Reactivity of η^2-CS_3Me Metal Complexes as Electrophiles

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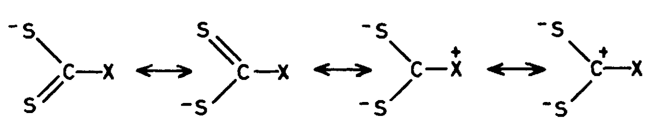
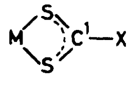
The CS_2 carbon atom of the η^2-CS_3Me ligand in the cobalt(II) and nickel(II) complexes [M(tppme)(S_2CSMe)][BPh_4] [M = Co (1) or Ni (2), tppme = 1,1,1-tris(diphenylphosphinomethyl)ethane] is an electrophilic centre, susceptible to attack by nucleophiles such as PEt_3 and H^-; as a result the new complexes [M(tppme){$S_2C(PEt_3)SMe$}][BPh_4] [M = Co or Ni] and [Co(tppme){$S_2C(H)SMe$}] are obtained. Reaction of an excess of $NaBH_4$ with (1) gives the complexes [Co(tppme)(S_2CS)], [Co(tppme)(η^2-CS_2)] (8), and [Co(tppme)(S_2CO)]. The C–SMe bond in both compounds (1) and (2) is cleaved by sodium to give the η^2-CS_2 complexes (8) and [Ni(tppme)(η^2-CS_2)] respectively. Replacement of the SMe group in complex (2) by NEt_2, followed by reaction of the resultant dithiocarbamate complex with $NaBH_4$, affords the nickel(I) thiolato-complex [Ni(tppme)(SH)], which reacts with CS_2 to give the trithiocarbonate complex [Ni(tppme)(S_2CS)]. All the products have been fully characterized. Mechanisms for the formation of the reaction products are proposed and discussed.

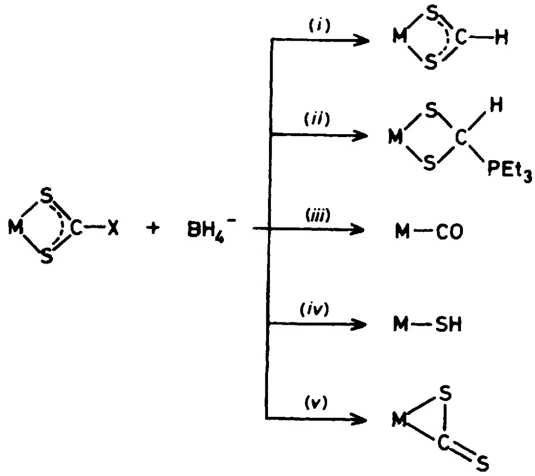
The overall electronic structure of chelated η^2-dithioacid ligands can be described by considering the resonance forms (I)—(IV). Which of these predominates will depend on the nature of the X substituent as well as of the metal–ancillary ligand fragment.[1] We have recently ascertained that the resonance form (IV) is important in describing the reactivity of a variety of η^2-dithioacid metal complexes toward nucleophiles.[2-9]


(I) (II) (III) (IV)

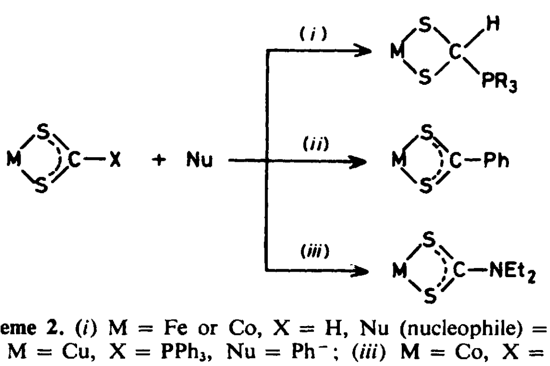
Iron–, cobalt–, nickel–, and copper–phosphine moieties give dithioformate, *S*-methyl trithiocarbonate, dithiocarbamate, *O*-ethyl dithiocarbonate, and triethylphosphoniodithiocarboxylate complexes, in which the dithio-ligand forms a four-membered ring (V) with the metal. Upon η^2-co-ordination to the metal, the C^1 carbon atom of the dithio-ligand becomes an electrophilic centre, susceptible to attack by nucleophiles such as H^- (Scheme 1),[2,5-8] PR_3,[3] Ph^-,[9] and $NHEt_2$[4] (Scheme 2), and RO^- (Scheme 3).[2,8] The nucleophile can add to the C^1 carbon atom, cause fragmentation of the dithio-ligand, displace the X substituent, or facilitate the attack by an appropriate reagent on the C^1 carbon. The electrophilic character of η^2-dithioacid complexes has been also confirmed by qualitative molecular-orbital arguments, which suggested that the main bonding interaction between the Co(tppme) and S_2CSMe fragments in the η^2-trithiocarbonate complex [Co(tppme)(S_2CSMe)][BPh_4] [tppme = 1,1,1-tris(diphenylphosphinomethyl)ethane] involves a significant charge delocalization from the CS_3Me grouping toward the metal, not counterbalanced by π-type back donation.[4]


X = H, SMe, NEt_2, OEt, or PEt_3

(V)

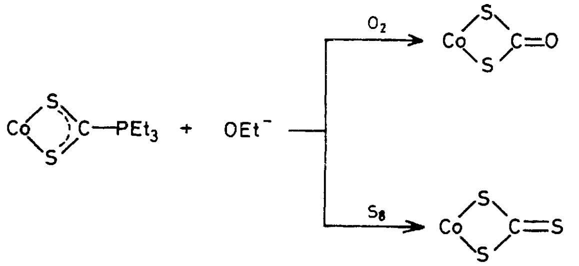


Scheme 1. (*i*) M = Fe, X = PEt_3; (*ii*) M = Fe, Co, or Ni, X = PEt_3; (*iii*) M = Ni, X = OEt; (*iv*) M = Ni, X = NEt_2; (*v*) M = Ni, X = SMe



Scheme 2. (*i*) M = Fe or Co, X = H, Nu (nucleophile) = PR_3; (*ii*) M = Cu, X = PPh_3, Nu = Ph^-; (*iii*) M = Co, X = SMe, Nu = $NHEt_2$

The variety and importance of the results obtained have prompted us to investigate in detail the reactivity of the *S*-methyl trithiocarbonato-cobalt(II) and -nickel(II) complexes [M(tppme)(S_2CSMe)][BPh_4] toward a series of nucleophilic agents. The reactions performed are summarized in Scheme 4; some of them represent a novel and potentially useful route to metal complexes with ligands such as $S_2C(PEt_3)SMe^-$, $S_2C(H)SMe^{2-}$, and S_2CO^{2-}, which do not exist in the free



Scheme 3.

form. The further reactivity of the products obtained has also been probed.

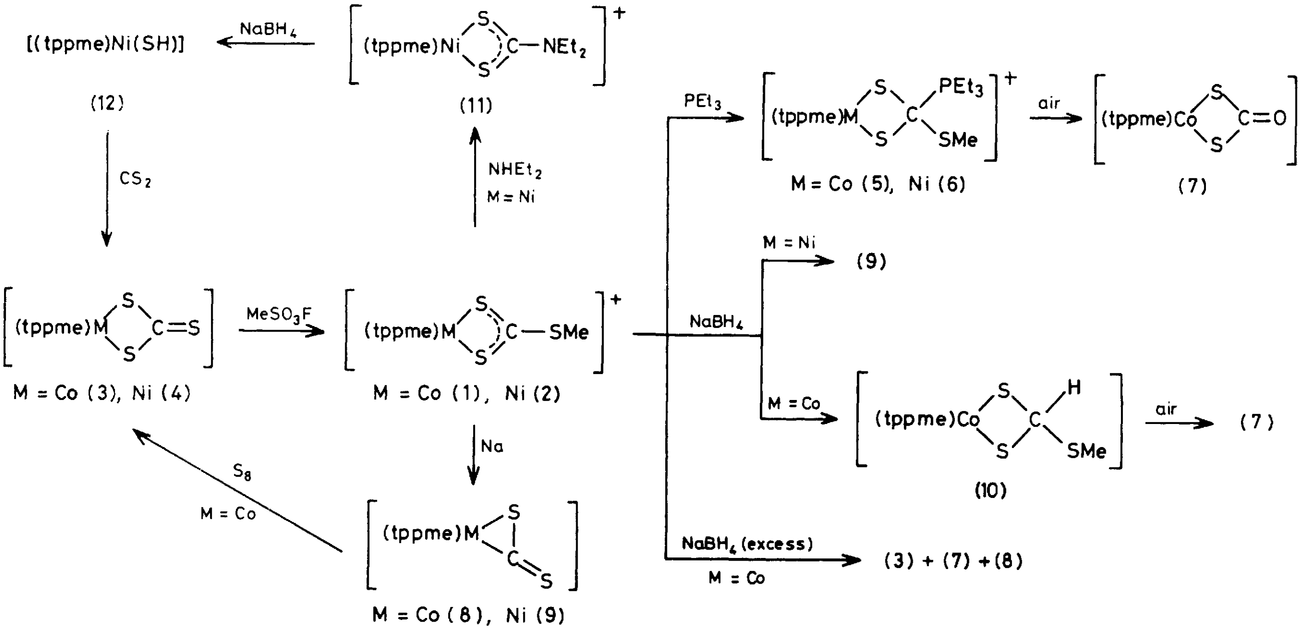
All complexes have been characterized and their physical properties studies by the usual methods and by ^{31}P n.m.r. spectroscopy.

Experimental

The ligand tppme [10] and the complexes [Co(tppme)(S_2CSMe)][BPh_4] (1)[4] and [Ni(tppme)(S_2CS)] (4)[11] were prepared according to published procedures. All other chemicals employed were of reagent-grade quality and were used without further purification. All operations were routinely performed under a nitrogen atmosphere except where stated otherwise. The solid complexes were collected on a sintered-glass frit, washed successively 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 between KBr plates. Proton and ^{31}P-{^1H} n.m.r. spectra of $CDCl_3$ solutions were recorded with a Varian CFT 20 spectrometer at 303 K. Peak positions are relative to tetramethylsilane and phosphoric acid respectively 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. Conductance measurements were made with a WTW model LBR/B conductivity bridge in *ca.* 10^{-3} mol dm^3 nitroethane solutions. The analytical, magnetic, and conductivity data of the complexes are reported in the Table.

Syntheses.—[Ni(tppme)(S_2CSMe)][BPh_4] (2). The compound $MeSO_3F$ (0.05 cm^3, 0.62 mmol) was pipetted into a solution of complex (4) (0.56 g, 0.5 mmol) in CH_2Cl_2 (30 cm^3). Immediately a red-violet solution was obtained. Addition of $NaBPh_4$ (0.30 g, 0.9 mmol) in ethanol (20 cm^3) and slow evaporation of the solvent gave red-violet crystals, yield 80%.



Scheme 4.

[M(tppme){$S_2C(PEt_3)SMe$}][BPh_4] [M = Co (5) *or* Ni (6)]. Into a solution of the appropriate *S*-methyl trithiocarbonate complex (1) or (2) (0.56 g, 0.5 mmol) in CH_2Cl_2 (30 cm^3) was pipetted a molar equivalent of PEt_3 (0.08 cm^3, 0.5 mmol) and the solution was stirred magnetically for *ca.* 1 h at room temperature. On addition of ethanol and slow concentration a yellow-brown and an orange product respectively separated, yields 50 and 55%. By exposing a dichloromethane–ethanol solution of (5) to the air, green crystals of [Co(tppme)(S_2CO)] (7) were obtained.

[Co(tppme){$S_2C(H)SMe$}] (10). A solution of complex (1) (0.56 g, 0.5 mmol) in acetone (40 cm^3) was treated with a molar equivalent of $NaBH_4$ (0.04 g, 0.5 mmol) dissolved in ethanol (10 cm^3). The solution immediately turned brown. Yellow-brown crystals precipitated on addition of n-butanol (30 cm^3), yield 60%. Green crystals of complex (7) were formed by exposing a dichloromethane–ethanol solution of (10) to the air.

[Ni(tppme)(S_2CNEt_2)][BPh_4] (11). A solution of complex (2) (0.56 g, 0.5 mmol) in CH_2Cl_2 (20 cm^3) was treated with an excess of $NHEt_2$ (5 mmol) in CH_2Cl_2 (10 cm^3). Within a few minutes an orange solution was obtained. Addition of ethanol and slow evaporation of the solvent produced orange crystals, yield 70%.

Reaction of Complex (1) *with an Excess of* $NaBH_4$.—A large excess of $NaBH_4$ (0.37 g, 10 mmol) in ethanol (20 cm^3)

Table. Analytical and physical data for the complexes

Complex	Analysis[a] (%)			Λ[b]/ Ω^{-1} cm^2 mol^{-1}	$\mu_{eff.}$/B.M.[c] (298 K)
	C	H	M		
(2) [Ni(tppme)(S_2CSMe)][BPh_4][d]	71.15 (71.45)	5.55 (5.55)	5.20 (5.20)	44	
(5) [Co(tppme){$S_2C(PEt_3)SMe$}][BPh_4][e]	70.2 (70.45)	6.20 (6.25)	4.75 (4.75)	45	2.01
(6) [Ni(tppme){$S_2C(PEt_3)SMe$}][BPh_4][f]	70.15 (70.5)	6.15 (6.25)	4.65 (4.70)	48	
(10) [Co(tppme){$S_2C(H)SMe$}][g]	63.8 (63.95)	5.30 (5.35)	7.20 (7.30)		2.04
(11) [Ni(tppme)(S_2CNEt_2)][BPh_4][h]	72.9 (73.05)	5.95 (6.05)	5.05 (5.10)	44	

[a] Calculated values are given in parentheses. [b] Molar conductance values for *ca.* 10^{-3} mol dm^{-3} nitroethane solutions at 20 °C. [c] 1 B.M. $\approx 9.27 \times 10^{-24}$ A m^2. [d] S, 8.5 (8.55)%. [e] S, 7.70 (7.75)%. [f] P, 9.85 (9.95)%. [g] S, 11.8 (11.9)%. [h] N, 1.20 (1.20)%.

was added to a magnetically stirred solution of complex (1) (0.56 g, 0.5 mmol) in acetone (30 cm^3). The solution immediately turned red-brown. Addition of n-butanol (20 cm^3) produced a red-brown crystalline product which was identified as a mixture of the three isomorphous complexes [Co(tppme)(S_2CS)] (3), (7), and [Co(tppme)(η^2-CS_2)] (8).

Reaction of Complexes (1) *and* (2) *with Sodium.*—To a suspension of complex (1) or (2) (0.56 g, 0.5 mmol) in tetrahydrofuran (thf) (40 cm^3) was added a large excess of sodium and the reaction mixture stirred at room temperature for 4 h. The resulting red-brown and orange-brown solutions were then filtered to eliminate the unreacted sodium and $NaSCH_3$ and treated with n-butanol (30 cm^3). Garnet-red and brown crystals of complex (8) and [Ni(tppme)(η^2-CS_2)] (9) respectively precipitated on standing, yield 50%.

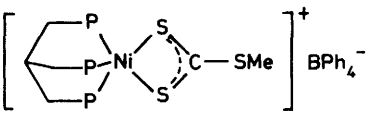
Reaction of [Ni(tppme)(SH)] (12) *with* CS_2.—Carbon disulphide (5 cm^3) was added to a yellow-orange solution of complex (12) obtained by treating (11) (0.34 g, 0.3 mmol) in acetone (30 cm^3) with $NaBH_4$ (0.04 g, 1 mmol) in ethanol (10 cm^3).[5] After 30 min the resultant red-brown solution was treated with n-butanol (20 cm^3) giving a crystalline precipitate which was identified as complex (9). The mother-liquor on standing gave red-orange crystals of (4) as the main product, yield 70%.

Results and Discussion

The complex [Co(tppme)(S_2CSMe)][BPh_4] (1) has recently been synthesized by reaction of [Co(tppme)(S_2CS)] (3) with MeI in the presence of $NaBPh_4$.[4] Similarly, the complex [Ni(tppme)(S_2CSMe)][BPh_4] (2) is obtained as red-violet crystals by reaction of [Ni(tppme)(S_2CS)] (4) with $MeSO_3F$ in the presence of $NaBPh_4$.

Compound (2) is diamagnetic, and air-stable both in the solid state and in solution. It is soluble in common organic solvents, in which it behaves as a 1 : 1 electrolyte. The electronic spectrum is practically identical in the solid state and in solution, showing absorption maxima at 13 200 (ε = 432) and 19 600 cm^{-1} (ε = 7 225 dm^3 mol^{-1} cm^{-1}), and is fully comparable with those of five-co-ordinate nickel(II) complexes with P_3S_2 donor sets.[5,11] The i.r. spectrum has a strong band at 990 cm^{-1} attributable to the C–S stretching mode of the η^2-trithiocarbonate ligand.[4,12,13] The ^{1}H n.m.r. spectrum exhibits a singlet at 2.67 p.p.m. characteristic of S–CH_3 protons, while the ^{31}P-{^{1}H} n.m.r. consists of a singlet at 0.77 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, as observed also for the precursor (4).[11]

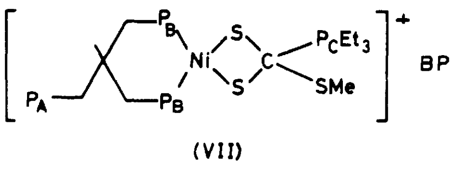
On the basis of all of these data it is reasonable to assign the structure (VI) to complex (2).



(VI)

Compounds (1) and (2) react with equimolecular amounts of PEt_3 producing solutions from which the complexes [M(tppme){$S_2C(PEt_3)SMe$}][BPh_4] [M = Co (5) or Ni (6)] can be obtained. These complexes, yellow-brown and orange 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 : 1 electrolytes. Compound (5) is paramagnetic with a magnetic moment corresponding to a doublet ground state, whereas (6) is diamagnetic. The electronic spectrum of (5) has bands at 10 550 (ε = 430), 16 500 (ε = 290), and 20 900 cm^{-1} (ε = 1 315 dm^3 mol^{-1} cm^{-1}), and is fully comparable with those of distorted five-co-ordinate cobalt(II) complexes with P_3S_2 donor sets,[2,4,7,8] whereas that of (6), with no band at <15 000 cm^{-1}, is typical of square-planar nickel(II) complexes.[5] The i.r. spectra of both compounds do not show any bands attributable to $\mathrm{C}\overset{\cdots}{-}\mathrm{S}$ stretching modes, but instead exhibit a band at 1 040 cm^{-1} indicative of the presence of the PEt_3 group.[14]

The structure of complex (6) has been unambiguously ascertained by means of variable-temperature ^{31}P-{^{1}H} n.m.r. spectroscopy. The ^{31}P n.m.r. spectra for the temperature range +30 to −55 °C are presented in the Figure. At −55 °C the spectrum indicates a ' frozen ' structure, in which the tppme ligand is functioning as a bidentate ligand with one of the terminal Ph_2P groups unbonded. The most likely structure of the complex cation is illustrated in (VII). The ^{31}P n.m.r. assignments are as follows: $\delta(P_C)$ 44.02, $\delta(P_B)$ 17.29, and $\delta(P_A)$ −30.01. As the temperature is raised, the bonded and free Ph_2P groups begin to exchange positions as evidenced by the simultaneous broadening of the above resonances. At +30 °C they give rise essentially to a broad absorption at *ca.* 1 p.p.m. Increase in temperature induces only a very small high-field shift of the resonance due to the phosphorus atom of the PEt_3 group (from 44.02 p.p.m. at −55 °C to 43.76 p.p.m. at +30 °C). Assignments have been made by reference to existing ^{31}P n.m.r. data for the two complexes [Ni(tppme){$S_2C(H)PEt_3$}][BPh_4][5] (13) and [(tppme)Ni(μ-CS_3)Ni(tppme)]-



(VII)

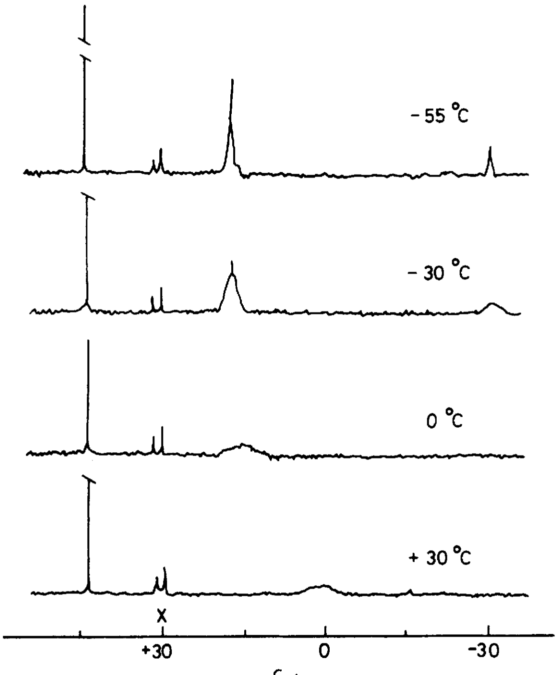


Figure. Variable-temperature ^{31}P-{^{1}H} n.m.r. spectra of [Ni(tppme){$S_2C(PEt_3)SMe$}][BPh_4] in $CDCl_3$; X = an impurity

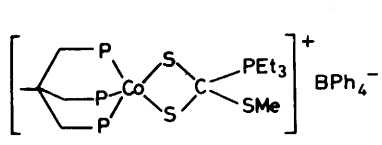
[BPh_4]$_2$ [11] (14). Both (13) and (14) exhibit dynamic behaviour as evidenced by their variable-temperature ^{31}P-{^{1}H} n.m.r. spectra. The spectrum of complex (13) at −65 °C indicates a structure where the co-ordination of the nickel atom is square-planar with the tppme acting in a bidentate manner ($\delta = +16.72$ p.p.m.) with one Ph_2P group unco-ordinated ($\delta = -31.77$ p.p.m.). Analogously, one nickel atom of the binuclear complex (14) has square-planar co-ordination with a bidentate tppme ligand ($\delta = 13.22$ p.p.m. at −60 °C) and two sulphur atoms of the bridging CS_3 ligand. The free Ph_2P group gives a singlet at −31.31 p.p.m.

On the basis of its spectroscopic properties, and of those of (6), compound (5) is assigned the structure (VIII), in which the cobalt atom is five-co-ordinated by the three phosphorus atoms of the tppme ligand and by two sulphur atoms of the new $S_2C(PEt_3)SMe$ ligand.

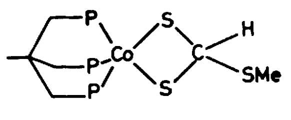
Useful comparisons can be made with the complexes [Co(tppme){$S_2C(H)PEt_3$}][BPh_4]$_x$ [$x = 1$ (15), or 2 (16)] [2,7] and [Co(tepme){$S_2C(H)PEt_3$}][BPh_4]$_x$ [$x = 1$ (17) or 2 (18)] [7] [tepme = 1,1,1-tris(diethylphosphinomethyl)ethane], the last of which has been characterized by *X*-ray analysis. These have been found to contain the dithio-ligand $S_2C(H)PEt_3^-$ which differs from that contained in complexes (5) and (6) only in having H in the place of SMe. The mechanism of their formation has been suggested to involve nucleophilic attack by hydride ion on the CS_2 carbon atom (see introduction), a reaction pattern which can be positively proposed for the formation of (5) and (6) just by replacing H with PEt_3.

Further support for the proposed structure (VIII) is provided by the fact that (5), when exposed to air, gives the dithiocarbonate complex [Co(tppme)(S_2CO)] (7), which has previously been synthesized by oxygen attack both on the product obtained by treatment of [Co(tppme)(S_2CPEt_3)][BPh_4]$_2$ (19) with sodium ethanolate [8] and on compound (15).[2,8]

The reaction of complex (2) with $NaBH_4$ has been reported to cause the extrusion of MeSH, followed by rearrangement of the CS_2 fragment to give the η^2-CS_2 complex, [Ni(tppme)(η^2-CS_2)] (9).[5] In contrast, complex (1) reacts with an equimolecular amount of $NaBH_4$ producing yellow-brown crystals of formula [Co(tppme){$S_2C(H)SMe$}] (10). Compound (10) is air-stable in the solid state, but decomposes in solution even under an inert atmosphere. It is paramagnetic with a magnetic moment corresponding to an unpaired spin. The electronic spectrum exhibits absorption maxima at 10 500, 16 300, and 22 000 cm^{-1}, and is fully comparable with that of complex (5), and, in general, with those of five-co-ordinate cobalt(II) complexes with P_3S_2 and P_3O_2 donor sets.[2,4,7,8,15] The i.r. spectrum does not show any band attributable to $C\overset{\cdots}{-}S$ stretching modes, or to the tetraphenylborate group.



(VIII)



(IX)

All the information gathered from the spectroscopic and magnetic measurements is suggestive of the structure (IX), where the cobalt atom is five-co-ordinated by the three phosphorus atoms of the tppme ligand, and by two sulphur atoms of the new $S_2C(H)SMe^{2-}$ ligand.

Exposure to air of a solution of (10) yields the dithiocarbonate complex (7). The detailed mechanisms for the formation of complex (13) [2,8] are not yet understood, however a mandatory condition seems to be the presence of 1,1-dithiolate ligands of the type $S_2C(X)PEt_3$ (X = H or OEt) η^2-co-ordinated to the Co(tppme) fragment.[8] The present results provide further evidence for this suggestion, complex (7) being formed also by exposure to the air of solutions of the complexes (5), (10), and [Co(tppme){$S_2C(H)OEt$}] (20).[16] Surely, it is not a coincidence that all of these complexes contain 1,1-dithiolate ligands of the above type, namely $S_2C(H)PEt_3^-$, $S_2C(H)SMe^{2-}$, $S_2C(PEt_3)SMe^-$, and $S_2C(H)OEt^{2-}$. It is noteworthy that the precursor dithioacid complexes (1), (19), and [Co(tppme)(S_2COEt)][BPh_4] (21), when exposed to the air, do not afford (7).

The reaction of complex (1) with an excess of $NaBH_4$ yielded red-brown crystals identified by means of i.r. spectroscopy as a mixture of the three isomorphous complexes (3),[2,8] [Co(tppme)(η^2-CS_2)] (8),[17] and (7).[2,8] The i.r. spectrum shows bands at 1 690 and 1 600 cm^{-1} attributable to η^2-S_2CO, at 1 045 and 865 cm^{-1} attributable to η^2-S_2CS, and at 1 120 and 630 cm^{-1} attributable to η^2-CS_2. The formation of the η^2-CS_2 complex (8) is not completely unexpected since the analogous complex (9) is obtained from the nickel trithiocarbonate complex (2) through an identical procedure.[5] The reaction mechanism proposed for complex (9) can probably be extended to (8). Both compounds (8) and (9) can also be synthesized by reaction of sodium with solutions of the *S*-methyl trithiocarbonate complexes (1) and (2), respectively. The trithiocarbonate reactions represent a facile and potentially useful route to η^2-CS_2 complexes, which usually require starting compounds containing the metals in low oxidation states.

In the absence of any kinetic measurements as well as of the detection of intermediates, a number of pathways to the formation of the η^2-CS_3 complex (3) are conceivable. These include: (*a*) extrusion of CH_4 from the intermediate complex (10); (*b*) formation of a CS_2 intermediate which could undergo reaction with sulphur or sulphides released in some manner in the reaction mixture; (*c*) formation of a thiolate complex which in turn could react with CS_2 released from the S_2CSMe grouping. While there is no experimental evidence in support of the hypothesis (*a*), it has been reported that complex (8) (see Scheme 4) reacts with elemental sulphur to give the η^2-CS_3 complex (3),[18] and that an intermediate of the type $[Mn(CO)_5S]^-$ has been suggested to undergo CS_2 insertion into the Mn–S bond to yield $[Mn(CO)_4(\eta^2\text{-}CS_3)]$.[12] Moreover, the thiolato-complex [Ni(tppme)(SH)] (12) has been isolated from the reaction of $NaBH_4$ with an acetone solution of the dithiocarbamate complex $[Ni(tppme)(S_2CNEt_2)][BPh_4]$ (11).[5]

The suggested transformation of M–SH into M–η^2-CS_3 invited an investigation of the effect of adding CS_2 to a solution of the thiolato-complex (12). A solution of the latter, obtained by the procedure summarized in Scheme 4, reacts with CS_2 producing a red-brown solution from which the η^2-CS_3 complex (4) can be isolated together with a minor amount of the η^2-CS_2 complex (9). This result may be viewed as providing support for the proposed mechanisms (*b*) and (*c*).

Finally, the formation of the dithiocarbonate complex (7) from the reaction of (1) with an excess of $NaBH_4$ is somewhat surprising. We are inclined to ascribe it to the fortuitous presence of oxygen in the mixture during the course of the reaction.

In a previous paper [11] we reported that the η^2-CS_2 and η^2-CS_3 metal complexes possess a similar reactivity toward a variety of nucleophilic and electrophilic reagents; the present report emphasizes a particular aspect of the chemistry of η^2-CS_2 and η^2-CS_3 complexes, that is their facile interconversion.

Acknowledgements

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