Journal of Organometallic Chemistry, 286 (1985) 259–270
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REACTIVITY OF (triphos)Ni(η^2-CS_2) TOWARDS GROUP VIB ELEMENTS, HBF_4, AND $MeOSO_2F$. CRYSTAL STRUCTURE OF THE DITHIOCARBONATE COMPLEX $[O{=}PPh_2CH_2C(CH_3)(CH_2PPh_2)_2]Ni(S_2CO) \cdot 0.5THF$

CLAUDIO BIANCHINI, CARLO A. GHILARDI, ANDREA MELI and ANNABELLA ORLANDINI

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, C.N.R., Via F.D. Guerrazzi, 27, 50132 Firenze (Italy)

(Received October 16th, 1984)

Summary

The chemistry of (triphos)Ni(η^2-CS_2) (**2**) (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) is compared and contrasted with that of the isostructural complex (triphos)Co(η^2-CS_2) (**1**). Reaction of **2** with O_2, S_8, and Se_n gives $[O{=}PPh_2CH_2C(CH_3)(CH_2PPh_2)_2]Ni(S_2CO) \cdot 0.5THF$ (**6**), $CH_3C(CH_2PPh_2S)_3$, $CH_3C(CH_2PPh_2Se)_3$, respectively. Methylation of **2** by $MeOSO_2F$, followed by addition of $NaBPh_4$ gives [(triphos)Ni(CS_2Me)]BPh_4. Compounds **1** and **2** react with HBF_4/diethyl ether to yield the dimers [(triphos)Co(μ-CS_2)Co(triphos)]$(BF_4)_2$ and [(triphos)Ni(μ-S)Ni(triphos)]$(BF_4)_2$, respectively. The CS_2 ligand in **2** is displaced by CO to give the carbonyl (triphos)Ni(CO). The structure of **6** has been determined from counter diffraction data. Crystal data are: *a* 25.937(15), *b* 15.560(8), *c* 23.186(13) Å, β 92.93(5)°, monoclinic, space group $C2/c$, $Z = 8$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations to $R = 0.087$ for 1464 observed reflections. The nickel atom shows a distorted square planar geometry, being surrounded by two phosphorus atoms of the triphos ligand and by the sulfur atoms of the dithiocarbonate group.

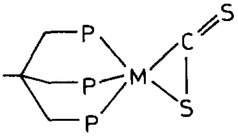
Introduction

As part of our investigation of the organometallic chemistry of carbon disulfide we have recently focused our attention on comparable η-$^2CS_2$ complexes; by comparable complexes we mean those which as far as possible, exhibit, similarities in the factors that are important for stabilization of the metal–CS_2 dihapto-bonding viz. the electronic configuration, the geometry of the metal–ligand fragment, and the nature of the coligands and of the metal [1]. The study of such compounds should provide information on the role played by each of the above factors in the reactions of the metal–η^2-CS_2 moiety.

0022-328X/85/$03.30

(Triphos)Co(η^2-CS_2) (**1**) [2], and (triphos)Ni(η^2-CS_2) (**2**) [3] (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) are comparable complexes. These have almost identical structures [1b], differing only in the nature of the metal centre, a d^9 cobalt(0) in **1** and a d^{10} nickel(0) in **2**. The cobalt compound **1** has one unpaired electron and is paramagnetic, while the nickel compound **2** is diamagnetic.

In this paper we compare and contrast the reactivity of **1** and **2** towards Group VIB elements, protic acids, alkylating agents, and electrophilic metal–ligand fragments.



(M = Co, **1**;
M = Ni, **2**)

Experimental

Compounds **1** [2], **2** [3], and (triphos)Ni(S_2CS) [4] were prepared by published procedures. Tetrahydrofuran was purified by refluxing over $LiAlH_4$ followed by distillation. All other chemicals and solvents employed were reagent grade and were used without further purification. All the reactions described were performed under dry nitrogen unless otherwise stated. The solid compounds were collected on a sintered-glass frit and washed successively with ethanol and petroleum ether (b.p. 40–70°C) before being dried in a stream of dry nitrogen. Infrared spectra were recorded on a Perkin–Elmer 283 spectrophotometer as Nujol mulls between KBr plates. Proton and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian CFT 20 spectrometer. Peak positions are relative to tetramethylsilane and phosphoric acid, respectively, with downfield shifts positive. Ultraviolet-visible spectra were recorded on a Beckman DK-2A spectrophotometer.

Preparation of the complexes

*(Triphos=O)Ni(S_2CO) · 0.5THF (**6**).* A. Dioxygen was slowly bubbled through a THF (40 ml) solution of **2** (0.38 g, 0.5 mmol) at room temperature for ca. 10 min. During this time the colour changed from red brown to orange brown. On addition of n-butyl ether (20 ml) and partial evaporation of the solvent, yellow orange crystals separated; yield 60%. Anal. Found: C, 63.74; H, 5.27; Ni, 6.99; S, 7.69. $C_{44}H_{43}NiO_{2.5}P_3S_2$ calcd.: C, 63.86; H, 5.24; Ni, 7.09; S, 7.75%.

B. A THF (40 ml) solution of **2** (0.38 g, 0.5 mmol) was exposed to air for 1 d, during which it turned orange. Addition of n-butyl ether (20 ml) followed by partial evaporation under nitrogen gave **6** in 60% yield.

C. A mixture of **2** (0.38 g, 0.5 mmol) and KO_2 (0.21 g, 3 mmol) in CH_2Cl_2 (40 ml) was stirred for 2 d. The excess of KO_2 was then filtered off and the filtrate was concentrated to ca. 5 ml. Addition of THF (10 ml) and n-butyl ether (10 ml) led to precipitation of **6**; yield 40%.

(Triphos=O)Ni(S_2CS). A mixture of (triphos)Ni(S_2CS) (0.39 g, 0.5 mmol) and nitrosobenzene (0.16 g, 1.5 mmol) in CH_2Cl_2 (50 ml) was heated under reflux for ca.

2 h. The resulting orange solution was cooled to room temperature, concentrated to ca. 10 ml, and then diluted with ethanol (30 ml) to precipitate yellow orange crystals; yield 80%. Anal. Found: C, 62.15; H, 4.79; Ni, 7.22; S, 11.88. $C_{42}H_{39}NiOP_3S_3$ calcd.: C, 62.46; H, 4.86; Ni, 7.27; S, 11.91%. IR: 1190, 1120, 580 cm^{-1} ν(P=O), 1055 cm^{-1} ν(C=S); ^{31}P $\{^1H\}$ NMR ($CDCl_3$): 24.22 ppm (P=O), 15.62 ppm (PPh_2), intensity ratio 1/2.

$CH_3C(CH_2PPh_2S)_3$ (7). Cyclo-octasulfur (0.26 g, 1 mmol of S_8) and **2** (0.38 g, 0.5 mmol) in THF (40 ml) were heated under reflux for 1 h. The dark brown solution was cooled to room temperature, filtered and concentrated to 20 ml under reduced pressure. Addition of butanol (30 ml) gave white crystals, which were recrystallized from CH_2Cl_2 and ethanol; yield 65%. Anal. Found: C, 68.29; H, 5.48; P, 12.71; S, 13.19. $C_{41}H_{39}P_3S_3$ calcd.: C, 68.31; H, 5.45; P, 12.88; S, 13.34%. IR: 620, 605 cm^{-1} ν(P=S), ^1H NMR ($CDCl_3$, 20°C): doublet at δ 3.78 (CH_2), singlet at δ 1.54 (CH_3); ^{31}P $\{^1H\}$ NMR ($CDCl_3$, 20°C): singlet at 34.87 ppm.

$CH_3C(CH_2PPh_2Se)_3$ (8). This white crystalline compound was obtained in 60% yield by a procedure analogous to that above, except for the use of amorphous selenium in place of cyclo-octasulfur. Anal. Found: C, 57.08; H, 4.42; P, 10.56; S, 27.21. $C_{41}H_{39}P_3Se_3$ calcd.: C, 57.15; H, 4.56; P, 10.78; S, 27.49%. IR: 550 cm^{-1} ν(P=Se); ^1H NMR ($CDCl_3$, 20°C): doublet at δ 4.01 (CH_2), singlet at δ 1.52 (CH_3); ^{31}P $\{^1H\}$ NMR ($CDCl_3$, 20°C): singlet at 23.44 ppm.

$[(Triphos)Co(\mu\text{-}CS_2)Co(triphos)](BF_4)_2$ (9). HBF_4 (54% in diethyl ether) (84 μl, 0.6 mmol) was added to a stirred solution of **1** (0.38 g, 0.5 mmol) in THF (40 ml). A black solution was immediately formed. Addition of butanol (30 ml) and slow evaporation of the solvent gave black crystals of **9** in 65% yield.

$[(Triphos)Ni(\mu\text{-}S)Ni(triphos)](BF_4)_2$ (10). Green crystals of **10** were obtained in 60% yield by a procedure analogous to that above except, for the use of **2** in place of **1**.

$[(Triphos)Ni(CS_2Me)]BPh_4$ (12). Neat $MeOSO_2F$ (50 μl, 0.6 mmol) was pipetted into a solution of **2** (0.38 g, 0.5 mmol) in CH_2Cl_2 (20 ml). There was an immediate color change from red brown to emerald green. Addition of acetone (20 ml) and $NaBPh_4$ (0.32 g, 1 mmol) in ethanol (30 ml) gave dark green crystals; yield 85%. Anal. Found: C, 73.39; H, 5.67; Ni, 5.29; S, 5.91. $C_{67}H_{62}BNiP_3S_2$ calcd.: C, 73.57; H, 5.71; Ni, 5.36; S, 5.86%.

(Triphos)Ni(CO) (14). A solution of $Cr(CO)_5(THF)$ formed in situ by UV irradiation of the corresponding hexacarbonyl complex (0.29 g, 0.87 mmol) in THF (60 ml) was added to a solution of **2** (0.50 g, 0.66 mmol) in THF (250 ml) which had been stored at −10°C. The mixture was kept for 2 h at room temperature. The solvent was removed under vacuum and the residue extracted with CH_2Cl_2 (30 ml). Addition of ethanol (30 ml) followed by slow evaporation of the solvent gave yellow crystals, yield 30%.

Crystal data and data collection

Accurate cell dimensions were determined by least-squares refinement of 20 carefully centered reflections. The crystals belong to the monoclinic system with systematic absences hkl for $h+k=2n+1$, $h0l$ for $l=2n+1$. Although both acentric Cc and centric $C2/c$ space groups were possible, the centric $C2/c$ was confirmed by the successful refinement of the structure. Details of crystal data and data collection are given in Table 1. The procedure used in the data processing has

TABLE 1

CRYSTAL DATA AND DETAILS OF THE DATA COLLECTION

Mol formula	$C_{44}H_{43}NiO_{2.5}P_3S_2$
Mol. wt.	827.59
a (Å)	25.937(15)
b (Å)	15.560(8)
c (Å)	23.186(13)
β (deg.)	92.93(5)
$d_{\text{calcd.}}$ (g cm^{-3})	1.176
V (Å^3)	9345.2
Space group	$C2/c$
Z	8
Habit	parallelepiped
Dimensions (mm)	0.25 × 0.075 × 0.075
Color	yellow-orange
Abs coeff. (μ(Mo-K_α)) (cm^{-1})	6.35
Diffractometer	Philips PW 1100
Monochromator	graphite crystal
Method	$\omega-2\vartheta$
Scan speed (deg s^{-1})	0.06
Scan width (deg.)	$0.70+0.3\tan\vartheta$
Bkgd	half the scan time
Stds	3 every 120 readings
Max. dev. of stds (%)	±5
2ϑ limits, (deg.)	5–40
No. of total data	4689
No. of data with $I \geqslant 3\sigma(I)$	1464
Final no. of variables	167

been described elsewhere [5]. The intensities were corrected for background and assigned a standard deviation $\sigma(I)$ calculated by using a value of 0.03 for the instability factor p [6]. The intensities were corrected for Lorentz-polarization effects, but not for absorption. An anomalous dispersion correction was applied in F_c calculations [7].

Determination and refinement of the structure

All the calculations were carried out using the SHELX76 crystallographic system of programs on a SEL 32/77 computer [8]. Neutral atom scattering factors for non-hydrogen atoms were taken from ref. 9, whereas those for hydrogen atoms from ref. 10. The refinements were based on F_0, the function minimized being $\Sigma w(|F_0| - |F_c|)^2$; the weighting scheme utilized was $w = 1/\sigma^2(F_0)$. The nickel atom was located by conventional Patterson synthesis. All remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. Full-matrix least-squares refinements were carried out, applying anisotropic thermal parameters for nickel, phosphorous, and sulfur atoms. The phenyl rings were treated as rigid bodies of D_{6h} symmetry. The hydrogen atoms, introduced in their calculated positions, (C–H 0.95 Å), were not refined. The final difference Fourier map was featureless apart from some positive electron density in the vicinity of the tetrahydrofuran molecule; the solvent molecule, in fact, appeared to be disordered and required a rigid-body refinement, with scattering factors for the carbon atom assigned to all the atoms.

TABLE 2. POSITIONAL PARAMETERS ($\times 10^4$)

Atom	x	y	z
Ni	7973(2)	1511(4)	7344(3)
P(1)	8544(4)	856(8)	7912(5)
P(2)	8132(4)	853(8)	6563(6)
P(3)	9507(4)	−1285(8)	6246(6)
S(1)	7363(5)	2269(10)	6904(6)
S(2)	7722(5)	2326(9)	8045(6)
O(1)	9657(10)	−590(21)	5919(14)
O(2)	6976(14)	3291(24)	7616(16)
C	7298(24)	2742(43)	7553(32)
C(1)	9359(13)	614(21)	6878(17)
C(2)	9036(13)	−134(25)	7008(16)
C(3)	8862(12)	−85(23)	7644(16)
C(4)	8538(11)	−111(21)	6621(15)
C(5)	9281(13)	−1018(22)	6931(15)
C(11)	9030(11)	1576(25)	8175(10)
C(21)	9085(11)	2393(25)	7937(10)
C(31)	9483(11)	2931(25)	8143(10)
C(41)	9827(11)	2652(25)	8587(10)
C(51)	9772(11)	1835(25)	8824(10)
C(61)	9374(11)	1297(25)	8618(10)
C(12)	8242(9)	491(14)	8539(15)
C(22)	8232(9)	1014(14)	9027(15)
C(32)	7969(9)	746(14)	9506(15)
C(42)	7716(9)	−45(14)	9496(15)
C(52)	7726(9)	−568(14)	9008(15)
C(62)	7988(9)	−300(14)	8530(15)
C(13)	8416(10)	1494(24)	6037(11)
C(23)	8528(10)	2356(24)	6150(11)
C(33)	8800(10)	2836(24)	5758(11)
C(43)	8959(10)	2453(24)	5253(11)
C(53)	8846(10)	1591(24)	5139(11)
C(63)	8574(10)	1111(24)	5532(11)
C(14)	7540(14)	489(15)	6196(13)
C(24)	7258(14)	977(15)	5786(13)
C(34)	6779(14)	685(15)	5564(13)
C(44)	6582(14)	−95(15)	5752(13)
C(54)	6865(14)	−583(15)	6162(13)
C(64)	7343(14)	−291(15)	6384(13)
C(15)	9027(9)	−1918(17)	5867(15)
C(25)	9148(9)	−2119(17)	5303(15)
C(35)	8821(9)	−2649(17)	4965(15)
C(45)	8374(9)	−2980(17)	5191(15)
C(55)	8253(9)	−2779(17)	5755(15)
C(65)	8579(9)	−2248(17)	6093(15)
C(16)	10038(13)	−1999(15)	6428(11)
C(26)	10537(13)	−1727(15)	6322(11)
C(36)	10956(13)	−2272(15)	6443(11)
C(46)	10876(13)	−3089(15)	6669(11)
C(56)	10377(13)	−3361(15)	6775(11)
C(66)	9958(13)	−2817(15)	6654(11)
C(1) [a]	1659(33)	4528(63)	3068(48)
C(2) [a]	1704(31)	5294(69)	2741(45)
C(3) [a]	1236(42)	5761(48)	2775(45)
C(4) [a]	889(24)	5263(71)	3099(51)
C(5) [a]	1148(43)	4499(55)	3277(47)

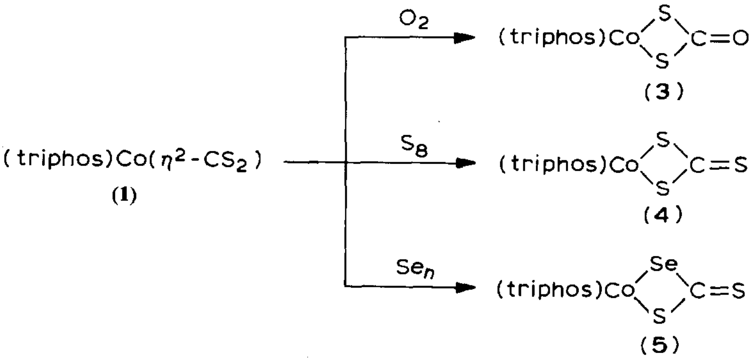
[a] Atoms belonging to the solvent molecule with population factors 0.5.

The refinement gave final agreement factors of $R = 0.087$ and $R_w = 0.082$, where $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ and $R_w = [\Sigma w||F_0| - |F_c||^2/\Sigma w|F_0|^2]^{1/2}$. Final positional parameters are listed in Table 2.

Results and discussion

In a previous paper we reported the reactions of **1** with molecular oxygen, cyclo-octasulfur, and amorphous selenium [11]. The results obtained are shown schematically in Scheme 1.

SCHEME 1



The mechanisms of formation of the dithiocarbonate **3**, trithiocarbonate **4**, and monoselenodithiocarbonate **5** derivatives were not understood. We tentatively suggested that these reactions might proceed in a manner similar to that noted for reactions of some Fischer-type carbene complexes with Group VIB elements [11,12]. Some support for this idea is provided by the proposed carbenoid nature of the metal–η^2-CS$_2$ moiety [13]. In a subsequent paper [1b], we suggested that the reactions of **1** with O_2, S_8, and Se_n might follow a pathway which depends upon splitting of these reagents into radicals. MO calculations of the extended Hückel-type strongly indicate the radical nature of **1**, with one electron populating a largely metallic orbital.

In order to obtain further information on this type of reaction, we treated **2** with O_2, S_8, and Se_n. A tetrahydrofuran solution of **2** reacts at room temperature with dioxygen to produce an orange brown solution from which yellow orange crystals of (triphos=O)Ni(S_2CO)·0.5THF (**6**) (triphos=O is $O{=}PPh_2CH_2C(CH_3)(CH_2PPh_2)_2$) are obtained in good yield after addition of n-butyl ether. Crystals of **6** can be also obtained by simple exposure of solutions of **2** to air, or by treating **2** with KO_2.

Compound **6** is diamagnetic, fairly air-stable, and soluble in chlorinated solvents in which it is non-conducting. The reflectance spectrum has no bands at frequencies < 15000 cm^{-1}, which is typical for square-planar nickel(II) complexes [14]. The IR spectrum shows no bands attributable to C=S stretching modes, but has two bands in the CO stretching region, at 1690 and 1600 cm^{-1}, which are indicative of a chelate dithiocarbonate ligand [15]. The spectrum also exhibits absorptions characteristic of P=O groups at 1190, 1120, and 580 cm^{-1} [16]. The ^{31}P{^{1}H}NMR spectrum ($CDCl_3$, 20°C) consists of two resonances at 23.96 and 15.40 ppm (intensity ratio 1/2). This pattern is consistent with the presence of a triphos=O ligand acting as a bidentate ligand through two phosphine donor atoms [16,17].

X-ray analysis has shown that the structure consists of monomers of (triphos=O)Ni(S_2CO) with tetrahydrofuran solvent molecules present in the lattice. A perspective view of the complex molecule is shown in Fig. 1. Selected bond distances and angles are given in Table 3.

The nickel atom has a distorted square planar geometry. It is coordinated to two phosphorus atoms of the triphos ligand and two sulphur atoms of the dithiocarbonate group. The nickel atom is displaced by 0.005 Å from the least-squares plane. The third phosphorus atom of the triphos ligand, which has undergone oxidation, remains uncoordinated. The distortion from the ideal square planar geometry is mainly due to the short "bite" of the S_2CO^{2-} ligand, in which the S(1)–Ni–S(2) angle is 78.4(5)°. The Ni–P and Ni–S bond distances average 2.16(2) and 2.186(1) Å, respectively. While the Ni–P distances are somewhat shorter than

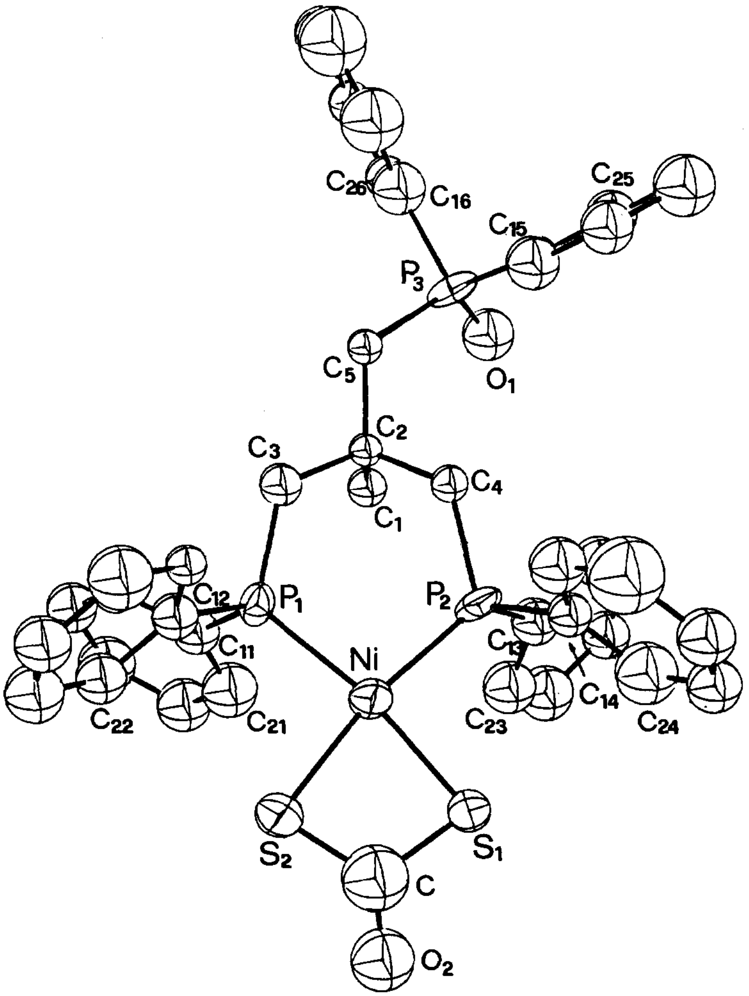


Fig. 1. Perspective view of the complex molecule (triphos=O)Ni(S_2CO). ORTEP drawing with 30% probability ellipsoids.

TABLE 3

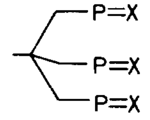
SELECTED BOND DISTANCES (Å) AND ANGLES (deg.)

Ni-P(1)	2.183(13)	P(3)-O(1)	1.39(3)
Ni-P(2)	2.139(14)	P(3)-C(5)	1.77(3)
Ni-S(1)	2.185(14)	P(3)-C(15)	1.78(3)
Ni-S(2)	2.187(13)	P(3)-C(16)	1.80(3)
P(1)-C(3)	1.81(3)	S(1)-C	1.69(7)
P(1)-C(11)	1.77(4)	S(2)-C	1.67(7)
P(1)-C(12)	1.78(3)	C-O(2)	1.21(6)
P(2)-C(4)	1.83(3)	C(1)-C(2)	1.47(4)
P(2)-C(13)	1.77(4)	C(2)-C(3)	1.57(4)
P(2)-C(14)	1.81(4)	C(2)-C(4)	1.53(4)
		C(2)-C(5)	1.53(4)
P(1)-Ni-P(2)	97.6(5)	Ni-P(2)-C(14)	103.0(13)
P(1)-Ni-S(1)	170.7(6)	O(1)-P(3)-C(5)	115.0(18)
P(1)-Ni-S(2)	92.4(6)	O(1)-P(3)-C(15)	111.7(17)
P(2)-Ni-S(1)	91.7(5)	O(1)-P(3)-C(16)	112.1(16)
P(2)-Ni-S(2)	170.0(6)	C(5)-P(3)-C(15)	108.4(15)
S(1)-Ni-S(2)	78.4(5)	C(5)-P(3)-C(16)	102.6(16)
Ni-P(1)-C(3)	118.7(13)	C(15)-P(3)-C(16)	106.3(13)
Ni-P(1)-C(11)	111.2(11)	Ni-S(1)-C	85.5(25)
Ni-P(1)-C(12)	109.2(9)	Ni-S(2)-C	85.9(25)
Ni-P(2)-C(4)	117.7(13)	S(1)-C-S(2)	110.3(38)
Ni-P(2)-C(13)	114.8(11)	S(1)-C-O(2)	121.1(61)
		S(2)-C-O(2)	128.6(62)

the sum of covalent radii (2.21 Å), the Ni–S distances are somewhat larger (2.17 Å). These small differences from the ideal values may be the result of a *trans* effect arising from the fact that the phosphorus ligands are *trans* to the sulphur ligands. It is noteworthy that the value for the P–O bond distance of 1.39(3) Å is shorter than that in free triphenylphosphine oxide (1.46 Å) [18]. The bond distances within the dithiocarbonate ligand, S–C(av) 1.68(1) and C–O(2), 1.21(6) Å, fall in the range of values found for other dithiocarbonate complexes, and indicate an overall electronic delocalization within the S_2CO group [15,19].

In an attempt to get information about the formation of **6**, we tried to synthesize the complex (triphos)Ni(S_2CO), in which triphos would have all its donor atoms coordinated to the metal, as in the cobalt derivative **3** [15]. The existence of such a complex would have helped to indicate whether the reaction of **2** with dioxygen might proceed, at least initially, through the formation of a dithiocarbonate complex, as was found for cobalt, which successively undergoes oxidation of one phosphorus atom of triphos to give **6**. The easy oxidation of one arm of triphos to give the triphos=O ligand is, a well known process for five-coordinate nickel(II) complexes with triphos [16,17]. Unfortunately, all our attempts to synthesize (triphos)Ni(S_2CO) were unsuccessful. For example, treatment of the five-coordinate trithiocarbonate complex, (triphos)Ni(S_2CS) [4], with PhNO, a reagent which is known to convert C=S groups into C=O groups, yields the square planar complex (triphos=O)Ni(S_2CS).

Compounds **1** and **2** differ greatly in their reactions with S_8 and Se_n. Insertion of a sulfur or a selenium atom into the metal–carbon bond occurs with the cobalt complex (Scheme 1), but the reaction of the nickel complex with S_8 and Se_n does not lead to metal complexes; the only isolable products of the reactions are $CH_3(CH_2PPh_2S)_3$ (**7**) and $CH_3(CH_2PPh_2Se)_3$ (**8**). Both of these results, in particular the reactions with S_8, are rather surprising. Nickel trithiocarbonates with triphos acting either as a tridentate ligand [4], or as a bidentate ligand are very stable compounds.

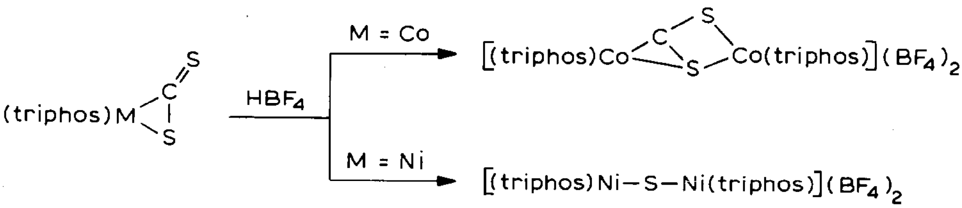


(X = S, 7;
X = Se, 8)

The oxidation of dihapto-bonded CS_2 to dithiocarbonate seems to depend neither on the geometry of the metal–ligand fragment nor on the nature of the metal centre. Such a reaction, in fact, has been observed to occur for a variety of η^2-CS_2 compounds: the d^9 and d^{10} distorted square-pyramidal complexes **1** and **2**, and the d^{10} square-planar $Pt(\eta^2\text{-}CS_2)(PPh_3)_2$ [20]. In contrast, the insertion of a sulfur or selenium atom from S_8 or Se_n into the metal–carbon bond, to give dithiocarbonate or trithiocarbonate derivatives, seems to depend on the nature of the metal. These facts suggest that the reaction of O_2 with **1** might involve a pathway different from that followed by the reactions of **1** with S_8 and Se_n.

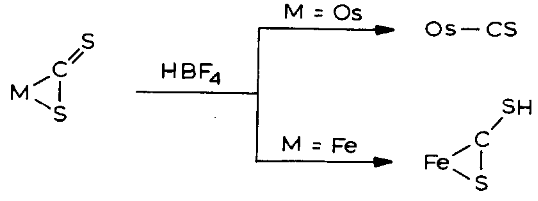
Tetrahydrofuran solutions of **1** and **2** react with HBF_4 to give the μ-CS_2 dimer $[(triphos)Co(\mu\text{-}CS_2)Co(triphos)](BF_4)_2$ (**9**), and the μ-S dimer $[(triphos)Ni(\mu\text{-}S)Ni(triphos)](BF_4)_2$ (**10**), respectively (Scheme 2). Both compounds have been previously synthesized by other methods [2,21].

SCHEME 2



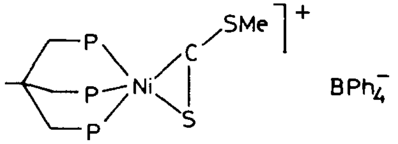
Only two reactions of η^2-CS_2 complexes with protic acids have been reported to give sulfur-containing products; viz. the reactions of $Os(\eta^2\text{-}CS_2)(CO)_2(PPh_3)_2$ [22] and $Fe(\eta^2\text{-}CS_2)(CO)_2L_2$ ($L = PMe_2Ph$; PPh_3) [23] with HBF_4 to yield the thiocarbonyl complex $OsCl_2(CO)(CS)(PPh_3)_2$ and the η^2-CS_2H complex $Fe(\eta^2\text{-}CS_2H)(CO)_2L_2$, respectively (Scheme 3).

SCHEME 3



In the reaction of the osmium η^2-CS_2 complex with HBF_4, which gives the thiocarbonyl and H_2S, a preliminary step may be the formation of an unstable η^2-CS_2H intermediate. Indeed, the stability of η^2-CS_2H complexes seems to be very low, as is reported to be the case for the iron derivative [23]. Moreover, MO calculations indicate that the electronic nature of the metal–η^2-CS_2H moiety is similar to that of the metal–η^2-COS moiety [24]. Stable compounds containing the latter moiety are very rare [25] and they usually break down to carbonyl and/or thiolo derivatives [26]. In light of these results and considerations, a reasonable mechanism for the formation of the μ-S complex **10** is one which implies the intermediacy of an unstable η^2-CS_2H complex. On the basis of the same arguments, the formation of the μ-CS_2 complex **9** is not as apparent as that of **10**. However, a labile complex of the type $[(\text{triphos})Co(\eta^2\text{-}CS_2H)]^+$ might lose the CS_2H group to give the metal fragment $(\text{triphos})Co^{2+}$, which is known to react with the starting η^2-CS_2 compound **1** to give μ-CS_2 dimer **9**.

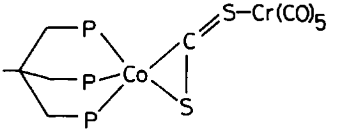
The chemical behaviour of **1** closely parallels that of **2** in the reactions with methylating agents; both compounds give η^2-dithiomethyl ester complexes. The physical and chemical properties of the cobalt derivative $[(\text{triphos})Co(\eta^2\text{-}CS_2Me)]BPh_4$ (**11**) have been already described [11]. The dark green nickel complex $[(\text{triphos})Ni(\eta^2\text{-}CS_2Me)]BPh_4$ (**12**) is formed in good yield by treating a CH_2Cl_2 solution of **2** with $MeOSO_2F$ then adding $NaBPh_4$ in ethanol. Compound **12** is diamagnetic and air-stable in the solid state. It is soluble in chlorinated solvents, in which it behaves as a 1 : 1 electrolyte (molar conductance value in 10^{-3} *M* nitroethane solution: 46 ohm^{-1} cm^2 mol^{-1}). The electronic spectra in the solid state and in 1,2-dichloroethane solution are almost identical, with absorption maxima at 18200 and 25000 cm^{-1}. They are similar to those of five-coordinate nickel(II) complexes [4]. The IR spectrum exhibits a band at 1120 cm^{-1}, attributable to ν(CS) of a dihapto-bonded CS_2Me group [13b]. The $^{31}P\{^1H\}$NMR spectrum in $CDCl_3$ at 25°C consists of a singlet at -0.16 ppm; this pattern, which is unchanged even at -60°C, is consistent with rapid intramolecular exchange of the three phosphorus atoms of triphos around the metal atom [4]. On the basis of all of the data, it is reasonable to assign to **12** the five-coordinate structure shown below.



(12)

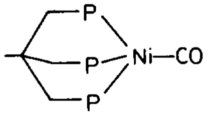
The nature of the metal fragment to which the dihapto-CS_2 ligand is attached does not seem greatly to influence the reactions with alkylating agents. Indeed, η^2-CS_2 complexes with metal fragment of the types $(C_5H_5)_2LM$, $(C_5H_5)_2M$, L_5M, and L_2M have been found to undergo the alkylation of the exocyclic sulfur to give dithioalkyl ester derivatives. This is not surprising, since these reactions occur at the atom of the CS_2 ligand which is less involved in bonding to the metal. Similarly, the first step of the reaction of η^2-CS_2 complexes with protic acids may always be the attack at the uncoordinated sulfur atom to give an η^2-CS_2H intermediate. Whether the product is stable or undergoes conversion of the metal–η^2-CS_2H moiety into other species should then depend on the nature of the metal–ligand fragment.

Another reaction which is common to a variety of η^2-CS_2 complexes is the displacement of the THF ligand from organometallic compounds by the uncoordinated sulfur atom to give μ-CS_2 dimers [2,27]. For instance, **1** reacts with a THF solution of $Cr(CO)_5(THF)$ to yield the dinuclear complex (triphos)Co(μ-CS_2)$Cr(CO)_5$ (**13**), whose structure has been determined by X-ray methods [2].



(13)

Under the conditions used for **1**, compound **2** does not form a stable μ-CS_2 dimer similar to **13**. The only isolable product of this reaction is the carbonyl (triphos)Ni(CO) (**14**) [28]. In an attempt to account for the formation of **14**, we treated **2** in THF with CO; displacement of CS_2 by CO to give **14** took place



(14)

immediately under very mild conditions. Compound **1**, however does not react with CO. Thus, the formation of **14** is due to the presence of free CO in solution rather then to the decomposition of an eventual Ni(μ-CS_2)Cr dimer.

The reactions of **1** and **2** with molecules such as CO, SO_2, CSe_2, COS, CO_2, SCNR, and OCNR are being studied. Preliminary results indicate that the displacement of CS_2 from **2** is quite common, and takes place as a thermal process in solution at room temperature. In contrast, displacement of CS_2 from **1** is observed in only a few cases (SO_2, CSe_2), and requires severe reaction conditions. This confirms that the reactions which involve the metal–η^2-CS_2 linkage depend greatly on the nature of the metal centre.

References

1 (a) C. Mealli, R. Hoffmann and A. Stockis, Inorg. Chem., 23 (1984) 56; (b) C. Bianchini, D. Masi, C. Mealli and A. Meli, Inorg. Chem., 23 (1984) 2838.
2 C. Bianchini, C. Mealli, A. Meli, A. Orlandini and L. Sacconi, Inorg. Chem., 19 (1980) 2968.
3 P. Dapporto, S. Midollini, A. Orlandini and L. Sacconi, Inorg. Chem., 15 (1976) 2768.
4 C. Bianchini, P. Innocenti and A. Meli, J. Chem. Soc., Dalton Trans., (1983) 1777.
5 A. Bianchi, P. Dapporto, G. Fallani, C.A. Ghilardi and L. Sacconi, J. Chem. Soc., Dalton Trans., (1973) 641.
6 P.W.R. Corfield, R.J. Doedens and J.A. Ibers, Inorg. Chem., 6 (1967) 197.
7 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, England, 1974, Vol. IV, p. 149.
8 G.M. Sheldrick, System of Computing Programs, University of Cambridge, Cambridge, 1976, adapted by Dr. C. Mealli.
9 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, England, 1974, Vol. IV, p. 99.
10 R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.

11 C. Bianchini and A. Meli, J. Chem. Soc., Chem. Commun., (1983) 156.

12 C. Bianchini, C.A. Ghilardi, A. Meli and A. Orlandini, J. Organomet. Chem., 270 (1984) 251.

13 (a) P. Conway, S.M. Grant and A.R. Manning, J. Chem. Soc., Dalton Trans., (1979) 1920; (b) G. Fachinetti, C. Floriani, A. Chiesi-Villa and C. Guastini, J. Chem. Soc., Dalton Trans., (1979) 1612.

14 A.B.P. Lever, Inorganic Electron Spectroscopy, Elsevier, Amsterdam, 1968, and references therein.

15 C. Bianchini, A. Meli and A. Orlandini, Inorg. Chem., 21 (1982) 4166.

16 C. Bianchini, C. Mealli, A. Meli and M. Sabat, Inorg. Chem., 23 (1984) 273.

17 C. Bianchini, A. Meli and G. Scapacci, Organometallics, (1984) in press.

18 G. Bandoli, G. Bartolozzo, D.A. Clemente, U. Croatto and C. Panattoni, J. Chem. Soc. A, (1970) 2778.

19 H. Werner, W. Bertleff, B. Zimmer-Gasser and U. Schubert, Chem. Ber., 115 (1982) 1004.

20 I. Ghatak, D.M.P. Mingos, M.B. Hursthouse and P.R. Raithby, Trans. Met. Chem., 1 (1976) 119.

21 C. Mealli, S. Midollini and L. Sacconi, Inorg. Chem., 17 (1978) 632.

22 K.R. Grundy, P.O. Harrison and W.R. Roper, J. Organomet. Chem., 90 (1975) C34.

23 H. Stolzenberg, W.P. Fehlhammer and P. Dixneuf, J. Organomet. Chem., 246 (1983) 105.

24 Dr. C. Mealli, private communication.

25 T.R. Gaffney and J.A. Ibers, Inorg. Chem., 21 (1982) 2860.

26 T.R. Gaffney and J.A. Ibers, Inorg. Chem., 21 (1982) 2857.

27 T.G. Southern, U. Oehmichen, J.Y. Le Marouille, H. Le Bozec, D. Grandjean and P.H. Dixneuf, Inorg. Chem., 19 (1980) 2976; J. Amaudrut, J. Sala-Pala, J.E. Guerchais, R. Mercier and J. Douglade, J. Organomet. Chem., 235 (1982) 301.

28 J. Chatt and F.A. Hart, J. Chem. Soc., (1965) 812.