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REACTIVITY OF $[\mathrm{N(CH_2CH_2PPh_2)_3]Ni}$ TOWARD $\mathrm{CS_2}$, SCNPh, AND COS. STRUCTURE OF THE η^2-*S,C*-BONDED PHOSPHONIODITHIOMETHYL ESTER COMPLEX $[\mathrm{Ph_2}\overline{\mathrm{PCH_2CH_2N(CH_2CH_2PPh_2)_2Ni(C}}\mathrm{S_2Me)]BPh_4}$

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Summary

Reaction of $\mathrm{(np_3)Ni}$ ($\mathrm{np_3}$ = tris(2-diphenylphosphinoethyl)amine) with $\mathrm{CS_2}$, SCNPh, or COS affords $\mathrm{(np_3)Ni(\eta^2\text{-}CS_2)}$ (**5**), $\mathrm{(np_3)Ni(\eta^2\text{-}SCNPh)}$ (**9**), and $\mathrm{(np_3)NiCO}$ (**12**), respectively. Methylation of **5** by $\mathrm{MeOSO_2F}$, followed by $\mathrm{NaBPh_4}$ addition, leads to $[\mathrm{Ph_2}\overline{\mathrm{PCH_2CH_2N(CH_2CH_2PPh_2)_2Ni(C}}\mathrm{S_2Me)]BPh_4}$ (**6**) through intramolecular attack by a phosphorus atom of $\mathrm{np_3}$ on a η^2-dithiomethyl ester group formed in situ. The structure of **6** has been determined from counter diffraction data. Crystal data are: *a* 28.148(16), *b* 14.448(8), *c* 33.922(17) Å, β 112.11(4)°, monoclinic, space group $C2/c$, $Z = 8$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares. Refinements converged at the conventional *R* factor value of 0.095 for the 1989 reflections having $I \geq 3\sigma(I)$.

Introduction

Much of current interest in the organometallic chemistry of carbon disulfide stems from the surprising reactivity that this molecule shows when it is dihapto-bonded to a metal center [1,2]. Electrophiles [3–12], nucleophiles [13–17], and dipolarophiles [18–21] have been found to react with η^2-$\mathrm{CS_2}$ complexes. In most instances the reagent adds directly to the $\mathrm{CS_2}$ group; in other cases fragmentation of $\mathrm{CS_2}$ to CS and S occurs [22,23].

The rationalization of the reactivity of η^2-$\mathrm{CS_2}$ complexes is in an early stage of development. Some reactions have not been understood, either partially or completely; meanwhile other workers attempt to find applications other than the prototype reaction.

In our opinion, for a better understanding of the reactions of η^2-$\mathrm{CS_2}$ complexes, and thus of the bonding in the M–η^2-$\mathrm{CS_2}$ moiety, it would be important to investigate both the reactivity and the structural implications of "comparable" metal complexes. Comparable complexes are those which exhibit similarities of the factors

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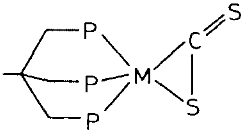
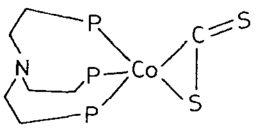
that are important for the stabilization of the dihapto-bonding of CS_2. Such factors are the total electron count, the geometry of the metal–ligand fragment, and the nature of the co-ligands and the metal [24,25].

A comparative study on the reactivity of η^2-complexes with the CS_2-like molecules SCNPh and COS should also be fruitful.

Recently we have characterized (by X-ray analyses and MO calculations of the extended Hückel-type) the two isomorphous complexes (triphos)Co(η^2-CS_2), **1** and (triphos)Ni(η^2-CS_2), **2** (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) [25]. In spite of having almost superimposable structures, **1** and **2** show some important differences in their reactivity. Such variations have been related to the different electron population at the metal atom(d^9 or d^{10}). The complex (np_3)Co(η^2-CS_2), **3** (np_3 = tris(2-diphenylphosphinoethyl)amine) has also been synthesized and characterized [12]. Its reactivity toward alkylating agents has also been probed.



(M = Co, 1 , Ni, 2)



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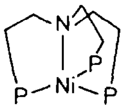
It therefore seemed that it would be interesting to try to synthesize the nickel complex analogous to **3**, and to investigate its reactivity. One of the methods for obtaining complexes with the electrophilic CS_2 molecule is to use metal fragments which are rich in electrons, that is with a high Lewis-basicity. The obvious starting compound for the preparation of a complex of the formula (np_3)Ni(CS_2) is, thus, the trigonal pyramidal nickel(0) complex (np_3)Ni, **4**. The latter compound, in fact, contains a nucleophilic metal center which is capable of adding a great variety of electrophiles [26].



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The present paper concerns the synthesis of the nickel(0) complex (np_3)Ni(η^2-CS_2), **5**. An X-ray crystal structure determination has been carried out on the alkylated product of **5**, $[Ph_2PCH_2CH_2N(CH_2CH_2PPh_2)_2Ni(CS_2Me)]BPh_4$, **6**.

The complex (np_3)Ni(η^2-SCNPh), **9** has also been prepared, and attempts to synthesize the COS analog are described.

A preliminary account of part of this work has already been published [27].

Experimental

Compound **4** was prepared according to a published procedure [26]. Reagent grade chemicals were used in the preparation of the complexes. Tetrahydrofuran

(THF) was purified by distillation over $LiAlH_4$ just before use. All operations were routinely performed under nitrogen, using deoxygenated solvents. The solid complexes 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 nitrogen. IR spectra were recorded on a Perkin–Elmer 283 spectrophotometer using Nujol mulls between KBr plates. $^{31}P\ \{^1H\}$ NMR spectra were taken on a Varian CFT 20 spectrometer. Peak positions are relative to phosphoric acid, with downfield values reported as positive. UV-VIS 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.

Preparation of the complexes

$(np_3)Ni(\eta^2\text{-}CS_2)$ (5). Carbon disulfide vapor was bubbled for ca. 5 min through a solution of **4** (1 mmol) in THF (50 ml); during this time the color changed from red-orange to black. After the addition of ethanol (20 ml), black crystals separated on standing; yield 45% (Found: C, 65.28; H, 5.24; N, 1.63; Ni, 7.41; S, 8.22. $C_{43}H_{42}NNiP_3S_2$ calcd.: C, 65.47; H, 5.36; N, 1.77; Ni, 7.47; S, 8.12%).

$[(np_3)Ni(CS_2Me)]BPh_4$ (6). (A) A suspension of **5** (0.5 mmol) in THF (30 ml) was treated with neat $MeOSO_2F$ (0.6 mmol), which caused the solid to dissolve to give a dark-brown solution. The solvent was then removed under reduced pressure and the oily residue gave crystals after the addition of acetone (30 ml) and $NaBPh_4$ (0.7 mmol) in ethanol (10 ml); yield 35%.

(B) Neat $MeOSO_2F$ (0.6 mmol) was pipetted into a magnetically-stirred mixture of **4** (0.5 mmol) and CS_2 (40 ml). After 30 min the solvent was removed under reduced pressure and the oily residue was extracted with acetone (30 ml). Addition of ethanol (10 ml) and $NaBPh_4$ (0.7 mmol) gave well-shaped brown crystals; yield 80% (Found: C, 72.59; H, 5.83; N, 1.13; Ni, 5.19; S, 5.75. $C_{68}H_{65}BNNiP_3S_2$ calcd.: C, 72.72; H, 5.83; N, 1.24; Ni, 5.24; S, 5.70%).

$(np_3)Ni(\eta^2\text{-}SCNPh)$ (9). SCNPh (1.2 mmol) was added to a solution of **4** (1 mmol) in THF (30 ml). After 1 h the resulting deep-red solution was concentrated to 10 ml under a stream of nitrogen. Addition of a 1 : 1 mixture of n-butyl ether and ethanol (20 ml) caused the separation in a few min of red crystals in a 70% yield (Found: C, 69.39; H, 5.55; N, 3.27; Ni, 6.89; S, 3.79. $C_{49}H_{47}N_2NiP_3S$ calcd.: C, 69.41; H, 5.58; N, 3.30; Ni, 6.95; S, 3.78%).

$(np_3)NiCO$ (12). COS was bubbled for ca. 2 min through a solution of **4** (1 mmol) in THF (30 ml) until a yellow solution was obtained. Yellow crystals were formed following the addition of n-butanol (30 ml) and the slow evaporation of the solvent; yield 90% (Found: C, 69.65; H, 5.74; N, 1.83; Ni, 7.85. $C_{43}H_{42}NNiOP_3$ calcd.: C, 69.78; H, 5.72; N, 1.89; Ni, 7.93%).

Crystal data and data collection

Diffraction data were collected on a Philips PW 1100 automated four-circle diffractometer, using graphite-monochromated Mo-K_α radiation. A brown prismatic crystal of approximate dimensions 0.40 × 0.20 × 0.05 mm was mounted in a random orientation on the diffractometer. Lattice constants were determined by least-squares refinement of the angular positions of 20 carefully centered reflections. The crystals are monoclinic, space group $C2/c$, with eight molecules in the unit cell of dimen-

TABLE 1
ATOMIC COORDINATES ($\times 10^4$)

Atom	x	y	z
Ni	2335(1)	4032(3)	853(1)
P(1)	2617(3)	5418(7)	1071(3)
P(2)	3000(3)	3111(6)	1084(2)
P(3)	1192(3)	3984(7)	873(2)
S(1)	1832(3)	2965(6)	513(2)
S(2)	1260(3)	4697(7)	71(3)
N	2433(7)	3937(17)	1642(6)
C(1)	2548(11)	5576(20)	1600(8)
C(2)	2701(11)	4745(21)	1870(9)
C(3)	3190(11)	3051(23)	1670(9)
C(4)	2724(10)	3056(22)	1797(9)
C(5)	1508(10)	3333(19)	1359(8)
C(6)	1933(10)	3868(22)	1713(8)
C(7)	1564(9)	4026(21)	535(8)
C(8)	872(12)	3820(24)	−313(10)
C(1,1)	2314(7)	6449(16)	767(5)
C(2,1)	2260(7)	7263(16)	968(5)
C(3,1)	2024(7)	8033(16)	725(5)
C(4,1)	1842(7)	7989(16)	282(5)
C(5,1)	1896(7)	7175(16)	81(5)
C(6,1)	2132(7)	6404(16)	324(5)
C(1,2)	3296(9)	5679(16)	1192(6)
C(2,2)	3442(9)	5719(16)	842(6)
C(3,2)	3955(9)	5866(16)	903(6)
C(4,2)	4322(9)	5972(16)	1314(6)
C(5,2)	4175(9)	5932(16)	1663(6)
C(6,2)	3663(9)	5786(16)	1602(6)
C(1,3)	2882(6)	1925(12)	901(5)
C(2,3)	2832(6)	1722(12)	485(5)
C(3,3)	2738(6)	815(12)	335(5)
C(4,3)	2695(6)	111(12)	600(5)
C(5,3)	2745(6)	314(12)	1016(5)
C(6,3)	2838(6)	1221(12)	1166(5)
C(1,4)	3602(7)	3328(14)	1001(6)
C(2,4)	3569(7)	3531(14)	589(6)
C(3,4)	4015(7)	3618(14)	504(6)
C(4,4)	4494(7)	3501(14)	831(6)
C(5,4)	4526(7)	3298(14)	1242(6)
C(6,4)	4081(7)	3212(14)	1327(6)
C(1,5)	1025(6)	5051(18)	1007(5)
C(2,5)	1153(6)	5885(18)	865(5)
C(3,5)	990(6)	6721(18)	977(5)
C(4,5)	699(6)	6723(18)	1231(5)
C(5,5)	571(6)	5888(18)	1373(5)
C(6,5)	734(6)	5052(18)	1261(5)
C(1,6)	601(8)	3371(11)	594(6)
C(2,6)	147(8)	3870(11)	407(6)
C(3,6)	−312(8)	3406(11)	188(6)
C(4,6)	−316(8)	2443(11)	156(6)
C(5,6)	138(8)	1944(11)	343(6)
C(6,6)	597(8)	2408(11)	562(6)
C(1,7)	1147(8)	1233(16)	1897(5)
C(2,7)	733(8)	1641(16)	1573(5)
C(3,7)	516(8)	2452(16)	1653(5)

TABLE 1 (continued)

Atom	x	y	z
C(4,7)	712(8)	2855(16)	2056(5)
C(5,7)	1126(8)	2447(16)	2380(5)
C(6,7)	1344(8)	1636(16)	2300(5)
C(1,8)	1161(9)	−538(14)	2051(7)
C(2,8)	841(9)	−287(14)	2264(7)
C(3,8)	621(9)	−969(14)	2432(7)
C(4,8)	721(9)	−1901(14)	2388(7)
C(5,8)	1040(9)	−2152(14)	2175(7)
C(6,8)	1260(9)	−1470(14)	2007(7)
C(1,9)	1201(7)	68(14)	1288(6)
C(2,9)	763(7)	−442(14)	1059(6)
C(3,9)	618(7)	−559(14)	621(6)
C(4,9)	912(7)	−166(14)	412(6)
C(5,9)	1350(7)	343(14)	641(6)
C(6,9)	1495(7)	460(14)	1079(6)
C(1,10)	2039(11)	251(17)	2032(7)
C(2,10)	2286(11)	−570(17)	2006(7)
C(3,10)	2821(11)	−605(17)	2161(7)
C(4,10)	3108(11)	180(17)	2344(7)
C(5,10)	2861(11)	1001(17)	2370(7)
C(6,10)	2326(11)	1036(17)	2214(7)
B(1)	1374(14)	259(29)	1842(12)

sions a 28.148(16), b 14.448(8), c 33.922(17) Å, β 112.11(4)°, V 12781.0 $Å^3$, d(calcd) 1.171 g cm^{-3}.

Intensity data within $2\vartheta \leqslant 40°$ were collected by using the ω-2ϑ scan technique, with the scan width varying with ϑ according to the expression $A + B \tan \vartheta$, where $A = 0.7°$ and $B = 0.69$, at a scan speed of 0.07°/s. Background counts were made for one half of the scan time at each end of the scan. During the collection, three standard reflections were recorded every 120 readings, to check the stability of the compound. The maximum deviation of the standards was 4%. The intensities, after correction for background, were rescaled and assigned a standard deviation $\sigma(I)$, calculated as described elsewhere [28], by using a value of 0.03 for the instability factor k. The raw intensity data were corrected for Lorentz-polarization effects and for absorption ($\mu(\text{Mo-}K_\alpha = 4.78\ \text{cm}^{-1}$). 1989 reflections with $I \geqslant 3\sigma(I)$ were considered observed.

Atomic scattering factors for the non-hydrogen atoms were taken from ref. 29, while those for hydrogen atoms from ref. 30. Both the $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were included for all non-hydrogen atoms [31].

Structure solution and refinement

All the calculations were carried out using the SHELX76 crystallographic system of programs on a SEL 32/7 computer installed in our institute [32].

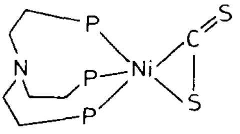
The structure was solved by the heavy-atom method and successive Fourier maps revealed all non-hydrogen atoms. Refinement was performed by using full-matrix least-squares techniques, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$, with $w = 1/\sigma^2(F_o)$. Throughout the refinement, the phenyl rings were treated as rigid bodies of D_{6h} symmetry. The hydrogen atoms, introduced in their calculated geometric positions, were not refined. Several cycles, with anisotropic thermal vibrations assigned to nickel, phosphorus and sulfur atoms and with isotropic ones to the remaining atoms, led to convergence at R and R_w of 0.095. A final ΔF Fourier map showed no particular features, apart from some residual electron densities in the regions of some phenyl rings, affected by high thermal motion. Final positional parameters are given in Table 1. Tables of thermal parameters and structure factors are available from the authors on request.

Results and discussion

Reaction of $(np_3)Ni$ *with* CS_2

A tetrahydrofuran solution of **4** reacts at room temperature with CS_2 vapor to give black crystals of the formula $(np_3)Ni(CS_2)$ (**5**), in 45% yield. This compound is fairly air-stable in the solid state but is rather unstable in solution. It is sparingly soluble in chlorinated solvents; unfortunately the concentrations are low, and so preclude any characterization in solution. It is diamagnetic and its reflectance spectrum, with absorption maxima at 17000, 20000, and 25000sh cm^{-1}, is comparable to that of the square-pyramidal nickel(0) η^2-CS_2 complex **2**, whose structure has recently been established by a complete X-ray analysis [25]. The IR spectrum shows two bands at 1150 and 630 cm^{-1}, which by comparison with the IR spectra of other η^2-CS_2 complexes such as **1**–**3**, are assigned to the out-of-ring $\nu(C{=}S)$ and to the in-ring $\nu(C{-}S)$ stretching vibrations, respectively. The IR spectrum also exhibits a band at 2800 cm^{-1} which is typical of metal complexes where np_3 acts as a tridentate ligand, the nitrogen atom not being coordinated to the metal [12].

On the basis of the analytical and spectroscopic data it is reasonable to formulate **5** as $(np_3)Ni(\eta^2$-$CS_2)$ and to assign a structure where the nickel atom is five-coordinated, by the three phosphorus atoms of np_3 and by a C=S linkage.



(5)

The treatment of a tetrahydrofuran suspension of **5** with $MeOSO_2F$ produces a dark brown oil. Crystallization from acetone/ethanol in the presence of $NaBPh_4$ affords brown crystals of the empirical formula $[(np_3)Ni(CS_2Me)]BPh_4$ (**6**), in 35% yield. The low yield is likely to be due to the low stability of **5** in solution. One of the possible causes of the instability of this compound in solution could indeed be the equilibrium $(np_3)Ni(CS_2) = (np_3)Ni + CS_2$. A remarkable improvement in the yield (up to 80%) can in fact be attained when the $MeOSO_2F$ is added directly to a carbon disulfide solution of **4**. Compound **6** is quite air-stable in the solid state, but rapidly decomposes in solution unless air is excluded. It is soluble in common organic solvents, in which it behaves as a 1 : 1 electrolyte (the molar conductance in a ca. 10^{-3} M nitroethane solution is 42 cm^2 ohm^{-1} mol^{-1}). It is diamagnetic and the electronic spectrum, which is practically the same both in the solid state and in 1,2-dichloroethane solution, consists of two bands at 17200 (ε 1030) and 22200 (ε

2300) cm^{-1}, and is comparable with those of five-coordinate nickel(II) complexes, as well as with those of **2** and **5**. The IR spectrum shows a band of medium intensity at 1110 cm^{-1}, which can be tentatively assigned to a C–S stretching vibration. At variance with the parent complex, **5**, the band at 2800 cm^{-1} is absent, thus indicating the coordination to the metal of the nitrogen atom of np_3.

The X-ray analysis has revealed that the structure consists of $[Ph_2PCH_2CH_2N(CH_2CH_2PPh_2)_2Ni(CS_2Me)]^+$ cations and BPh_4^- anions. A perspective view of the complex cation is given in Fig. 1. The final values of selected bond distances and angles are listed in Table 2.

The metal atom displays a distorted square-pyramidal geometry, being surrounded by two phosphorus atoms of the np_3 ligand and by the carbon atom and the un-methylated sulfur atom of a phosphoniodithiomethyl ester group. The third phosphorus atom of the np_3 ligand is attached to the CS_2Me carbon atom, lying at 3.24(1) Å from the metal center. The apex of the pyramid is occupied by the np_3 nitrogen atom, which displays a bond distance from the metal of 2.592(18) Å. This value, much larger than the sum of covalent radii (1.90 Å), but significantly shorter than the sum of the Van der Waals radii (3.18 Å), can be indicative of some nickel–nitrogen interaction. Indeed, the electronic and IR spectra are suggestive of a significant N–Ni interaction.

The nitrogen atom is displaced from the ideal apical position of the square pyramid, with the angle between the Ni–N line and the perpendicular to the basal plane being 16.8°. Such a displacement seems to be essentially due to the asymmetry of the chains; indeed, a six-membered ring is formed upon attachment of the phosphorus to the CS_2Me carbon atom.

The distortion of the square pyramid is also indicated by the values of the basal angles, P(1)–N(1)–S(1) 159.7(3)° and P(2)–Ni–C(7) 142.0(9)°, which are conditioned by the small angle of the phosphoniodithiomethyl ester fragment (S(1)–Ni–C(7) 49.0(8)°).

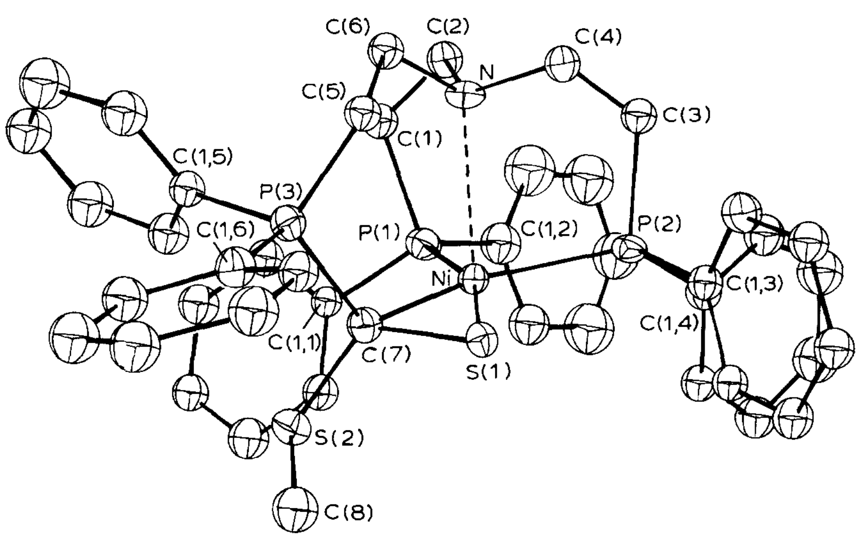


Fig. 1. Perspective view of the complex cation. ORTEP drawing with 30% probability ellipsoids.

TABLE 2

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

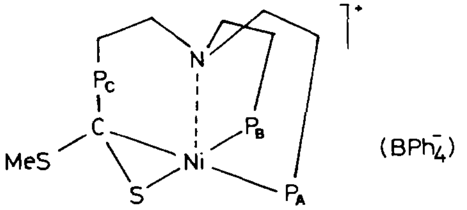
Ni-P(1)	2.179(10)	P(2)-C(1,4)	1.85(2)
Ni-P(2)	2.188(9)	P(3)-C(5)	1.81(2)
Ni-S(1)	2.117(9)	P(3)-C(7)	1.82(2)
Ni-C(7)	2.027(24)	P(3)-C(1,5)	1.72(2)
Ni-N	2.592(18)	P(3)-C(1,6)	1.81(2)
P1-C(1)	1.89(3)	S(1)-C(7)	1.72(3)
P1-C(1,1)	1.83(2)	S(2)-C(7)	1.77(3)
P1-C(1,2)	1.84(3)	S(2)-C(8)	1.85(3)
P2-C(3)	1.86(3)	N-C(2)	1.45(3)
P2-C(1,3)	1.81(2)	N-C(4)	1.50(3)
		N-C(6)	1.52(3)
P(1)-Ni-P(2)	106.5(3)	C(1,3)-P(2)-C(1,4)	99.8(9)
P(1)-Ni-S(1)	159.7(3)	C(5)-P(3)-C(7)	113.0(12)
P(1)-Ni-N	79.2(6)	C(5)-P(3)-C(1,5)	108.2(11)
P(1)-Ni-C(7)	111.4(9)	C(5)-P(3)-C(1,6)	105.1(11)
P(2)-Ni-S(1)	93.4(3)	C(7)-P(3)-C(1,5)	114.5(12)
P(2)-Ni-N	81.6(5)	C(7)-P(3)-C(1,6)	108.7(11)
P(2)-Ni-C(7)	142.0(9)	C(1,5)-P(3)-C(1,6)	106.7(9)
S(1)-Ni-N	108.3(5)	Ni-S(1)-C(7)	62.7(8)
S(1)-Ni-C(7)	49.0(8)	C(7)-S(2)-C(8)	102.1(14)
N-Ni-C(7)	103.1(8)	Ni-N-C(2)	109.9(15)
Ni-P(1)-C(1)	106.3(10)	Ni-N-C(4)	103.8(15)
Ni-P(1)-C(1,1)	121.6(6)	Ni-N-C(6)	115.1(14)
Ni-P(1)-C(1,2)	118.6(8)	C(2)-N-C(4)	113.2(19)
C(1)-P(1)-C(1,1)	104.2(11)	C(2)-N-C(6)	107.2(21)
C(1)-P(1)-C(1,2)	103.5(11)	C(4)-N-C(6)	107.8(21)
C(1,1)-P1-C(1,2)	100.6(10)	Ni-C(7)-P(3)	114.7(12)
Ni-P(2)-C(3)	106.0(10)	Ni-C(7)-S(1)	68.2(9)
Ni-P(2)-C(1,3)	115.5(6)	Ni-C(7)-S(2)	122.2(14)
Ni-P(2)-C(1,4)	123.5(7)	P(3)-C(7)-S(1)	111.2(15)
C(3)-P(2)-C(1,3)	105.4(12)	P(3)-C(7)-S(2)	112.2(14)
C(3)-P(2)-C(1,4)	105.1(11)	S(1)-C(7)-S(2)	121.5(14)

The bond lengths involving the metal atom, i.e. the Ni–S distance of 2.117(9) Å and the Ni–P distances, which average 2.183(4) Å, fall in the lower range of values reported for Ni–S–C and NiPMe$_3$ fragments, respectively [33].

A particular comment must be made about the carbon atom of the CS$_2$ group. Indeed, a look at its bond distances and angles shows a geometrical environment characteristic of an *sp*^{3} hybridization. Apart from the Ni–C(7)–S(1) angle, which is constrained to the value of 68.2(9)°, the angles range from 111.2(15) to 122.2(14)°. The angle between the planes P3C7S2 and NiS1C7 is 88.3°. Moreover the bond distances involving C(7) appear systematically larger than those reported for the η^2-CS$_2$ complexes **1** and **2**, (where the M–C, C–S(1), C–S(2) bonds are 1.86(1), 1.63(1), 1.61(1) Å, and 1.88(1), 1.68(1), 1.62(1) Å, respectively [25]). No bonding interaction between the nickel and the phenyl carbon atoms is apparent.

The singularity of the phosphoniodithiomethyl ester complex **6** does not allow a direct comparison with any other compound reported in the literature (the cobalt analog has not been characterized by X-ray methods [12]). However, **6** shows some structural analogies with the complex Ni(SC(S)SC(PMe$_3$)S)(PMe$_3$) recently reported by Ibers et al. [33]. In this compound the nickel atom is coordinated by a PMe_3 group and by the $SC(S)SC(PMe_3)S$ ligand, formed in situ, through a sulfur atom and a C–S linkage of the S_2C–PMe_3 fragment. However Ibers's compound displays a shortening of the Ni–C distance compared to that in complex **6** (1.92(1) vs. 2.037(24) Å), which may be attributed to ligand constraints.

The $^{31}P\{^1H\}$NMR spectrum in CD_2Cl_2 is compatible with the structure found in the solid state. The presence of three types of phosphorus is revealed, giving resonances in a 1/1/1 ratio. A doublet of doublets with a chemical shift of 7.48 ppm is assigned to the P_A phosphorus atom which is *trans* to the carbon atom of the PCS_2Me group, while two doublets at 17.79 ppm ($^3J(P_A$–$P_B)$ 14 Hz), and 20.21 ppm ($^2J(P_A$–$P_C)$ 8 Hz) are assigned to the P_B phosphorus atom which is *cis* to P_A and to the P_C phosphonium atom, respectively.

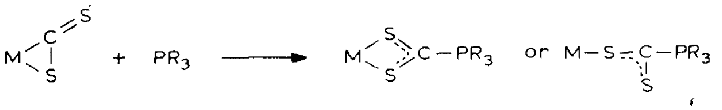


The mechanism for the formation of **6** may be envisaged as involving the initial methylation of the exo-cyclic sulfur atom of **5** to give a dithiomethyl ester group, followed by nucleophilic attack by a phosphorus atom of np_3 on the CS_2Me carbon atom. During this second step the nitrogen atom of np_3 approaches the metal; even though not completely coordinated, this nitrogen should contribute significantly to stabilize the complex by increasing the electron density at the metal center.

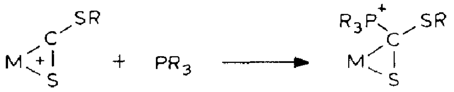
Support for this pathway is provided by the following pieces of experimental information. (a) The η^2-CS_2 complexes **1** and **2** react with $MeOSO_2F$ to give the stable η^2-dithiomethyl ester complexes $[(\text{triphos})M(\eta^2\text{-}CS_2Me)]BPh_4$ (M = Co, **7**; Ni, **8**) [11]. (b) The carbon atom of some η^2-CS_2 complexes undergoes nucleophilic attack by tertiary phosphine or hydride ion, to give phosphoniodithioformate [15,16], or dithioformate complexes [17] (the nature of the metal-η^2-CS_2Me bonding can be regarded in the same way as that of the η^2-CS_2 precursor [7,11]). (c) Nucleophiles like RO^- and RS^- have been found to attack the carbon atom of η^2-CS_2R groups [34].

The results presented in this paper and those reported as points (b) and (c) clearly indicate that the carbon atom of the dihapto-bonded CS_2 and CS_2R groups in an electrophilic center, susceptible to attack by nucleophiles. Tertiary phosphines react with carbon disulfide [15,16] or dithioalkyl ester complexes to give phosphoniodithioformate (eq. 1) [12] or phosphonioalkyldithioformate (eq. 2); hydride ion from $LiHBEt_3$ reduces the η^2-CS_2 group to η^1-SC(H)S (eq. 3) [17]; alkoxides and alkylsulfides cause the fragmentation of the dithioalkyl ester ligand to CS(XR′) (X = O, S; R′ = Me, Et) and SR groups (eq. 4) [34].

All of these findings may contribute to rationalize the bonding of the M–η^2-CS_2 and M–η^2-CS_2R moieties, for which a carbenoid character has been proposed on the basis of the structural data [5,7], the M–C distances being shorter than those found in η^2-acetylene and olefin complexes. Indeed, there are many experimental results

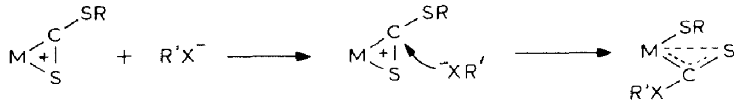


(1)



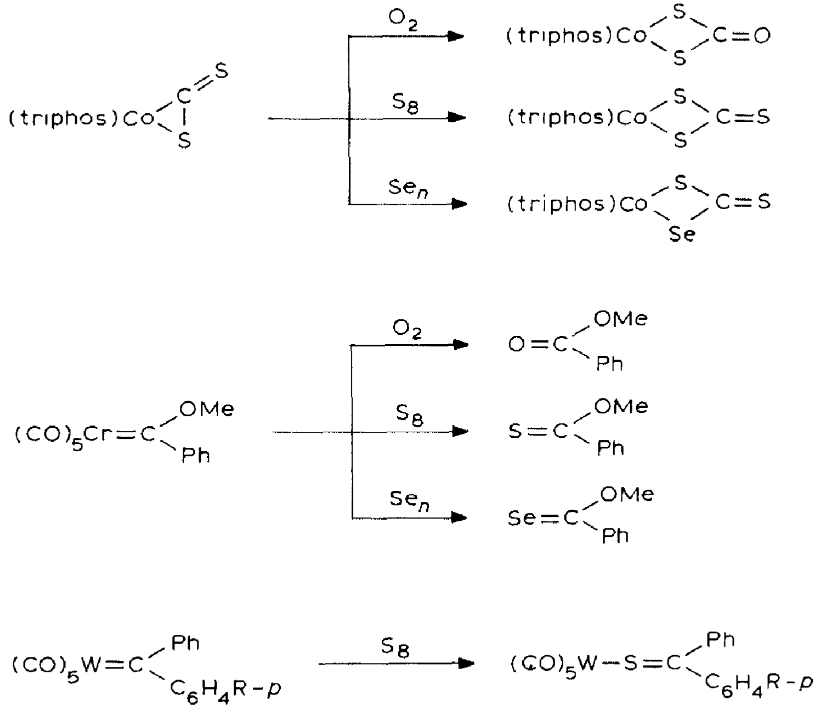
(2)

(3)



(4)

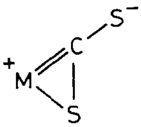
which, at least, apparently suggest a carbenoid nature for the M–η^2-CS_2 and M–η^2-CS_2R moieties. In particular, the reactions of the η^2-CS_2 complex **1** and of the η^2-CS_2Me complex **7** with oxygen, sulfur and selenium [11] show some analogies with those of Fischer-type carbene complexes with the later Group VIB elements [35], and more closely with those of the carbene complexes $(CO)_5W[C(p\text{-}C_6H_4R)(C_6H_5)]$ (R = Me, OMe, H, Br, CF_3) with elemental sulfur [36] (Scheme 1).



SCHEME 1

Further support for the carbenoid nature of CS_2 and CS_2R complexes is provided by the analogies existing between their reactivity and that of some dithiocarbenemetal complexes toward nucleophiles. Yu and Angelici have, in fact, clearly demonstrated that tertiary phosphines, alkoxides, alkyl sulfides, and other nucleophilic agents, can attack the carbene carbon atom [37].

Conversely, recent MO calculations on the bonding capabilities of CS_2 suggest that the contribution of the carbenoid canonical representation **A** to the description

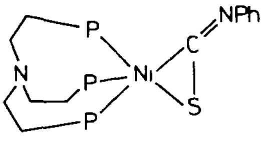


(**A**)

of the electron structure of the M–η^2-CS_2 moiety is meaningless [24,25]. In particular, the presence of a double bond between the metal and the carbon atom seems to be ruled out. As for the short M–C bond distance, this is ascribed rather to the prevailing involvement of the carbon orbital (π_u^* of CS_2), in the π back-donation process. On the basis of the same MO arguments, the similarity between carbene and η^2-CS_2 or η^2-CS_2R complexes with respect to nucleophilic attack may depend on the fact that both types of complexes have LUMOs centered at the α-carbon atom [38].

Reaction of $(np_3)Ni$ *with SCNPh and COS*

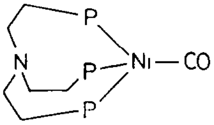
A tetrahydrofuran solution of **4** reacts with SCNPh to give diamagnetic red crystals of formula $(np_3)Ni(SCNPh)$ (**9**) in 70% yield. Complex **9** is fairly air-stable in the solid state but is unstable in solution unless air is excluded. The electronic spectra, both in the solid state and in solution, are almost identical to those of **5**. The IR spectrum shows bands at 1640 and 650 cm^{-1}, attributable to the C=N stretching vibration and the $\overline{\mathrm{MSC}}$ vibration of a dihapto-*S,C* bonded SCNPh [12]. The band at 1640 cm^{-1} is somewhat broadened by a phenyl vibration at ca. 1620 cm^{-1}. Re-inforced phenyl vibrations appear at 1580 and 1485 cm^{-1}. Also present is the band at 2800 cm^{-1}, indicative of the uncoordination of the nitrogen atom of np_3. These IR absorptions perfectly match those found for the complexes $(np_3)Co(\eta^2$-$SCNPh)$ (**10**) [12] and $(triphos)Ni(\eta^2$-$SCNPh)$ (**11**) [39], whose structures have been elucidated by means of complete X-ray diffraction analyses. On the basis of all of these data it therefore seems reasonable to formulate **9** as $(np_3)Ni(\eta^2$-$SCNPh)$ and to assign a structure in which the nickel atom is five-coordinated, by the three phosphorus atoms of np_3 and by the C=S linkage of the SCNPh group.



(**9**)

Compound **9** reacts with hard alkylating agents such as $MeOSO_2F$ and $MeOSO_2CF_3$, but any attempt to isolate a product from the reaction mixtures was unsuccessful. This is in contrast to the cobalt analog **10**, which on treatment with methylating agents forms the thiocarbonyl complex cation $[(np_3)CoCS]^+$ [40].

A tetrahydrofuran solution of **4** reacts with COS to afford yellow crystals of the known complex (np$_3$)NiCO (**12**) in 90% yield. This result is in line with those of most of the reported reactions of COS with metal fragments [12].



(12)

The intermediacy of labile η^2-COS species has often been invoked to explain the fragmentation of carbonyl sulfide to carbon monoxide and sulfur [12,41,42]. In many instances, the fate of the sulfur has not been determined [12,42]. Phosphine co-ligands can often function as sulfur acceptors [41]. The presence of np$_3$ sulfides has not been found in the reaction mixture. This may be ascribed to the well-known rigidity of the np$_3$-metal moiety.

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