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**INSERTION OF CS₂ AND CSe₂ INTO METAL—AMIDO BONDS.
MONO- VERSUS BI-DENTATE DITHIOCARBAMATES FORMED BY
REACTIONS OF CS₂ + NHR₂ WITH {CpM(CO)_n}₂ (M = Fe, n = 2; M = Mo,
n = 3)**

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Summary

The reaction of Cp₂Fe₂(CO)₄ with NHEt₂ and CS₂ gives the monodentate dithiocarbamate CpFe(CO)₂-η¹-SC(S)NEt₂ (Ia), whereas the same reaction with Cp₂Mo₂(CO)₆ gives the chelate CpMo(CO)₂-η²-S₂CNEt₂ (II). New complexes of amines CpFe(CO)₂(NHR₂)⁺PF₆⁻ (III, R = Me, Et, SiMe₃) have been synthesized by treating CpFe(CO)₂Cl with NHR₂. They do not react with CS₂ and give only [CpFe(CO)₂]₂ upon refluxing with bases such as t-BuOK or NEt(i-Pr)₂, but concerted CS₂ insertion in the presence of a base immediately gives I at 20°C. This clean route is used to synthesize the monodentate diselenocarbamate CpFe(CO)₂-η¹-SeC(Se)NMe₂ (IV) by reaction of CSe₂ with III (R = Me) in the presence of t-BuOK. Whereas the known reaction of CpFe(CO)₂Cl with Na⁺S₂CNMe₂⁻ gives Ib (R = Me), the analogous reaction of C₅Me₅Me(CO)₂Br gives specifically the thermally stable chelate C₅Me₅Fe(CO)-η²-S₂CNMe₂ (Vb').

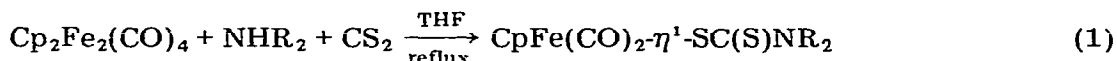
Many binary inorganic dithiocarbamate (dtc) complexes have been synthesized during the last three decades [1–7]. Their ability to stabilize exceptionally high oxidation numbers [8–12] and their redox properties are well-known [13]. Some interesting electronic properties have been found, such as spin cross overs [14,15] and antiferromagnetic coupling [16,17]. Dithiocarbamate is occasionally a useful ancillary ligand in bioinorganic models aimed at mimicking enzymes for the fixation of small molecules such as acetylene [18,19]. Organometallic complexes of dithiocarbamate are less numerous, however [20–23]; in particular only a few complexes are known in which the mode of coordination of this ligand is monodentate [22,23]. We were especially interested in the large scale syntheses of easily accessible complexes of monodentate dithiocarbamates to permit further study of the reactions of this ligand through the uncoordinated sulfur atom, and we now describe the reactions of Fp₂ (Fp = CpFe(CO)₂) and

$\text{Cp}_2\text{Mo}_2(\text{CO})_6$ with $\text{CS}_2 + \text{NHR}_2$, the first of which is found to be a convenient route to the monodentate *dtc* complex $\text{Fp-}\eta^1\text{-dtc}$. We also describe another convenient route to monodentate dithio- and diseleno-carbamates, namely the insertion of CS_2 and CSe_2 into metal—amido bonds [7]. Interestingly, the reaction of $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ with NHR_2 and CS_2 provides not a monodentate but a bidentate mononuclear complex. The reactivity of monodentate dithiocarbamate complexes has been the subject of a preliminary communication [24] and will be considered in detail later [25], as will their physical properties [26a]. It should be noted that Wilkinson reported in 1969 the synthesis of $\text{Fp-}\eta^1\text{-SC(S)-NMe}_2$ by reaction of FpCl with $\text{Na}^+ \text{S}_2\text{CNMe}_2^-$, the only known synthesis of a monodentate complex of iron [22]. We also show in this paper that the analogous reaction with $\text{C}_5\text{Me}_5\text{Fe}(\text{CO})_2\text{Br}$ follows a different path. On the other hand, Abel's syntheses [21] from $\text{Me}_3\text{SnSC(S)NMe}_2$ and organometallic halides provided the chelates $\text{CpFe}(\text{CO})\text{-}\eta^2\text{-S}_2\text{CNMe}_2$ and $\text{CpMo}(\text{CO})_2\text{-}\eta^2\text{-S}_2\text{CNMe}_2$.

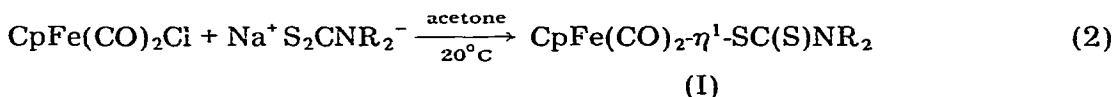
Results and discussion

Reactions of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ and $\text{CpMo}_2(\text{CO})_6$ with $\text{CS}_2 + \text{NHEt}_2$

The reaction between $\text{Cp}_2\text{Fe}_2(\text{CO})_4$, CS_2 and the secondary amine NHEt_2 in refluxing THF gives a 50% yield of the new monodentate complex $\text{Fp-}\eta^1\text{-SC(S)-NEt}_2$ (Ia), after chromatographic separation and recrystallization, (eq. 1), and



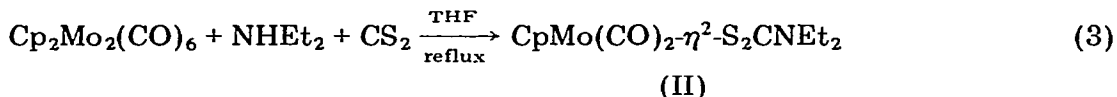
minor amounts of $\text{Fe}^{\text{III}}(\text{dte})_3$, of the starting materials Fp_2 and traces ($\approx 5\%$) of the chelate $\text{CpFe}(\text{CO})\text{-}\eta^2\text{-dte}$ (Vb). This reaction is convenient with diethylamine but not with gaseous dimethylamine unless an autoclave is used. The most convenient route to I remains Wilkinson's reaction [22] of $\text{CpFe}(\text{CO})_2\text{Cl}$ with the commercially available NaS_2CNR_2 ($\text{R} = \text{CH}_3$) or ammonium salts obtained by treating NHR_2 (other R groups) with CS_2 (eq. 2). After one day at 20°C in



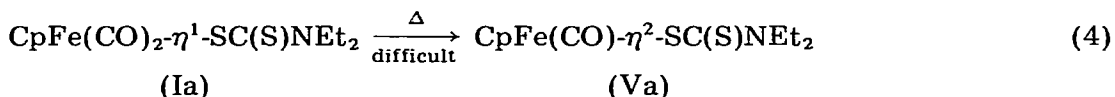
acetone, the reaction between FpCl and $\text{Na}^+ \text{dte}^-$ affords the desired products in excellent yields without the formation of side products, thus avoiding the need for chromatographic separation. The monodentate structure can be checked by IR spectroscopy using Bonati's criteria [27,28]; thus, the chelate shows only one CS_2 stretching band in the $1000\text{--}1100\text{ cm}^{-1}$ region whereas the dissymmetrical complex exhibits a doublet. The thiouroid CN band is located at a higher frequency for the chelates ($1500\text{--}1530\text{ cm}^{-1}$) than for the monodentate complexes ($1440\text{--}1495\text{ cm}^{-1}$) which corresponds to a higher delocalization of the nitrogen lone pair. Definitive evidence for a monodentate structure is provided by the rotation barrier observed in ^1H and ^{13}C NMR [26a] (in contrast to the symmetrical chelates), and by elemental analysis. A very simple criteria is the location of the Cp peak in the ^1H NMR spectrum at δ 5–5.1 ppm for monodentate I and at δ 4.5–4.8 for the chelate V. Rapid monitoring is possible by analytical thin-layer chromatography, the difference

in R_f between the two kinds of products being large with a mixture of hexane and ether (4/1) as eluant ($R_{f1} = 0.3$, $R_{f2} = 0.7$).

The reaction of $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ with NHEt_2 and CS_2 in refluxing THF proceeds cleanly, giving a 90% yield of the dark red crystalline chelate $\text{CpMo}(\text{CO})_2\text{-}\eta^2\text{-S}_2\text{CNEt}_2$ (II) after extraction and recrystallization from hexane (eq. 3).



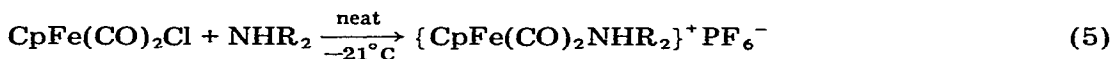
The structure of II is confirmed by an X-ray crystal structure study [26b]. This reaction provides the cheapest and most convenient route to II. Attempts to trap or characterize an intermediate monodentate complex analogous to Ia were unsuccessful and so chelation must be fast under the conditions used. It was also not possible to obtain such a monodentate complex by treating $\text{CpMo}(\text{CO})_3\text{Br}$ with $\text{Na}^+ \text{dtc}^-$ at lower temperatures. The driving force to chelation seems much stronger than for iron, which is readily accounted for in terms of the larger electronegativity difference between early transition metals and chalcogens. It is noteworthy that thermal chelation of I is extremely difficult and proceeds only at temperatures of 100°C or above and also accompanied by decomposition, giving very low yields of $\text{CpFe}(\text{CO})\text{-}\eta^2\text{-S}_2\text{CNEt}_2$ (Va) (eq. 4).



This reaction is even more difficult with the selenium analogue $\text{Fp-}\eta^1\text{-SeC}(\text{Se})\text{NMe}_2$ (IV), which under such drastic conditions, gives only trace amounts of the chelate $\text{CpFe}(\text{CO})\text{-}\eta^2\text{-Se}_2\text{CNMe}_2$ (VI). These findings are in accord with precedents which clearly showed that *dtc* ligands stabilize high oxidation states of late transition metals (Cu^{III} , Fe^{IV} , Ni^{V}) [8–12]. It is relevant to note that $\text{CpMo}(\text{CO})_2\text{-}\eta^1\text{-SC(O)NMe}_2$ [29] could be made, and that $\text{Fp-}\eta^1\text{-SC(O)NMe}_2$ [26] does not give the chelate even under drastic conditions.

Synthesis of $\text{Fp}(\text{amine})^+$; insertion of CS_2 and CSe_2 into Fe—amido bonds

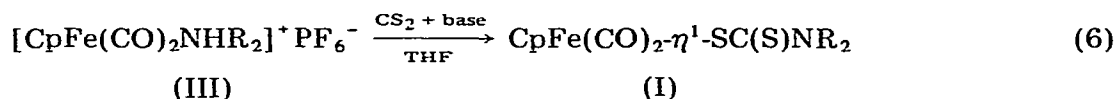
Although mechanistic studies are beyond the scope of this paper, it was of synthetic interest to examine the possibility of synthesizing monodentate dithiocarbamates by insertion of CS_2 into metal—amido bonds. Such extension of this reaction to CSe_2 turned out to be useful as a clean route to monodentate diselenocarbamates. This process also mimics part of the reaction of Fp_2 with amine and CS_2 and thus sheds some light on possible mechanistic alternatives. Therefore, we synthesized the unknown simple complexes $\text{Fp}(\text{NHR}_2)^+ \text{PF}_6^-$ for $\text{R} = \text{CH}_3$, C_2H_5 , SiMe_3 by an extension of the synthesis of $\text{Fp}(\text{NH}_3)^+ \text{PF}_6^-$ from FpCl and NH_3 reported by Fischer and Moser [30] (eq. 5). We find



that these amine complexes become less easily accessible as the size of the nitrogen substituents R is increased (yields: $\text{R} = \text{Me}$, 35%; $\text{R} = \text{Et}$, 20%; $\text{R} = \text{SiMe}_3$, 10%). Although these reactions were performed at low temperature

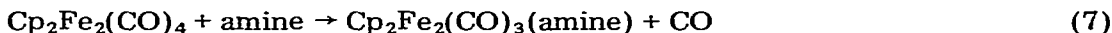
(-21°C), it seems that extensive electron transfer from bulky amines to "Fp⁺" competes with the formation of the amino complex, a limitation which becomes serious when R is large. However, good amounts of these cationic amino complexes are easily synthesized and separated from Fp₂, the electron-transfer product, since only cheap starting materials are used. Attempts to deprotonate these Fp(amino)⁺ complexes by t-BuOK or NEt-i-Pr₂ to synthesize neutral Fp-amido complexes resulted instead in the liberation of the free amine and formation of Fp₂ (in refluxing THF) either by electron transfer from the base to the organometallic cation or by decomposition of the transient Fp-amido complexes, which are unknown.

Reaction of Fp(amino)⁺ with CS₂ in THF does not occur even on prolonged reflux. Thus, insertion is not possible into Fe—amino bonds. However, when the amino complexes are treated with a mixture of CS₂ and t-BuOK (or NEt-i-Pr₂), immediate insertion proceeds at 20°C, giving monodentate dithiocarbamates I (R = Me, Et, SiMe₃) in 90–92% yields of isolated complexes (eq. 6).

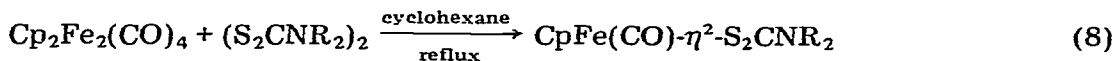


It thus seems that this insertion is a concerted process [31,32] since both the base and CS₂ are necessary. This procedure was used to synthesize Fp-η¹-SeC-(Se)NMe₂ (IV) since the reaction of Fp₂ with NHMe₂ and CSe₂ is neither clean nor quantitative. Insertion of CSe₂ is as clean and easy as that of CS₂, and this route probably is the best one to IV.

The concerted formation of monodentate dithiocarbamate ligands by insertion of CS₂ into metal—amido bonds indicates this path is a possible mechanism for the reaction of Fp₂ with amine and CS₂. It is known that Fp₂ reacts with amines to bring about replacement of one carbonyl by a two-electron amine ligand [33] (eq. 7).



In these media, amines can also play the role of a base in a subsequent concerted insertion. Whether this process occurs before or after breaking the metal—metal bond is unclear, however. Initiation of formation of a dithiocarbamate-metal complex by the radical Fp[•] would favour the synthesis of a chelate rather than that of a monodentate dtc complex, as indicated by the reaction of Fp₂ with dithiuram disulfide, which is known to give CpFe(CO)-η²-dtc [21] (eq. 8).

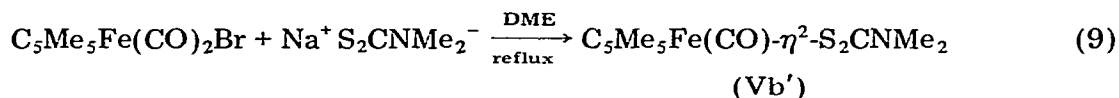


On the contrary, the fact that the yield of the reaction is limited to 50% and that some Fp₂ (20%) is always recovered after the reaction indicates the fate of the two Fp moieties may be different. This is not the case, however for the reaction with Cp₂Mo₂(CO)₆ which certainly follows a different, more straightforward path. The formation of I not only occurs when Fp₂ is first treated with amine and then with CS₂, but also when both reagents are added at the start of the reaction, the amine being in excess. Since the driving force for the

formation of I is strong, it is also possible that two possible mechanisms are operative, e.g. the possibility also exists that dtc^- directly reacts with $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ or $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{NHEt}_2)_2$. More work is needed before the mechanism can be considered in detail.

Reaction of $\text{C}_5\text{Me}_5\text{Fe}(\text{CO})_2\text{Br}$ with Na^+dtc^-

Since we wished to extend the synthesis of monodentate dithiocarbamates to the C_5Me_5 series, we attempted to use Wilkinson's method. No reaction was found to occur at 20°C , even after one day, between $\text{C}_5\text{Me}_5\text{Fe}(\text{CO})_2\text{Br}$ and $\text{Na}^+\text{S}_2\text{CNMe}_2^-$ in acetone. Even in refluxing DME no trace of the expected monodentate complex was found, but the chelate $\text{C}_5\text{Me}_5\text{Fe}(\text{CO})-\eta^2\text{-S}_2\text{CNMe}_2$ was formed (eq. 9). Evidence for its structure was obtained from the absence



of a rotational barrier in variable temperature ^1H and ^{13}C NMR spectra, from the elemental analysis and by application of Bonati's criteria to the IR spectrum (vide supra). Thus Wilkinson's reaction gives the monodentate complex with C_5H_5 and the chelate with C_5Me_5 . This dramatic change can be attributed to the difficulty of removing the halide in the presence of the C_5Me_5 ligand on iron, combined with the enhanced thermal stability of the chelate complex containing permethylated Cp. There are many precedents for stabilization of organometallic complexes [34] as well as changes in reactivity [34,35] upon permethylation of Cp.

Experimental

General data

All manipulations were carried out by Schlenk techniques under purified N_2 or Ar. Reagent grade THF and DME were predried on Na foil and distilled from sodium benzophenone ketyl just before use. Benzene and toluene were distilled and stored under nitrogen. Reagent grade pentane and hexane were degassed with N_2 or Ar before use. 1,2,3,4,5-Pentamethylcyclopentadiene was prepared as described by Threlkel and Bercau [36]. All other chemicals were used as received. Infrared spectra were recorded with a Pye Unicam SP 1100 infrared spectrophotometer which was calibrated with polystyrene. Samples were prepared between KBr disks in Nujol. ^1H NMR spectra were obtained with a Varian EM 360 spectrometer. Proton decoupled ^{13}C NMR spectra were obtained at 25 MHz in the pulsed Fourier transform mode with a Varian H100 spectrometer. All chemical shifts are reported in parts per million (δ) relative to internal SiMe_4 .

Preparations of $\text{CpFe}(\text{CO})_2-\eta^1\text{-SC(S)N}(\text{Et})_2$ (Ia) from Fp_2 , NHEt_2 and CS_2

4.42 g of Fp_2 (12.5 mmol) is dissolved in 60 ml THF under N_2 and 50 mmol (excess) of the secondary amine is added. The mixture is refluxed for 3 h before 25 mmol CS_2 is added slowly at 25°C , alternatively this addition can be made immediately after that of the amine. The formation of Ia is monitored by TLC ($R_f = 0.35$ with hexane/ether 85/15 as eluent). The initially purple reaction mix-

ture turns red-brown. After removal of the solvent in vacuo, the solid residue is dissolved in 20 ml ether and the solution is passed through a short chromatographic column of silica gel to remove impurities and submitted to preparative thin-layer chromatography (eluent: hexane/ether 4/1). The major, orange-red band is separated and, after recrystallization from hexane/ether, red crystals of Ia are obtained in 40.7% yield, m.p. 83°C. Analysis. Found: C, 41.67; H, 4.70; Fe, 17.19; N, 4.37; S, 19.65. $C_{12}H_{15}O_2FeNS_2$ calcd.: C, 44.32; H, 4.61; Fe, 17.19; N, 4.00; S, 19.70%. NMR (δ ppm, $CDCl_3$) 1H : 5.08 (Cp), 4.06 (q, CH_2); 1.26 (t, CH_3); ^{13}C : 86.3 (Cp), 211.9 (CO), 205.3 (CS_2), 63.3 and 66.9 (CH_2), 12.4 (CH_3). $Fe(dtc)_3$ is also isolated from this reaction as black crystals in 25% yield after crystallization from acetone following extraction by this solvent of the ether-insoluble residue from the reaction mixture. It is identified by its melting point and elemental analysis, as is the white, air stable salt $NEt_2H_2^+S_2CNET_2^-$.

CpMo(CO)₂- η^2 -S₂CNEt₂ (II) from Cp₂Mo₂(CO)₆, NH₂Et and CS₂

A procedure analogous to the one described above for Ia is used, starting from 0.98 g of $Cp_2Mo_2(CO)_6$ (2 mmol). It gives, after 5 h reflux, 85% of II after recrystallization, m.p. 134°C; $R_f = 0.43$ (hexane/ether 85/15 as eluent). Analysis. Found: C, 39.61; H, 4.20; Mo, 26.21; S, 17.13; N, 3.77. $C_{12}H_{15}NO_2S_2Mo$ calcd.: C, 39.40; H, 4.11; Mo, 26.30; S, 17.50; N, 3.83%. NMR (δ ppm, $CDCl_3$) 1H : 4.59 (Cp), 3.08 (q, CH_2), 1.03 (t, CH_3); ^{13}C : 94.1 (Cp), 256.7 (CO), 206.2 (CS_2), 42.5 (CH_2), 12.4 (CH_3).

Fp(NHR₂)⁺PF₆⁻ from FpCl and NHR₂ (R = Me, Et, SiMe₃)

Fischer's synthesis of $Fp(NH_3)^+PF_6^-$ from $FpCl$ and NH_3 [30] was used with secondary amines. The amine served as the solvent. 1.06 g of $FpCl$ (5 mmol) is dissolved in 50 ml $NHMe_2$ (liquified at $-78^\circ C$), and the mixture is stirred for 1 h at $-21^\circ C$, the reaction being monitored by TLC. The reaction is stopped when Fp_2 appears. 1.2 g of precipitate is obtained, and is dissolved in 20 ml water; this solution is filtered and added to an aqueous solution of $NaPF_6$. The precipitate is dried in vacuo and purified by preparative thin layer chromatography (eluent: CH_2Cl_2 /ether 8/3) on silica plates (1 mm). The yellow band is eluted to provide 0.617 g of the air-stable salt $Fp(NHMe_2)^+PF_6^-$ (IIIb) (35% yield), m.p. 170°C (dec.). Analysis. Found: C, 29.08; H, 3.77; Fe, 15.40. $C_9H_{12}NFeO_2PF_6$ calcd.: C, 29.44; H, 3.27; Fe, 15.22%. IR (Nujol): $\nu(CO)$: 2040, 2090, $\nu(N-H)$: 3340 cm^{-1} .

Under identical conditions, the reaction with NH_2Et and 2.12 g of $FpCl$ (10 mmol), followed by thick layer chromatography (CH_2Cl_2 /ether 4/3) gives 0.810 g of $Fp(NH_2Et)^+PF_6^-$ (20% yield), m.p. 40°C (dec.). Analysis. Found: C, 33.26; H, 4.53; N, 3.77; Fe, 14.10. $C_{11}H_{16}NFeO_2PF_6$ calcd.: C, 33.43; H, 4.65; N, 3.54; Fe, 14.14%. IR (Nujol) $\nu(CO)$: 2010, 2060; $\nu(N-H)$: 3300 cm^{-1} .

Refluxing 2.12 g of $FpCl$ (10 mmol) with neat $NH(SiMe_3)_2$ (10 ml) for 3 h gives 0.450 g of pale-yellow air-stable $FpNH(SiMe_3)_2^+PF_6^-$ (IIIc) (10% yield), m.p. 120°C (dec.). IR (Nujol) $\nu(CO)$: 2060, 2105; $\nu(NH)$: 3350 cm^{-1} .

Reaction of Fp(NHR₂)⁺PF₆⁻ with CS₂ and a base (R = Me, Et)

No reaction is observed between $Fp(NHR_2)^+PF_6^-$ and base (t-BuOK,

NEt-i-Pr₂) or CS₂ at 20°C after 24 h in THF. Reaction with a base under reflux gives Fp₂.

To a solution of 0.733 g of Fp(NHR₂)⁺PF₆⁻ (III) in 40 ml acetone, is added 1 ml of CS₂. No reaction is observed at 20°C. NEt-i-Pr₂ (1 ml) is added dropwise by syringe. The yellow solution immediately turns red, the colour of Fp-η¹-dtc. After stirring 1/2 h and removal of acetone in vacuo, extraction with ether, preparative thin-layer chromatography and recrystallization gives a 90 to 92% yield of Fp-η¹-dtc. The ether-insoluble residue is identified by ¹H NMR and IR spectroscopy (ν(NH): 3350 cm⁻¹) as (NH*i*-Pr₃)⁺PF₆⁻. Use of *t*-BuOK instead of NH*i*-Pr₂ also gives yields of I close to 90%. Treatment of III with either CS₂ or a base alone at 20°C in THF does not give any reaction. Reactions with bases in refluxing THF lead to the slow formation of Fp₂.

*Reaction of Fp(NHMe₂)⁺PF₆⁻ with CSe₂ and *t*-BuOK*

To an acetone solution of (FpNHMe₂)⁺PF₆⁻ (IIIb, 0.59 g, 1.6 mmol) at -20°C is added 0.27 g of CSe₂ (1.6 mmol) and then 0.18 g of *t*-BuOK (1.6 mmol). After stirring 1 h at -20°C and removal of acetone in vacuo, the residue is dissolved in 10 ml ether and chromatographed on a short column of silica gel. Crystallization from ether/hexane at -21°C gives Fp-η¹-SeC(Se)NMe₂ (IV) as brick-red crystals in 88% yield (0.53 g). The elemental analysis was not determined. ¹H NMR (δ ppm, CDCl₃): 5.20 (Cp), 3.68 (NMe₂). IR (Nujol) ν(CO): 2055, 1995; ν(CN): 1500 cm⁻¹. Variable temperature ¹H and ¹³C spectra (rotation about the C-N bond) will be reported later, together with ¹⁵N NMR data.

C₅Me₅Fe(CO)-η²-S₂CNMe₂ (Vb) from C₅Me₅Fe(CO)₂Br and Na⁺S₂CNMe₂⁻

No reaction occurs when 2.7 g of C₅Me₅Fe(CO)₂Br (10 mmol), 2.16 g of Na⁺S₂CNMe₂⁻ · H₂O (12 mmol) are stirred together at 20°C in 30 ml of 1,2-dimethoxyethane. This mixture is refluxed for 12 h, and the solvent is then removed in vacuo. The solid residue is submitted to preparative thin-layer chromatography on silica gel with hexane/ether 4/1 as eluent. The red band is eluted, and recrystallization in pentane gives 2.68 g (67%) of Vb' as black plates. ¹H NMR (δ ppm, CDCl₃): 1.67 (C₅Me₅); 3.11 (NMe₂). IR (Nujol) ν(CO): 1925; ν(CN): 1540; ν(CS): 1000 cm⁻¹. Analysis. Found: C, 49.58; H, 6.14; N, 4.16; Fe, 16.74; S, 18.40. C₁₄H₂₁NFeOS₂ calcd.: C, 49.56; H, 6.24; N, 4.18; Fe, 16.46; S, 18.90%.

Acknowledgements

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