Reactivity of η^2-Trithiocarbonate Metal Complexes as Nucleophiles. Intramolecular Mobility of the Trithiocarbonate Group in μ-CS_3 Binuclear Complexes †

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The reactivity of the trithiocarbonate nickel(II) complex [Ni(tppme)(S_2CS)] (1) [tppme = 1,1,1-tris(diphenylphosphinomethyl)ethane] toward a series of electronically and co-ordinatively unsaturated metal–ligand moieties has been investigated; as a result, the homo- and hetero-metal complexes [(tppme)Ni(μ-CS_3)Ni(tppme)][BPh_4]$_2$ (2), [(tppme)Ni(μ-CS_3)Co(tppme)][BPh_4]$_2$ (3), and [(tppme)Ni(μ-CS_3)Cr(CO)$_5$] (4) have been synthesized. Complex (2) gives a temperature-dependent ^{31}P-{^1H} n.m.r. spectrum indicative of fluxional behaviour. This is due both to the rotation of the bridging CS_3 group and to a tppme ligand, which displays an unco-ordinated phosphorus atom. The reaction of (1) with [V(η-C_5H_5)$_2$] results in the formation of the nickel(0) η^2-CS_2 complex [Ni(tppme)(η^2-CS_2)] through sulphur abstraction from the η^2-CS_3 ligand. The further reactivity of the binuclear complexes toward $NaBH_4$ has been investigated. The chemical analogies between η^2-CS_3 and η^2-CS_2 metal complexes are discussed.

As part of our investigations on the reactivity of co-ordinated ligands, we have recently focused our attention on η^2-CS_3 metal complexes. η^2 Co-ordination of the trithiocarbonato-ion to the metal generates two potentially reactive sites, the unco-ordinated sulphur atom and the carbon atom, susceptible to attack by electrophilic and nucleophilic agents, respectively. Reactions of the exocyclic sulphur atom include displacement of halide ion from alkyl halides to give sulphur-alkylated trithiocarbonate complexes,[1,2] or weakly bound ligands from organometallic derivatives to form CS_3-bridged binuclear complexes.[1,2] However, 1,2-cycloaddition of dimethyl acetylenedicarboxylate to η^2-CS_3 has clearly demonstrated the dual nature of the metal–CS_3 moiety as an electrophilic and nucleophilic reagent.[3]

The present paper concerns the reactions of the trithiocarbonate nickel(II) complex [Ni(tppme)(S_2CS)] (1) [tppme = 1,1,1-tris(diphenylphosphinomethyl)ethane] with a variety of electronically and co-ordinatively unsaturated metal–ligand moieties (Scheme).

The further reactivity of the binuclear complexes obtained toward $NaBH_4$ has been also studied. This has helped to elucidate the structures of the complexes and the reaction mechanism for their formation.

Experimental

tppme [4] and $Na_2CS_3 \cdot H_2O$ [5] were prepared as previously described. [Cr(CO)$_6$] was purchased from Strem Chemicals Inc. and used without further purification. All other chemicals employed were of reagent grade quality. Reagent grade tetrahydrofuran (thf) was further purified by distillation over $LiAlH_4$. All operations were performed under nitrogen using deoxygenated solvents. The solid complexes were collected on a sintered-glass frit and washed with ethanol and light petroleum (b.p. 40—70 °C) before being dried in a stream of nitrogen. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer as Nujol mulls. ^{31}P-{^1H} n.m.r. spectra of $CDCl_3$ solutions were recorded at 303 K with a Varian CFT 20 spectrometer. Peak positions are relative to phosphoric acid with downfield values reported as positive. Ultraviolet-visible spectra were recorded on a Beckman DK-2A spectrophotometer. Magnetic susceptibilities of solid samples were measured on a Faraday balance. Conductivity measurements were made using a WTW model LBR/B conductance bridge. The analytical, magnetic, and conductivity data of the complexes are reported in Table 1. Table 2 lists the electronic spectral data.

Synthesis of [Ni(tppme)(S_2CS)] (1).—A mixture of Ni[BF_4]$_2 \cdot 6H_2O$ (0.34 g, 1 mmol) in ethanol (10 cm^3) and tppme (0.62 g, 1 mmol) in CH_2Cl_2 (30 cm^3) was added to a solution of $Na_2CS_3 \cdot H_2O$ (0.17 g, 1 mmol) in ethanol (10 cm^3). Addition of ethanol (20 cm^3) to the resulting orange-brown solution and slow evaporation of the solvent produced orange crystals; yield 90%.

Synthesis of [(tppme)Ni(μ-CS_3)Ni(tppme)][BPh_4]$_2$ (2).—A CH_2Cl_2 solution (20 cm^3) of (1) (0.39 g, 0.5 mmol) was allowed to react with a mixture of Ni[BF_4]$_2 \cdot 6H_2O$(0.17 g, 0.5 mmol) in ethanol (10 cm^3) and tppme (0.31 g, 0.5 mmol) in CH_2Cl_2 (10 cm^3). On addition of $NaBPh_4$ (0.34 g, 1 mmol) in ethanol (20 cm^3) and slow evaporation of the solvent, red-brown crystals were obtained; yield 70%.

Synthesis of [(tppme)Ni(μ-CS_3)Co(tppme)][BPh_4]$_2$ (3).—This brown complex was prepared by the same procedure as (2) except for substitution of Co[BF_4]$_2 \cdot 6H_2O$ for the nickel analogue; yield 70%. Alternatively, (3) was synthesized by the same procedure as above by reacting [Co(tppme)(S_2CS)] [6] with a mixture of Ni[BF_4]$_2 \cdot 6H_2O$ and tppme in the presence of $NaBPh_4$; yield 75%.

Synthesis of [(tppme)Ni(μ-CS_3)Cr(CO)$_5$] (4).—A solution of [Cr(CO)$_5$(thf)] formed by u.v. irradiation of the corresponding hexacarbonyl complex [7] (0.15 g, 0.7 mmol) in thf (50 cm^3) was added to a suspension of (1) (0.47 g, 0.6 mmol) in thf (200 cm^3). Within 2 h the solid dissolved and a red-brown solution was obtained. After evaporation of the solvent at reduced pressure the solid residue was extracted with CH_2Cl_2 (20 cm^3). Red-orange crystals were separated by addition of ethanol (20 cm^3) and slow evaporation of the solvent; yield 85%.

Synthesis of [Ni(tppme)(η^2-CS_2)] (8).—A suspension of (1) (0.39 g, 0.5 mmol) in thf (100 cm^3) was treated with a solution

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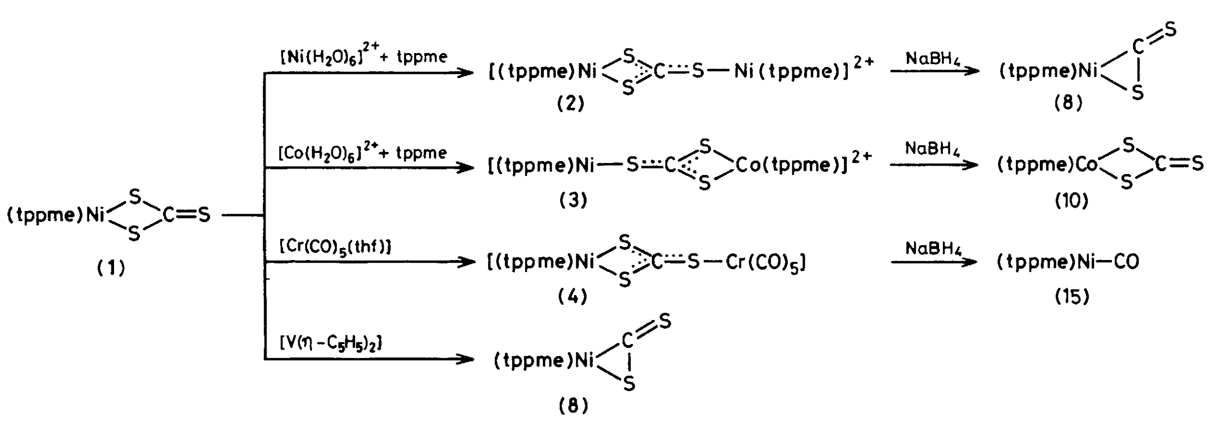
† *Non-S.I. unit employed:* B.M. = 0.927×10^{-23} A m^2.



Scheme.

Table 1. Analytical and physical data for the complexes

Complex	Analysis[a] (%) C	H	Ni	Λ[b]/ Ω^{-1} cm^2 mol^{-1}
(1) $[Ni(tppme)(S_2CS)]$	63.65 (63.7)	4.9 (4.95)	7.35 (7.4)	
(2) $[(tppme)Ni(\mu-CS_3)Ni(tppme)][BPh_4]_2$ [c]	74.2 (74.45)	5.65 (5.6)	5.5 (5.55)	103
(3) $[(tppme)Ni(\mu-CS_3)Co(tppme)][BPh_4]_2$ [d,e]	74.3 (74.45)	5.6 (5.6)	2.75 (2.75)	108
(4) $[(tppme)Ni(\mu-CS_3)Cr(CO)_5]$ [f]	57.3 (57.4)	3.95 (4.0)	5.9 (5.95)	

[a] Calculated values are given in parentheses. [b] Molar conductance values for *ca.* 10^{-3} mol dm^{-3} nitroethane solutions at 20 °C. [c] S, 4.5 (4.55)%. [d] Co, 2.75 (2.8)%. [e] $\mu_{eff.}$(293 K) = 2.12 B.M. [f] Cr, 5.25 (5.3)%.

Table 2. Electronic spectral data [a] for the complexes

Complex	$\lambda_{max.}$/cm^{-1}
(1)	13 350, 20 400, 23 800 (sh) [b]
	13 150 (74), 20 800 (740), 24 100 (2 290) [c]
(2)	12 800, 16 000 (sh), 19 250 [b]
	12 750 (800), 16 100 (sh), 19 300 (24 700) [c]
(3)	9 250, 12 800, 14 800, 17 700 (sh), 22 000 [b]
	9 550 (665), 12 900 (819), 15 150 (sh), 18 000 (sh), 23 200 (sh) [c]
(4)	13 300, 20 000, 24 100 [b]
	13 200 (95), 20 300 (810), 24 100 (2 400) [c]

[a] Molar absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses. [b] Solid at room temperature. [c] 1,2-Dichloroethane solution.

of $[V(\eta-C_5H_5)_2]$ (0.09 g, 0.5 mmol) in thf (15 cm^3). Within 6 h the solid dissolved to give a black-brown solution. After evaporation of the solvent at reduced pressure to 30 cm^3, n-butanol (20 cm^3) was added. Black-brown crystals separated on standing; yield 60%.

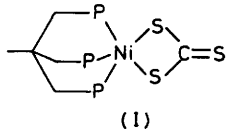
Reaction of (2) *with* $NaBH_4$.—An acetone solution (30 cm^3) of (2) (0.63 g, 0.3 mmol) was treated with $NaBH_4$ (0.02 g, 0.6 mmol) in ethanol (15 cm^3). On addition of n-butanol (20 cm^3) to the resulting deep brown solution crystals of (8) were obtained; yield 40%.

Reaction of (3) *with* $NaBH_4$.—$NaBH_4$ (0.02 g, 0.6 mmol) in ethanol (10 cm^3) was added dropwise to an acetone solution (25 cm^3) of (3) (0.63 g, 0.3 mmol). Red-orange crystals of $[Co(tppme)(S_2CS)]$ (10) precipitated on addition of n-butanol (20 cm^3); yield 85%.

Reaction of (4) *with* $NaBH_4$.—$NaBH_4$ (0.2 g, 0.6 mmol) in ethanol (10 cm^3) was added dropwise to an acetone (20 cm^3) suspension of (4) (0.49 g, 0.5 mmol) producing a yellow-brown solution. Ethanol (20 cm^3) was then added. Yellow crystals of $[Ni(tppme)(CO)]$ (15) formed on standing; yield 50%.

Results and Discussion

The diamagnetic complex (1) is obtained as red-orange crystals by reaction of $Na_2CS_3\cdot H_2O$ with nickel(II) aqua-cations and tppme. It is air-stable and soluble in chlorinated solvents in which it behaves as a non-electrolyte. The electronic spectrum, almost identical both in the solid state and in 1,2-dichloroethane solution is fully comparable with those of five-co-ordinate nickel(II) complexes with a P_3S_2 donor set such as $[Ni(tppme)(S_2COEt)]BPh_4$, $[Ni(tppme)(S_2CNEt_2)]BPh_4$, and $[Ni(tppme)(S_2CSMe)]BPh_4$.[8] The i.r. spectrum exhibits two bands at 1 045 and 865 cm^{-1} attributable to ν(C=S) and ν_{sym}(C–S) stretching vibrations respectively, and consistent with those reported for a variety of dihapto-co-ordinated CS_3 complexes.[1,2,6,9] The $^{31}P-\{^1H\}$ n.m.r. spectrum shows a singlet at −0.04 p.p.m. This pattern, unchanged even at −60 °C, is consistent with rapid intramolecular exchange of the three phosphorus atoms of tppme around the nickel atom.* On the basis of all of these data it is reasonable to assign the structure (I) to complex (1).



(I)

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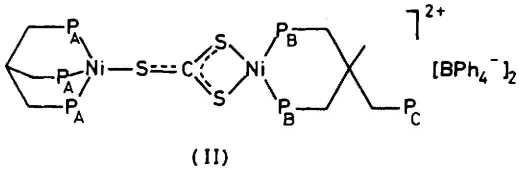
* A distorted square-pyramidal structure with an axial phosphorus atom is expected at very low temperature, based on the *X*-ray crystal structure of the isomorphous $[Co(tppme)(S_2CO)]$ complex.[6]

In previous work from this laboratory it has been shown that the metal–ligand moieties formed by some transition metals, particularly cobalt and nickel and the triphosphine tppme, are capable of reacting with appropriate complexes to form homo- and hetero-metal binuclear complexes [(tppme)-M(μ-X)M′L]$^{n+}$ where L = tppme or another ligand, and X is an appropriate bridging group.[10–12] The formation of these complexes usually exploits the reaction of the M(tppme) moiety with a complex containing a ligand whose ligating properties are not completely exhausted. It therefore seemed of interest to investigate the reactivity of (1) toward a variety of unsaturated complex compounds since the exocyclic sulphur atom is expected to have the capability of bonding to an appropriate metal species.

We have thus observed that (1) reacts with equimolecular amounts of Ni^{II} or Co^{II} aqua-cations and tppme, in the presence of NaBPh$_4$, producing intensely coloured solutions from which the binuclear complexes [(tppme)Ni(μ-CS$_3$)Ni-(tppme)][BPh$_4$]$_2$ (2), and [(tppme)Ni(μ-CS$_3$)Co(tppme)]-[BPh$_4$]$_2$ (3) can be obtained respectively. These complexes, red-brown and brown in colour respectively, are air-stable in the solid state but decompose in solution unless air is excluded. They are soluble in common organic solvents where they behave as 1 : 2 electrolytes. Compound (2) is diamagnetic, whereas (3) is paramagnetic with a magnetic moment corresponding to a doublet ground state. The electronic spectra, almost identical both in the solid state and in solution, show several absorption edges in the range 12 000—20 000 and 9 000—24 000 cm^{-1} for (2) and (3) respectively, but are not easily interpretable in the absence of more detailed studies. However, useful comparisons can be made with other metal complexes with tppme and sulphur-containing ligands (see below). The i.r. spectra of both compounds exhibit a strong absorption at 1 000 cm^{-1}, which is assigned to the C=S stretching frequency. The lowering in the C=S frequency compared with that of the precursor (1) is not unexpected since the co-ordination of another nickel or cobalt atom to the dihapto-CS$_3$ group should decrease the C=S force constant. Moreover, bands in the range 1 025—960 cm^{-1} have been found in metal complexes containing CS$_3$ bridges.[1,2,13,14]

The structure of (2) has been ascertained by variable-temperature ^{31}P n.m.r. spectroscopy. The ^{31}P-{^{1}H} n.m.r. spectra for the temperature range +55 to −60 °C are presented in the Figure. At −60 °C the spectrum indicates a ' frozen ' structure in which a tppme ligand is functioning as a bidentate ligand with one of the terminal Ph$_2$P− groups unbonded to the metal, while the CS$_3$ group chelates a nickel atom through two sulphur atoms and links the other nickel by means of the third sulphur. The most likely structure is illustrated in (II).



(II)

The ^{31}P n.m.r. assignments are as follows: δ(P$_A$) = −0.50, δ(P$_B$) = +13.22, δ(P$_C$) = −31.37 p.p.m. As the temperature is raised, the free Ph$_2$P− group (P$_C$) begins to switch its position with the other two arms of the bidentate tppme ligand, as evidenced by the broadening of these resonances. They give rise to a weak, broad absorption at +55 °C. Simultaneously the CS$_3$ group begins to rotate around the carbon atom, thus making the two differently co-ordinated Ni(tppme) moieties indistinguishable in the ^{31}P n.m.r. spectrum; at +55 °C only one signal is registered for the two tppme molecules at −1.26 p.p.m. An intramolecular motion is clearly taking place in which the two Ni(tppme) fragments rapidly exchange their sites and function.

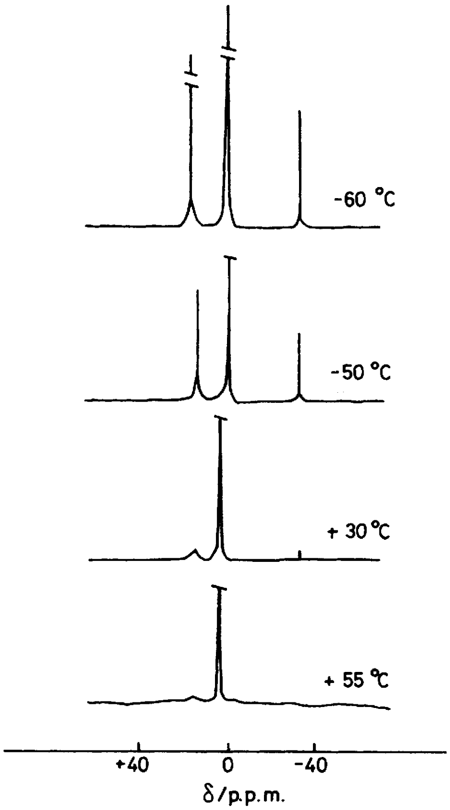


Figure. Variable-temperature ^{31}P-{^{1}H} n m.r. spectra of [(tppme)-Ni(μ-CS$_3$)Ni(tppme)][BPh$_4$]$_2$ in CDCl$_3$

The assignments at −60 °C have been made by taking into account the ^{31}P-{^{1}H} n.m.r. spectra of the nickel complexes (1), [(tppme)Ni(μ-CS$_3$)Cr(CO)$_5$] (4), [Ni(dppp)(S$_2$CS)] (5) [dppp = 1,3-bis(diphenylphosphino)propane],* and [Ni(tppme)-{S$_2$C(H)PEt$_3$}]BPh$_4$ (6).[8] Only one signal each is registered for the phosphine ligands in (1), (4), and (5) at −0.04, −1.56, and +15.04 p.p.m. respectively. Complex (5) has been assigned a planar geometry around the nickel atom. This is co-ordinated by the two sulphur atoms of the trithiocarbonate ligand and by the two phosphorus atoms of the dppp molecule, which thus forms a six-membered metallo-ring as does the bidentate tppme ligand in (2).

The physical and chemical properties of the binuclear complex (4) will be discussed later in this paper, however we can anticipate that the nickel atom is five-co-ordinated by a tridentate tppme molecule and by two sulphur atoms of a bridging CS$_3$ unit.

Conversely (6), where the nickel atom is four-co-ordinated by two phosphorus atoms of the tppme ligand and by the sulphur atoms of the S$_2$C(H)PEt$_3^-$ ligand, shows variable-temperature ^{31}P n.m.r. spectra indicating dynamic behaviour. At −65 °C the spectrum in methylene chloride solution indicates a ' frozen ' structure, where the tppme ligand acts as bidentate (δ = +16.72 p.p.m.) with one Ph$_2$P− group not co-ordinated to the metal (δ = −31.77 p.p.m.).

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* Unpublished results from this laboratory; compound (5) was synthesized by adding under nitrogen Na$_2$CS$_3$·H$_2$O (1 mmol) in ethanol (10 cm^3) to a mixture of Ni[BF$_4$]$_2$·6H$_2$O (1 mmol) in ethanol (20 cm^3), and dppp (1 mmol) in CH$_2$Cl$_2$ (20 cm^3).

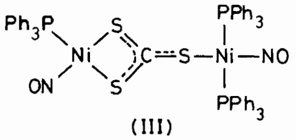
It would have been very interesting to record the ^{31}P n.m.r. spectrum of the binuclear complex [(tppme)Ni(μ-S)Ni(tppme)][BPh$_4$]$_2$[15] (7) where each nickel atom is tetrahedrally co-ordinated by a tppme molecule and by a sulphur atom. Unfortunately, its solubility in chloroform is too poor so as to preclude a good spectrum. The ^{31}P-{^{1}H} n.m.r. spectrum has been registered in acetone solution and shows a singlet at +3.92 p.p.m.

The electronic spectrum of (2) certainly cannot offer any decisive argument in favour of the proposed structure (II), however we wish to report that some analogies can be seen in the spectra of (2) and (7).

Finally, the reactivity toward NaBH$_4$ shown by (2) is compatible with the bonding formulation (II). NaBH$_4$, in fact, reacts with (2) producing black-brown crystals of [Ni(tppme)(η^2-CS$_2$)] (8)[16] (Scheme). Complex (8) has been recently obtained by treatment of the nickel(II) *S*-methyl trithiocarbonate complex [Ni(tppme)(S$_2$CSMe)]BPh$_4$ with NaBH$_4$ with a reaction mechanism that we suggested to involve nucleophilic attack by hydride ion on the $^-$CS$_2$ carbon atom, followed by expulsion of MeSH.[8] By analogy, a similar mechanism cannot be excluded for the formation of (8) from the reaction of (2) with NaBH$_4$, the only difference being the leaving group, which should be the thiolo-complex [Ni(tppme)(SH)]. Indeed this complex has been recently synthesized by treatment of a solution of the nickel(II) complex [Ni(tppme)(S$_2$CNEt$_2$)]BPh$_4$ with NaBH$_4$.[8] This compound is very unstable even in an inert atmosphere and can be isolated only if the supernatant solution is immediately removed from the reaction vessel. Unfortunately this procedure cannot be applied in the present reaction. However, the chemical evidence indicates that when the exocyclic sulphur atom of η^2-CS$_3$ complexes is attacked by an electrophilic agent, the carbon–sulphur bond is weakened. The concomitant presence of a reducing reagent thus may lead to the formation of the η^2-CS$_2$ complex. A further experimental confirmation of this suggestion is the reaction of (2) with [V(η-C$_5$H$_5$)$_2$] (see below).

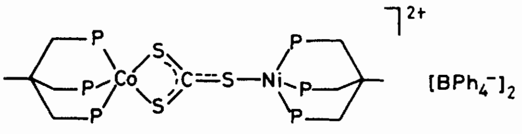
The diamagnetism of (2) could be rationalized in the same way as that of (7). The CS$_3$ group bridges two d^8 metal ions differently co-ordinated. In particular, the tetrahedrally co-ordinated d^8 entity would be paramagnetic. A superexchange mechanism through the CS$_3$ bridge, utilizing $p\pi$ orbitals of the sulphur atom and orbitals of higher energy of the metal, might be involved.[15]

Metal complexes containing CS$_3$ bridging groups are limited to a restricted number of compounds. One of them, namely [(PPh$_3$)$_2$(NO)Ni(μ-CS$_3$)Ni(NO)(PPh$_3$)] (9), seems to have close analogies with (2). Complex (9) has been suggested to have the structure (III) where a nickel atom is square-planarly co-ordinated by two sulphur atoms of the CS$_3^{2-}$ anion, and by the PPh$_3$ and NO groups, whereas a tetrahedral co-ordination is achieved by the other nickel atom by means of two PPh$_3$, NO, and the remaining sulphur atom.[14]

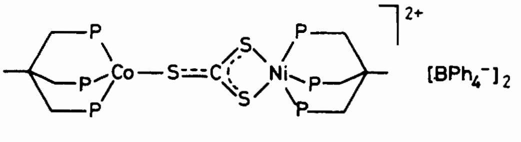


(III)

The heterometal derivative (3), being paramagnetic, could not be studied by ^{31}P n.m.r. spectroscopy. However, a reasonable structure can be proposed on the basis of its physical and chemical properties, and of those already reported, of (2). A number of conceivable structures can be formulated by varying the arrangement of the nine donor atoms available for the two metal centres. We are left with the possibility that (3) has the structural arrangement of either (IV) or (V). Either structure



(IV)



(V)

is sterically and electronically acceptable, and probably, owing to the mobility of the CS$_3$ bridge, (3) has a fluxional behaviour in solution. However, there are several observations that lead us to believe the correct solid-state formulation is that given by (IV).

The value of the magnetic moment corresponding to an unpaired spin for the overall complex cation is clearly not conclusive but the electronic spectrum below 10 000 cm^{-1} is very similar to that of the complex [Co(tppme)(S$_2$CS)] (10), which has been assigned a distorted square-pyramidal co-ordination around the cobalt atom by the three phosphorus atoms of tppme and by two sulphur atoms of the η^2-CS$_3$ group.[6]

Decisive support to (IV) is provided both by the reaction of (3) with NaBH$_4$ leading to (10), and by the reaction of (10) with nickel(II) aqua-cations in the presence of tppme and NaBPh$_4$ leading to (3).

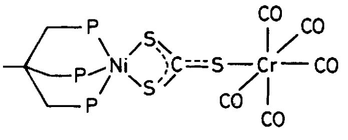
The formation of (3) clearly involves as a first-step nucleophilic attack by the exocyclic sulphur atom of the η^2-CS$_3$ group of (1) on the cobalt atom of the Co(tppme) moiety, followed then by the transposition of the dihapto-CS$_2$ bite from nickel to cobalt.

In contrast to (2), the binuclear complex (4) does not give a temperature-dependent ^{31}P n.m.r. spectrum. A single resonance at −1.56 p.p.m. is observed for the three phosphorus atoms of the tppme even at −60 °C.

Complex (4) is obtained as diamagnetic red-orange crystals from the reaction of (1) with [Cr(CO)$_5$(thf)]. It is stable both in the solid state and in solution, and soluble in common organic solvents in which it behaves as a non-electrolyte. The electronic spectrum, virtually unchanged both in the solid state and in solution, is very similar to that of (1). The i.r. spectrum shows a band at 1 020 cm^{-1} attributable to the C=S stretch which agrees well with those found in the complexes [(tppme)Co(μ-CS$_3$)Cr(CO)$_5$] (11) and [(dppe)Ni(μ-CS$_3$)Cr-(CO)$_5$] (12) (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$), containing CS$_3$ bridges.[2] The bands in the ν(CO) stretching region at 2 055, 1 982, 1 935, and 1 865 cm^{-1} are typical of the C_{4v} symmetry SCr(CO)$_5$ structural units. Comparison with the spectra of (11), (12), [(tppme)-Co(μ-CS$_2$)Cr(CO)$_5$] (13),[10] and [Cr(S$_2$CPEt$_3$)(CO)$_5$] (14)[17] is striking. These frequencies compared with those observed for a variety of [CrL(CO)$_5$] derivatives[18] indicate that (1) behaves as a strong electron-donating ligand when bonded to chromium in (4).

On the basis of all of these data it is therefore reasonable to assign the structure (VI) to complex (4).

Of particular interest is the reaction of (4) with NaBH$_4$. Instead of the expected cleavage of the carbon–exocyclic sulphur bond leading to the nickel(0) η^2-CS$_2$ complex (8),



(VI)

the nickel(0) carbonyl complex [Ni(tppme)(CO)] (15)[19] can be isolated in fairly good yield. The reaction mechanism for the formation of (15) has been rationalized by considering that the η^2-CS_2 complex (8) reacts both with [Cr(CO)$_5$(thf)] and with CO affording (15).[20] Thus we suggest that $NaBH_4$ produces the cleavage of the carbon–exocyclic sulphur bond to form (8), which in turn undergoes displacement of the CS_2 group with CO. This fact is surely interesting since displacement of η^2 co-ordinated carbon disulphide with carbon monoxide is generally not observed as a thermal step in solutions at ambient temperature.[21]

Carbonyl sulphide, COS, has been reported to react with [V(η-C_5H_5)$_2$] to form the binuclear complex [(η-C_5H_5)$_2$V(μ-S_2CO)V(η-C_5H_5)$_2$] containing a bridging dithiocarbonate ligand.[22] Since vanadocene is an electronically and co-ordinatively unsaturated molecule, capable of adding different small molecules as the M(tppme)(M = Fe, Co, or Ni) moieties do, we have treated it with (1) with the aim of synthesizing a μ-CS_3 complex. However, our efforts have met without success because the only product we succeeded in isolating from the reaction mixture was (8). The course of the reaction suggests that at first the expected heterometal complex could have been formed. The proven capability of the CS_3 bridge to transfer electrons from one metal to the other and the great stability of (8) may be then responsible for the decomposition of the binuclear intermediate.

It is interesting to note that sulphur extraction from the CS_3 ligand is an unprecedented reaction path of η^2-trithiocarbonate metal complexes.

To conclude we wish to note the close analogies existing in the chemistry of η^2-CS_3 and η^2-CS_2 metal complexes. They, in fact, can participate in almost the same reactions, which can be summarized as follows: (*a*) alkylation at the exocyclic sulphur atom;[1,2,23] (*b*) displacement of weakly bound ligands from metal complexes or reaction with co-ordinatively unsaturated complex species to give binuclear complexes;[2,10,24] (*c*) cycloaddition of activated alkynes;[3,25] (*d*) sulphur extraction to generate carbon disulphide (see earlier) or thiocarbonyl complexes;[26] (*e*) sulphur addition to give CS_4^{2-}[27] or trithiocarbonate[28] complexes.

These analogies and the fact that η^2-CS_2 and η^2-CS_3 complexes can be transformed directly[28] or indirectly[8,29] into each other make this area of chemistry of increasing interest. Moreover, it should never be forgotten that, despite some differences, the chemistry of CS_2 seems to be so far the only key we have to understand the activation of the most important heterocumulene, namely CO_2.

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