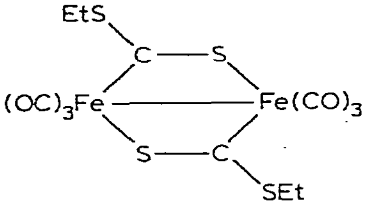
* See footnote p. 196.

the sulfur atom of the bridging thiocarboxamido ligand. Thus the bridging ligand in this complex behaves similarly to chelating thiocarboxamido ligands in other complexes where *S*-methylation is also observed.

Reactions of I with several other iron carbonyl anions were also attempted, but none were successful. $Fe_3(CO)_{11}H^-$ could not be induced to react with I even under ultraviolet radiation, while $Fe_2(CO)_8H^-$ and $Fe_3(CO)_{11}^{2-}$ yielded no isolable products.

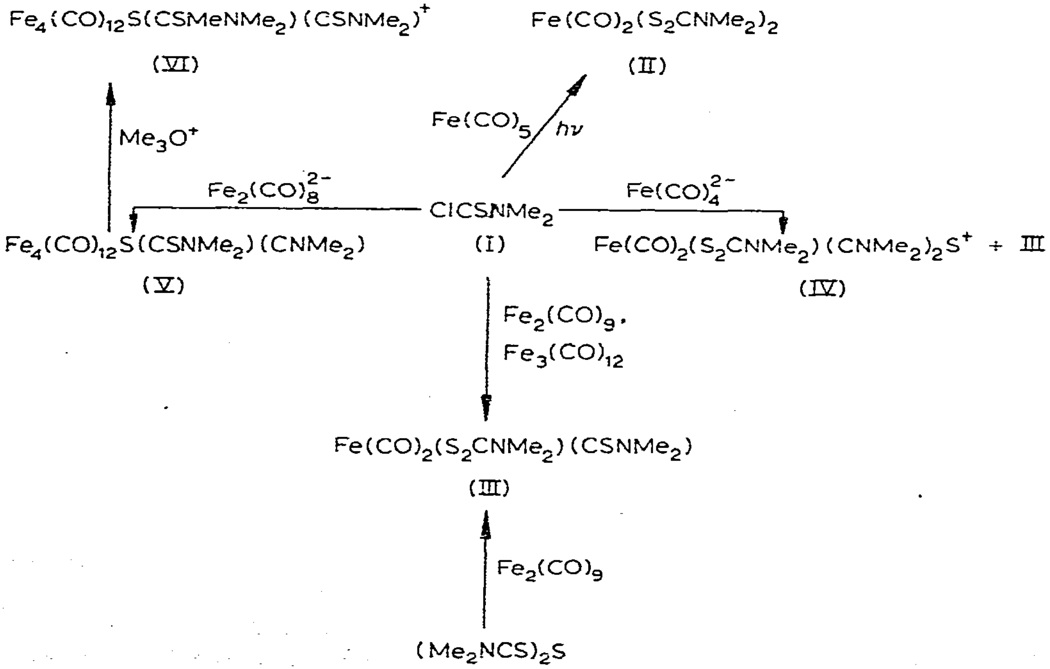
Several similar reactions were attempted using ethyl dithiochloroformate, ClCSSEt, in place of I, in the hope of obtaining similar products. In general, the reactivity of ClCSSEt seems to be much greater than that of $ClCSNMe_2$. In only one case was any identifiable product obtained; the reaction with $Fe_2(CO)_9$ yielded a product formulated as $Fe_2(CO)_6(CSSEt)_2$ (VII). This compound has only three C—O stretching frequencies in its infrared spectrum, indicating a symmetrical structure; for this reason the structure shown below is proposed:



(VII)

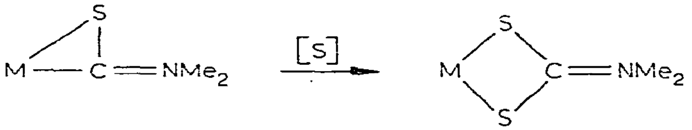
The reactions of iron carbonyl complexes with $ClCSNMe_2$ may be summarized as in the Scheme 1. While it is interesting that such a variety of products should

SCHEME 1



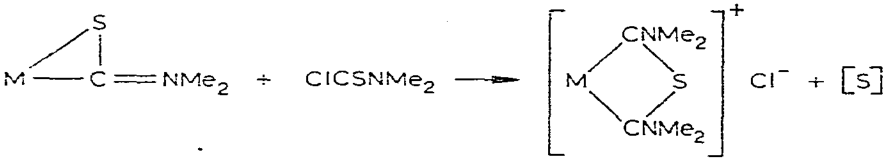
arise from the reactions of a single reagent, it is not at all obvious why this should be the case, nor how these reactions may be related to one another.

The one common factor which is immediately apparent in all these reactions is the remarkable mobility of the sulfur atom. In every case the formal carbon—sulfur double bond in at least one $ClCSNMe_2$ molecule is broken by the time it appears as a ligand in the product; in all but one case a sulfur atom joins a thiocarboxamido group to become a dithiocarbamate ligand. In some cases (IV, V) this may occur by an intramolecular migration of a sulfur atom to a new position, leaving the $C{=}NMe_2$ group behind, itself to appear in rather remarkable configurations. However, in other cases (II and III) where the S/N ratio in the product exceeds that in the starting material, it is clear that at some point a sulfur atom is being picked up from outside. It seems at least possible that this happens via the insertion of a sulfur atom into the metal—carbon bond of a chelating thiocarboxamido group:



We have suggested this possibility in one other case (the reaction of $Ph_3PMn(CO)_4^-$ and $ClCSNMe_2$ giving $Ph_3PMn(CO)_3S_2CNMe_2$ as a side-product) [7]. Because detailed mechanistic information is difficult or impossible to obtain for low-yield reactions such as those discussed here, we are presently studying the above step (and its reverse) in isolation, to determine what types of molecules may serve as sulfur-donating substrates.

One attractive possibility in the case of the formation of IV is that it arises by the insertion of a $CNMe_2$ group into a metal—sulfur bond of III:



(III) (IV)

Efforts to carry out this reaction in isolation using $Fe(CO)_2(S_2CNMe_2)(CSNMe_2)$ and $ClCSNMe_2$ were not successful; however, it may be that such an insertion takes place at an earlier stage in the reaction, before the formation of the dithiocarbamate ligand, with the sulfur atom migrating to form that ligand.

Perhaps the most surprising result is the formation of V from the reaction of $ClCSNMe_2$ with $Fe_2(CO)_8^{2-}$, instead of the expected dimethylamino analog of VII, $Fe_2(CO)_6(CSNMe_2)_2$. The latter compound should certainly be capable of existence, considering both the stability of VII and the presence of a bridging thiocarboxamido group in V, and presumably its formation is prevented at an early stage, possibly by the migratory propensity of the sulfur atom.

Experimental

All reagents were obtained from commercial sources or prepared by methods in the literature. Dimethylthiocarbamoyl chloride was recrystallized from diethyl ether before use. Tetrahydrofuran was distilled from calcium hydride. All operations were performed under a nitrogen atmosphere.

Infrared spectra were recorded on a Perkin—Elmer model 467 spectrophotometer, calibrated with gaseous CO and DBr. Proton NMR measurements were made with Jeol JNM-MH-100 and Varian EM-360 instruments; ^{13}C NMR spectra were recorded on a Varian CFT-20 instrument. Molecular weights were measured in benzene solution using a Mechrolab vapor pressure osmometer. Microanalyses were performed by Atlantic Microanalytical Laboratories, Atlanta, Ga.

Synthesis of the complexes

$Fe(CO)_2(S_2CNMe_2)_2$ (II). A. $Fe(CO)_5$ (5.00 g, 25.5 mmol) and $ClCSNMe_2$ (I) (3.15 g, 25.5 mmol) were treated with 100 ml tetrahydrofuran. No reaction occurred until the solution was irradiated (General Electric H100PSP44-4 lamp). After 24 h the solvent was removed and the residue was chromatographed over alumina. The product was eluted as a brown band with benzene, and recrystallized from toluene/heptane. Yield, 0.374 g of II (1.06 mmol, 16.6% based on S). Brown crystals; decomposition without melting ~150°C. Analysis: Found: C, 27.4; H, 3.45; N, 8.03, S, 36.7; mol. wt., 347. $C_8H_{12}N_2O_2S_4$ calcd.: C, 27.3; H, 3.41; N 7.95, S, 36.4%; mol. wt. 352.

B. II was also obtained from the reaction of $Fe(CO)_4I_2$ [8] (3.50 g, 8.3 mmol) with $NMe_2H_2(S_2CNMe_2)$ (2.75 g, 16.6 mmol) in 200 ml of acetone. The reaction proceeded rapidly at room temperature with gas evolution. After 18 h the reaction was stopped and the product worked up as above. Yield, 2.00 g of II (5.7 mmol, 69%).

$Fe(CO)_2(S_2CNMe_2)(CSNMe_2)$ (III). A. $Fe_2(CO)_9$ (10.0 g, 27.5 mmol) and I (3.4 g, 27.5 mmol) were stirred at room temp. in 200 ml of tetrahydrofuran. After 25 h the solvent was removed and the residue was chromatographed over alumina. The product was eluted as an orange band with benzene and recrystallized from toluene/heptane. Yield, 0.620 g of III (1.94 mmol, 21.0% based on S). Brown crystals, m.p. 125—130°C. Analysis: Found: C, 30.2; H, 3.84; N, 8.81; S, 30.1%; mol. wt. 314. $C_8H_{12}N_2O_2S_3$ calcd.: C, 30.0; H, 3.75; N, 8.75; S, 30.0%; mol. wt., 320.

B. $Fe_3(CO)_{12}$ (5.25 g, 10.4 mmol) and I (7.72 g, 62.5 mmol) were treated with 100 ml of tetrahydrofuran. After 120 h at room temperature the solvent was removed and the product was isolated and purified as above. Yield, 0.40 g (1.25 mmol, 6.0% based on available S).

C. $Fe_2(CO)_9$ (5.00 g, 13.7 mmol) and $(Me_2NCS)_2S$ (2.90 g, 13.7 mmol) were stirred overnight at room temp. in 100 ml of toluene. The solvent was removed and the residue was chromatographed over alumina. Benzene eluted an orange band of III, which was recrystallized as above. Yield, 0.77 g (2.41 mmol, 18% based on $(Me_2NCS)_2S$).

$[Fe(CO)_2(S_2CNMe_2)(CNMe_2)_2S]BPh_4$ (IV-BPh_4). $Fe_3(CO)_{12}$ (4.70 g, 9.33 mmol) was reduced to $Fe(CO)_4^{2-}$ in 250 ml of tetrahydrofuran by stirring with sodium amalgam. I (6.90 g, 56 mmol) was added and the mixture was stirred at room temperature overnight. The solution was then filtered and the solvent was removed. The residue was extracted with benzene and the extracts were passed over an alumina column, yielding 0.35 g of III (1.09 mmol, 5.9% based on S).

The benzene-insoluble residue was taken up in water, filtered, and precipitated by the addition of aqueous $NaBPh_4$. The precipitate was filtered, dried, and recrystallized from acetone/ether. Yield, 0.60 g (0.86 mmol, 4.6% based on S). Yellow crystals, m.p. 105—110°C. Analysis: Found: C, 60.6; H, 5.69; N, 5.99; S, 13.7. $C_{35}H_{38}BN_3O_2S_3Fe$ calcd.: C, 60.4; H, 5.47; N, 6.04; S, 13.8%.

This complex could also be obtained as the hexafluorophosphate salt (IV-PF_6) by using NH_4PF_6 in place of $NaBPh_4$. The product was worked up as above. Yellow crystals, m.p. 135—138°C. Analysis: Found: C, 25.1; H, 3.34; N, 8.08; S, 18.5. $C_{11}H_{18}N_3O_2S_3FePF_6$ calcd.: C, 25.3; H, 3.45; N, 8.06; S, 18.4%.

$Fe_4(CO)_{12}S(CSNMe_2)(CNMe_2)$ (V). $(NEt_4)_2Fe_2(CO)_8$ [9] (10.35 g, 17.3 mmol) and I (4.20 g, 33.9 mmol) were treated with 200 ml of tetrahydrofuran at room temperature. After 72 h the reaction was complete, the solvent was removed and the residue was chromatographed over alumina. The product was eluted as a red-brown band with benzene and was recrystallized from toluene/heptane. Yield, 0.80 g (1.08 mmol, 13% based on Fe). Red-purple crystals, m.p. 163—165°C (dec.). Analysis: Found: C, 29.4; H, 1.71; N, 3.91; S, 8.51; mol. wt. 702. $C_{18}H_{12}N_2O_{12}S_2Fe_4$ calcd.: C, 29.3; H, 1.63; N, 3.80; S, 8.70%; mol. wt. 736.

$[Fe_4(CO)_{12}S(CSMeNMe_2)(CNMe_2)]BF_4$ (VI). V (0.342 g, 0.465 mmol) was stirred with a large excess of $(Me_3O)BF_4$ at room temp. in 35 ml of chloroform. After several days the infrared spectrum showed no further change. The solution was filtered, the solvent was removed, and the residue was recrystallized from acetone/ether. Yield, 0.146 g (0.175 mmol, 38%). Red-orange crystals; decomposition without melting ~135°C. Analysis: Found: C, 27.6; H, 1.80; N, 3.34; S, 7.70%. $C_{19}H_{15}N_2O_{12}S_2Fe_4$ calcd.: C, 27.2; H, 1.80; N, 3.34; S, 7.64%.

$Fe_2(CO)_6(CSSEt)_2$ (VII). $Fe_2(CO)_9$ (10.0 g, 27.5 mmol) was stirred in 150 ml of tetrahydrofuran with ClCSSEt [10] (3.86 g, 27.5 mmol) overnight at room temp. The solvent was then removed and the residue was chromatographed over alumina. The product was eluted with 10% $CHCl_3$/hexane as a brown band, and was recrystallized from heptane. Yield, 0.41 g (0.42 mmol, 6.0%). Brown crystals, m.p. 96—98°C. Analysis: Found: C, 29.1; H, 2.03; S, 25.7; mol. wt. 486. $C_{12}H_{10}O_6S_4Fe_2$ calcd.: C, 29.3; H, 2.04; S, 26.1%; mol. wt. 490.

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