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Reactions of CS_2 with Nickel–Phosphine Complexes: Structure of $Ni(SC(S)SC(PMe_3)S)(PMe_3)$

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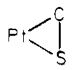
The reactions of carbon disulfide with a number of nickel(0)–phosphine complexes (generated from $Ni(COD)_2$ and added phosphine) afford two classes of Ni–CS_2 coordination compounds. For L = PPh_3, $P(p\text{-tol})_3$, and PCy_3 compounds characterized as $[Ni(CS_2)L]_2$ are formed. The compounds $Ni(C_2S_4PR_3)(PR_3)$ are produced when R = CH_3 or C_2H_5, as deduced from spectroscopic and X-ray analysis. The complex $Ni(SC(S)SC(PMe_3)S)(PMe_3)$ crystallizes in the orthorhombic space group D_2^4-$P2_12_12_1$ (a = 13.486 (3) Å, b = 13.500 (2) Å, c = 17.670 (3) Å) with two enantiomorphically related molecules per asymmetric unit. This crystal structure is a rare example of a racemic mixture crystallizing in an acentric space group. The final agreement indices, based on 271 variables and 6034 unique reflections collected at −151 °C on an automatic diffractometer, are $R(F^2) = 0.051$ and $R_w(F^2) = 0.082$. The conventional R index on F for 5197 reflections having $F_o^2 > 3\sigma(F_o^2)$ is 0.034. The complex displays a NiPSCS coordination (mean Ni–P 2.165 (7) Å; mean Ni–S 2.156(5) Å; mean Ni–C 1.92 (1) Å) that is severely distorted from square planar with a mean S–Ni–S angle of 138.9 (2)°, a mean C–Ni–P angle of 161.7 (2)°, mean C–Ni–S angles of 50.4 (3) and 92.9 (6)°, and deviations from the NiPSCS plane as large as 0.34 (3) Å. The $SC(S)SC(PMe_3)S$ linkage contains a planar SC(S)S fragment (largest deviation 0.026 (3) Å) and a nonplanar SC(P)S fragment (largest deviation 0.265 (6) Å). The bond length pattern found for this ligand (S–C range 1.662 (7)–1.793 (6) Å) is consistent with $^{13}C\{^1H\}$ NMR results that show that the carbon atom of the SC(S)S fragment is coupled to the metal-bound phosphine but not to the carbon-bound phosphine. This lack of coupling can be ascribed to a S–C single bond (S–C = 1.793 (6) Å) within the ligand that blocks communication between the phosphine and the carbon atom.

Introduction

The coordination chemistry of carbon disulfide has been extensively studied since the first preparation of transition-metal carbon disulfide complexes in 1967.[1] Carbon disulfide has proved to be a versatile ligand: it forms complexes with almost every transition metal; it is capable of coordinating to one or more metals; it shows a variety of insertion and disproportionation reactions.[2]

One of the first complexes of CS_2 to be prepared, $Pt(CS_2)(PPh_3)_2$,[1,3] contains an η^2-CS_2 ligand; that is, the CS_2 molecule is bound to the Pt through a



linkage. This mode of coordination also occurs in the analogous Pd complex, $Pd(CS_2)(PPh_3)_2$,[1,4] and in every other monometallic CS_2 complex structurally characterized by X-ray diffraction (see below). Our interest was attracted to the report that the related nickel complex, $Ni(CS_2)(PPh_3)_2$, could not be synthesized, but rather a compound of empirical formula $Ni(CS_2)(PPh_3)$ was formed.[1] Here we explore the influence of the phosphine on the resultant Ni–CS_2 complex.

Experimental Section

All reactions were performed under an atmosphere of prepurified N_2 with use of standard Schlenkware. Solvents were refluxed under N_2 and distilled from Na-benzophenone immediately prior to use, except CH_2Cl_2, which was distilled from P_2O_5 and stored under N_2. The compounds PPh_3, PEt_3, PMe_3, Cy_3PCS_2, and $P(p\text{-tol})_3$ (Me = methyl, Et = ethyl, Ph = phenyl, Cy = cyclohexyl, p-tol = p-tolyl) were purchased from Strem Chemicals, Inc. Reagent grade CS_2 was obtained from Mallinckrodt, Inc., and either used without further purification or purified according to published methods with no change in results. Enriched $^{13}CS_2$ (90%) was purchased from Prochem Chemicals, Inc. A literature procedure was used to prepared $Ni(COD)_2$[5] (COD = 1,5-cyclooctadiene). Elemental analyses were performed by Microtech Laboratories, Inc., Skokie, IL, and Galbraith Laboratories, Inc., Knoxville, TN. The results of these analyses are shown in Table I. Molecular weights were determined cryoscopically with the use of an apparatus described elsewhere.[6] Infrared spectra from Nujol mulls were recorded on a Perkin-Elmer 283 spectrometer. The $^{31}P\{^1H\}$ NMR and ^1H NMR spectra were obtained on a JEOL FX90Q spectrometer operating at 36.2 and 89.56 MHz, respectively. A JEOL FNM-FX270 NMR spectrometer operating at 67.8 MHz was used to obtain the $^{13}C\{^1H\}$ NMR spectra. The samples were contained in 10-mm tubes. Positive chemical shifts are reported as downfield from external 85% H_3PO_4 (^{31}P) or Me_4Si (^1H, ^{13}C).

Table I. Analytical Data for Nickel Carbon Disulfide Complexes

		% found (calcd)			
compd	color	C	H	P	S
$[Ni(CS_2)(PPh_3)]_2$	red-violet	57.45 (57.46)	4.05 (3.81)	7.63 (7.80)	16.17 (16.15)
$[Ni(CS_2)(P(p\text{-tol})_3)]_2$	red	59.86 (60.16)	5.22 (4.82)	6.71 (7.05)	13.92 (14.60)
$[Ni(CS_2)(PCy_3)]_2$	red	54.50 (54.95)	8.10 (8.01)	7.30 (7.46)	15.25 (15.44)
$Ni(C_2S_4PMe_3)(PMe_3)$	dark red	27.01 (26.48)	5.06 (4.92)		36.19 (35.35)
$Ni(C_2S_4PEt_3)(PEt_3)$	dark red	37.30 (37.59)	6.73 (6.76)		30.27 (28.67)

$[Ni(CS_2)(PPh_3)]_2$. The compounds $Ni(COD)_2$ (0.81 g, 3.0 mmol) and PPh_3 (1.54 g, 5.9 mmol) were dissolved in 10 mL of THF, and 2.5 mL of CS_2 was added. The resultant solution was stirred at room temperature overnight. The $[Ni(CS_2)(PPh_3)]_2$ complex was filtered out, washed with THF, and dried in vacuo: yield 76%; IR $\nu_{C=S}$ 1122 cm^{-1}.

$[Ni(CS_2)(P(p\text{-tol})_3)]_2$. The compounds $Ni(COD)_2$ (1.05 g, 3.8 mmol) and $P(p\text{-tol})_3$ (2.33 g, 7.6 mmol) were dissolved in 10 mL of THF, and 2.5 mL of CS_2 was added. After being stirred overnight, the reaction mixture was filtered. The collected $[Ni(CS_2)(P(p\text{-tol})_3)]_2$ compound was washed with THF and dried in vacuo: yield 75%; IR $\nu_{C=S}$ 1125 cm^{-1}; $^{31}P\{^1H\}$ NMR δ 21.2 ($CDCl_3$).

$[Ni(CS_2)(PCy_3)]_2$. The compounds $Ni(COD)_2$ (0.61 g, 2.2 mmol) and Cy_3PCS_2 (0.82 g, 2.3 mmol) were dissolved in 10 mL of THF,

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and the solution was stirred at room temperature for 4 h. The $[Ni(CS_2)(PCy_3)]_2$ complex was filtered out, washed with THF, and dried in vacuo: yield 74%; IR $\nu_{C=S}$ 1122 cm^{-1}.

R_3PCS_2 (R = Me, Et). Carbon disulfide was added to an ether solution of PR_3. The R_3PCS_2 compound was filtered out, washed with ether, and dried in vacuo. R = Me: IR ν_{CS} 1045 cm^{-1}; $^{31}P\{^1H\}$ NMR δ 14.1; ^1H NMR δ 2.02 (d, $^2J_{PH} = 13.4$ Hz); $^{13}C\{^1H\}$ NMR δ_{CH_3} 10.05 (d, $J_{PC} = 56.6$ Hz), δ_{PCS_2} 233.4 (d, $J_{PC} = 51.3$ Hz). R = Et: IR ν_{CS} 1065 cm^{-1}; $^{31}P\{^1H\}$ NMR δ 28.3; $^{13}C\{^1H\}$ NMR δ_{CH_2} 14.10 (d, $J_{PC} = 48.83$ Hz), δ_{CH_3} 4.74 (s), δ_{PCS_2} 229.51 (d, $J_{PC} = 43.95$ Hz).

$Ni(C_2S_4PEt_3)(PEt_3)$. Method 1. The compounds $Ni(COD)_2$ (0.66 g, 2.4 mmol) and Et_3PCS_2 (0.94 g, 4.8 mmol) were dissolved in 10 mL of THF, and after 4 h 40 mL of hexane was added and the solution cooled to −35 °C. The product was collected, washed with hexane, and dried in vacuo: yield 79%, molecular weight 362 (calculated 447); IR ν_{CS} 831, 854, 888, 998 cm^{-1}; $^{31}P\{^1H\}$ NMR (30 °C) δ_{P_1} 47.2 (s), δ_{P_2} 30.0 (s); $^{31}P\{^1H\}$ NMR (−80 °C) δ_{P_1} 49.0 (d), δ_{P_2} 30.2 (d, $J_{PP} = 6.1$ Hz); $^{13}C\{^1H\}$ NMR $(PEt_3)_1$: δ_{CH_2} 11.23 (d, $J_{PC} = 51.89$ Hz), δ_{CH_3} 5.10 (s). $^{13}C\{^1H\}$ NMR $(PEt_3)_2$: δ_{CH_2} 17.21 (d, $J_{PC} = 24.41$ Hz), δ_{CH_3} 7.04 (s).

Method 2. The compound $Ni(COD)_2$ (0.21 g, 0.8 mmol) was dissolved in 10 mL of THF, and PEt_3 (0.21 mL, 1.4 mmol) was added. After 1 h, 2 mL of CS_2 was added and the resulting solution was treated as above to give the identical product.

$Ni(C_2S_4PMe_3)(PMe_3)$. The compounds $Ni(COD)_2$ (0.67 g, 2.4 mmol) and Me_3PCS_2 (0.74 g, 4.8 mmol) were mixed in 10 mL of THF. The solution was stirred at room temperature for 2 h and then filtered to collect the product, which was washed with THF and dried in vacuo: molecular weight 361 (calculated 363); IR ν_{CS} 850, 1010 cm^{-1}; $^{31}P\{^1H\}$ NMR (30 °C) δ_{P_1} 32.9 (s), δ_{P_2} −9.5 (s); $^{31}P\{^1H\}$ NMR (−68 °C) δ_{P_1} 34.7 (d), δ_{P_2} −8.0 (d, $^2J_{PP} = 8.5$ Hz); ^1H NMR δ 1.80 (d, $^2J_{PH} = 13.4$ Hz), δ 1.31 (d, $^2J_{PH} = 8.5$ Hz), $^{13}C\{^1H\}$ NMR (30 °C) δ_{C_1} 42.6 (d, $J_{P_1C_1} = 73.3$ Hz), δ_{C_2} 251.2 (s); Hz, NMR (−80 °C) δ_{C_1} 42.4 (dd, $J_{P_1C_1} = 74.4$ Hz, $J_{P_2C_1} = 28.1$ Hz), $\delta_{C_2} = 250.9$ (d, $J_{P_2C_2} = 26.9$ Hz).

X-ray Study of $Ni(SC(S)SC(PMe_3)S)(PMe_3)$. Crystals suitable for X-ray work were obtained by recrystallization from CH_2Cl_2. The systematic extinctions ($h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$) and the symmetry of the intensity-weighted reciprocal lattice, as observed on preliminary Weissenberg and precession photographs, were indicative of the orthorhombic space group D_2^4-$P2_12_12_1$. Accurate unit cell parameters were determined by least-squares refinement of 15 high-angle reflections that had been automatically centered on a Picker FACS-1 diffractometer. Data collection was performed at −151 °C in a manner standard in this laboratory.[7] Six standard reflections measured at 100 reflection intervals showed no indication of crystal decay during the course of data collection. Crystallographic and experimental details are given in Table II.

All calculations were performed on a CDC Cyber 170-730 computer by use of programs standard in this laboratory. Conventional atomic scattering factors were used for the non-hydrogen[8] and hydrogen[9] atoms. Anomalous dispersion corrections[10] were applied to the nickel, sulfur, and phosphorus atoms with use of values of $\Delta f'$ and $\Delta f''$ of Cromer and Waber.[8]

The initial phase determination was carried out with use of MULTAN80.[11] A starting model of eight atoms was obtained from an E map calculated from the phase set with the best figures of merit. The remaining non-hydrogen atoms were found by standard Fourier and refinement techniques.

Enantiomeric determination was made after a full isotropic refinement based on F with reflections having $F_o^2 > 3\sigma(F_o^2)$ and with no correction for anomalous dispersion. Solution A was obtained by including anomalous dispersion and continuing the isotropic refinement. The residuals for solution A were $R = 0.087$ and $R_w = 0.107$. Solution B was obtained by including anomalous dispersion, reversing the signs of all atomic coordinates, and proceeding with the refinement. The residuals for solution B of $R = 0.080$ and $R_w = 0.099$ indicate that solution B is the correct enantiomer.

Table II. Crystallographic Details for $Ni(SC(S)SC(PMe_3)S)(PMe_3)$

formula	$C_8H_{18}NiP_2S_4$
fw	363.15
space group	D_2^4-$P2_12_12_1$
a, Å	13.486 (3)
b, Å	13.500 (2)
c, Å	17.670 (3)
V, Å^3	3217
Z	8
density(calcd) (−151 °C), g/cm^3	1.499
cryst shape	octahedron extended along [100] and with {101} and {011}
cryst vol, mm^3	0.0296
radiation	Mo Kα (λ(Kα_1) = 0.7093 Å, graphite monochromator)
linear abs coeff, cm^{-1}	18.8
transmission factors[a]	0.642-0.704
temp,[b] °C	−151
detector aperture	4.0 mm wide × 4.5 mm high, 32 cm from cryst
takeoff angle, deg	3.0
scan speed, deg/min	2 (in 2θ)
2θ limits, deg	$3.5 < 2\theta \leqslant 63.5$
bkgd counts, s	10 at each end of scan with rescan option[c]
scan range, deg	1.0 below Kα_1 to 1.35 above Kα_2
data collected	$+h, +k, +l$
unique data (including $F_o^2 < 0$)	6034
unique data with $F_o^2 > 3\sigma(F_o^2)$	5197
final no. of variables	271
$R(F^2)$	0.051
$R_w(F^2)$	0.082
error in observn of unit wt, e^2	1.21
R (on F for $F_o^2 > 3\sigma(F_o^2)$)	0.034

[a] A Gaussian grid of 4 × 4 × 4 was used for the absorption correction. [b] The low-temperature system is based on a design by: Huffman, J. C. Ph.D. Thesis, Indiana University, 1974. [c] The diffractometer was run under the Vanderbilt disk oriented system: Lenhert, P. G. *J. Appl. Crystallogr.* 1975, *8*, 568–570.

After anisotropic refinement of the model, hydrogen atoms were located in difference electron density maps. Idealized hydrogen positions (C–H = 0.95 Å; H–C–H = 109.5°) were obtained from a least-squares adjustment of the observed positions and were added as fixed contributions to the structure factors. Each hydrogen atom was assigned an isotropic thermal parameter 1 Å^2 greater than the equivalent isotropic thermal parameter of the atom to which it is attached. The final cycle of refinement (F_o^2) involved 271 variables and the 6034 unique intensities. The final residuals are $R(F_o^2) = 0.051$ and $R_w(F_o^2) = 0.082$, and the error in an observation of unit weight is 1.21 e^2. The conventional R indices on F_o for the 5197 reflections having $F_o^2 > 3\sigma(F_o^2)$ are $R(F_o) = 0.034$ and $R_w(F_o) = 0.040$. The largest peak in the final difference electron density map has a magnitude of 0.4 (1) e/Å^3.

The positional parameters for the non-hydrogen atoms are listed in Table III. The anisotropic thermal parameters (Table IV) and the final values of $10|F_o|$ and $10|F_c|$ (Table V) are available.[12] A negative entry in Table V implies that F_o^2 was observed to be negative.

Results and Discussion

Although for transition-metal carbon disulfide complexes a number of bonding modes have been proposed primarily on the basis of spectroscopic data,[1-3,13-35] we shall rely on known

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Table III. Positional Parameters[a] for the Non-Hydrogen Atoms of Ni(SC(S)SC(PMe$_3$)S)(PMe$_3$)

ATOM	X	Y	Z
NI	0.548757(29)	0.843756(29)	0.401806(21)
S(1)	0.535380(62)	0.930460(61)	0.503737(45)
S(2)	0.544704(58)	0.701606(59)	0.537248(39)
S(3)	0.511025(73)	0.512330(64)	0.461610(52)
S(4)	0.557434(71)	0.690702(60)	0.368423(41)
P(1)	0.727391(58)	0.821464(67)	0.510802(46)
P(2)	0.498237(65)	0.923326(69)	0.302300(48)
NI'	1.071096(33)	0.834751(31)	0.141640(23)
S(1)'	1.167768(61)	0.822908(62)	0.238966(55)
S(2)'	0.943152(55)	0.829318(55)	0.284795(40)
S(3)'	0.749481(64)	0.783025(76)	0.222593(64)
S(4)'	0.914678(72)	0.836340(72)	0.117027(44)
P(1)'	1.057851(64)	1.013137(56)	0.250164(47)
P(2)'	1.14112(10)	0.785727(81)	0.038300(61)
C(1)	0.59567(21)	0.81513(23)	0.50244(16)
C(2)	0.53933(24)	0.63129(24)	0.45323(16)
C(3)	0.77497(24)	0.90206(31)	0.43941(20)
C(4)	0.76412(26)	0.86851(42)	0.60115(19)
C(5)	0.78014(31)	0.70112(36)	0.49813(36)
C(6)	0.46697(30)	0.84912(32)	0.22084(21)
C(7)	0.59080(29)	1.00969(29)	0.26635(24)
C(8)	0.38870(35)	1.00091(40)	0.31303(26)
C(1)'	1.05260(21)	0.88155(21)	0.24274(16)
C(2)'	0.86593(22)	0.81756(22)	0.20514(19)
C(3)'	1.14193(29)	1.06183(23)	0.18137(19)
C(4)'	1.09824(33)	1.05025(27)	0.34209(19)
C(5)'	0.93885(28)	1.06591(24)	0.23247(27)
C(6)'	1.05924(53)	0.76724(49)	-0.04307(27)
C(7)'	1.23281(45)	0.87231(41)	0.00227(30)
C(8)'	1.20338(55)	0.67011(37)	0.04350(41)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. The unprimed atoms belong to molecule 1, and the primed atoms belong to molecule 2.

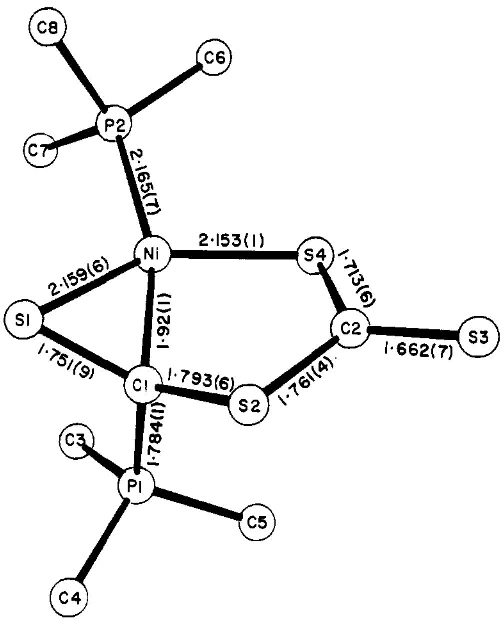
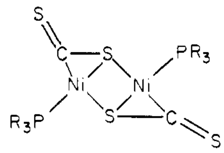


Figure 1. Drawing of Ni(SC(S)SC(PMe$_3$)S)(PMe$_3$), molecule 2. The hydrogen atoms have been omitted for clarity, and the atoms have been drawn as spheres with arbitrary radii. Averaged bond lengths (Å) for the two independent molecules are given.[48]

crystal structures.[3,4,17,23-25,27,31-36] Table VI lists those structures, along with spectroscopic data, when available. For monometallic complexes only the η^2-CS$_2$ coordination mode has been characterized by X-ray crystallography. The observed C=S stretching vibration for these complexes falls in the range 1120–1176 cm^{-1}. For polymetallic complexes many bonding modes have been observed, but owing to the limited data reliable correlations between $\nu_{C=S}$ and structure type cannot be made.

In 1967 Baird and Wilkinson[1] synthesized [Ni(CS$_2$)(PPh$_3$)]$_2$ according to eq 1. On the basis of a C=S stretching frequency of 1122 cm^{-1} and the fact that the compound appeared to be dimeric in chloroform (though of very low solubility) the following structure was assigned:

$$2\mathrm{Ni(CO)_2(PPh_3)_2} + 2\mathrm{CS_2} \rightarrow [\mathrm{Ni(CS_2)(PPh_3)}]_2 + 4\mathrm{CO} \qquad (1)$$



We have found that this class of Ni–CS$_2$ complexes can also be prepared with other monodentate phosphine ligands. The reaction shown in eq 2 was carried out for R = Ph, *p*-tol, Cy.

$$2\mathrm{Ni(COD)_2} + 2\mathrm{PR_3} + 2\mathrm{CS_2} \rightarrow [\mathrm{Ni(CS_2)(PR_3)}]_2 + 4\mathrm{COD} \qquad (2)$$

These three complexes all exhibit a Ni:CS$_2$:PR$_3$ ratio of 1:1:1 (see Table I) and are obtained even if a 2:1 (PR$_3$:Ni) ratio of starting materials is used. Their similar C=S stretching frequencies (1122–1125 cm^{-1}) and color (deep red) are indicative of similar structures. The compound [Ni(CS$_2$)(PCy$_3$)]$_2$[19] is even less soluble than [Ni(CS$_2$)(PPh$_3$)]$_2$ so characterization by other than IR spectroscopy and elemental

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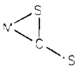
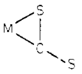
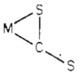
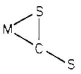
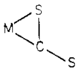
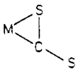
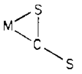
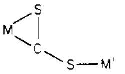
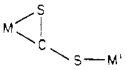
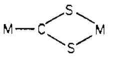
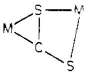
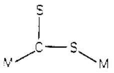
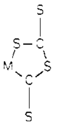
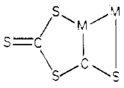
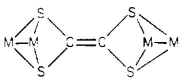
Table VI. Structures of Transition-Metal Carbon Disulfide Complexes Determined by Diffraction Methods

structure type[a]	compd	C=S str freq, cm^{-1}	ref
	$Pt(CS_2)(PPh_3)_2$	1160, 1141[b]	3
	$Pd(CS_2)(PPh_3)_2$	1176, 1151[b]	4
	$Nb(\eta^5-C_5H_5)_2(\eta^1-C_3H_5)(CS_2)$	1135[c]	33
	$V(\eta^5-C_5H_5)_2(CS_2)$	1141[c]	34
	$Co(\eta^5-C_5H_5)(CS_2)(PMe_3)$	1146[d]	23
	$Co(CS_2)(triphos)$[e]	1120[b]	24
	$Fe(CO)_2(CS_2)(PMe_3)(PPh_3)$	1160[b]	17
	$Co(triphos)(\mu-CS_2)Cr(CO)_5$	1110[b]	24
	$Fe(CO)_2(PMe_2Ph)_2(\mu-CS_2)Mn(\eta^5-C_5H_5)(CO)_2$	1159[b]	27
	$[PtCl(PPh_3)_2(\mu-CS_2)Pt(PPh_3)_2][BF_4]$	939, 874[d]	35
	$[Co(triphos)]_2(\mu-CS_2)$	*f*	24
	$Pt_2Cl_2(\mu-CS_2)(dppm)_2$[g]	985[b]	31
	$Rh(\eta^5-C_5H_5)(PMe_3)(C_2S_4)$	1060, 1039, 1000, 911[b]	25
	$Rh_2Cl_2(C_2S_4)(dppm)_2$	1050, 995, 980[b]	32
	$Fe_4(CO)_{12}(C_2S_4)$	*h*	36

[a] Connectivity, but not bond type, is displayed in the sketches. [b] Nujol mull. [c] CS_2 solution. [d] KBr pellet. [e] triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane. [f] Not located. [g] dppm = bis(diphenylphosphino)methane. [h] Not reported.

analysis was impossible. Though $[Ni(CS_2)(P(p\text{-tol})_3)]_2$ is soluble in chlorinated hydrocarbons, the solutions are unstable, thus making it impossible to determine a molecular weight for the compound. However, a $^{31}P\{^1H\}$ NMR spectrum was obtained. This spectrum, which is invariant with temperature, consists of a singlet at 21.2 ppm. The NMR spectral evidence of a single phosphine environment and the infrared stretching frequency in the range expected for a carbon–sulfur double bond are both consistent with the structure proposed earlier,[1] but other structures are consistent with these data, especially if the compounds are not dimeric.

Products of different stoichiometry are formed with small trialkylphosphines (eq 3; R = Me, Et). From NMR spectroscopic studies (^1H, $^{31}P\{^1H\}$, and ^{13}C) of these species we reached the following conclusions: (i) the Me and Et compounds have similar structures; (ii) in each the two PR_3 groups are nonequivalent, with a Ni–P and an $R_3P–CS_2$ interaction occurring in each; (iii) the second CS_2 molecule possesses a Ni–C interaction. The molecular weights of these complexes, measured in 1,2-dichloroethane, are those expected for monomers. From these observations we could draw no unique structure. But from solution and solid-state IR spectra we established that the solid-state structures persist in solution. Accordingly, we turned to a crystallographic study of the Me complex in order to establish unequivocally the connectivity in these complexes.

$$Ni(COD)_2 + 2PR_3 + 2CS_2 \rightarrow Ni(C_2S_4PR_3)(PR_3) + 4COD \quad (3)$$

As illustrated in Figure 1, the molecular structure of this compound consists of a monomeric Ni complex with a PMe_3 ligand and a multidentate $SC(S)SC(PMe_3)S$ ligand. We first show that these results are consistent with the spectroscopic data. The $^{31}P\{^1H\}$ NMR spectrum of the Me complex at 30 °C consists of two singlets at 32.9 and −9.5 ppm that resolve into doublets upon cooling the solution to −68 °C (J_{PP} = 8.5 Hz). These spectral changes are reversible. The low frequency of the CS stretching vibrations at 1010 and 850 cm^{-1} and the

Table VII. Phosphorus–Hydrogen Coupling Constants for Trimethylphosphine Derivatives

compd	$^2J_{PH}$, Hz	ref
PMe_3	2.7	*a*
$Ni(COCH_3)(acac)(PMe_3)$	9.8	*b*
$Fe(CH_2{=}C(CH_3){-}CH_2{=}CH_2)(PMe_3)_3$	6.1	*c*
$CoCl(CO)(PMe_3)_3$	8.9	*d*
Me_3PO	13.4	*a*
Me_3PS	13.0	*a*
$[Me_4P]I$	14.4	*a*
Me_3PCS_2	13.4	*e*
$Ni(C_2S_4PMe_3)(PMe_3)$	8.5, 13.4	*e*

[a] Hendrickson, J. B.; Maddox, M. L.; Sims, J. J.; Kaesz, H. D. *Tetrahedron* **1964**, *20*, 449–459. [b] Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1976**, *109*, 2524–2532. [c] Karsch, H. H.; Klein, H. F.; Schmidbaur, H. *Ibid.* **1977**, *110*, 2200–2212. [d] Klein, H. F.; Karsch, H. H. *Inorg. Chem.* **1975**, *14*, 473–477. [e] This work.

small value of J_{PP} are consistent with a phosphoniodithiocarboxylato ($R_3P{-}CS_2$) type ligand. Precedent for free and liganded R_3PCS_2 species exists.[37–44] The addition of CS_2 to a solution of PMe_3 results in immediate formation of Me_3PCS_2. These phosphine–CS_2 complexes are formed for all basic trialkylphosphines.[37] The structure of Et_3PCS_2 has been determined.[38] There are four equal P–C bond lengths (within experimental error), indicative of a full P–CS_2 bond. The $^{13}C\{^1H\}$ NMR spectrum of Et_3PCS_2 displays a doublet resonance at 229.5 ppm ($^1J_{PC}$ = 43.95 Hz) for the C (of CS_2) atom. The magnitude of the coupling constant is similar to that observed for the methylene carbon atoms of the ethyl groups, $^1J_{PC}$ = 48.8 Hz. For Me_3PCS_2 the $^{13}C\{^1H\}$ NMR spectrum consists of a doublet at 233.4 ppm ($^1J_{PC}$ = 51.3 Hz) and a doublet at 10.04 ppm ($^1J_{PC}$ = 56.6 Hz) assignable to the CS_2 carbon atom and the methyl carbon atom, respectively. The ^{13}C chemical shift observed for R_3PCS_2 complexes is almost identical with that observed for $MeOCS_2K$ (234.68 ppm) and $EtOCS_2K$ (233.95 ppm).[45] The bonding in R_3PCS_2 complexes presumably involves donation of the phosphorus lone pair of electrons into the vacant $2\pi_u$ orbital (LUMO) of the CS_2 fragment. The existence of stable R_3PCS_2 complexes depends on the donor ability of the phosphine; less basic phosphines are incapable of forming stable complexes because not enough electron density is transferred to the CS_2 molecule.

Nine examples of complexes in which there is a phosphoniodithiocarboxylato ligand have been reported. The compounds $[Mo(CO)_2(PEt_3)(\mu\text{-}S_2CPEt_3)]_2$,[44] $[Ir(CO)(PPh_3)_2(Ph_3PCS_2)][BPh_4]$,[39] $RuCl_2(PEtPh_2)_2(EtPh_2PCS_2)$,[40] $[Fe(CO)_2(PPh_3)_2(Ph_3PCS_2)][PF_6]_2$,[41] $[PdR(PMe_3)_2(Me_3PCS_2)][BPh_4]$[21] (R = CH_3, $COCH_3$, C_6H_5), $PdI(COCH_3)(PMe_3)(Me_3PCS_2)$,[21] $[Fe(depe)_2(Et_3PCS_2)][BPh_4]_2$,[42] and $[RuH(CO)(R_3PCS_2)(PCy_3)_2][BPh_4]$[43] (R = Cy, Et) exist. It is interesting that three of these contain aryl-substituted phosphoniodithiocarboxylato linkages that cannot be prepared in the absence of the metal species.

The presence of a phosphoniodithiocarboxylato type ligand in $Ni(C_2S_4PMe_3)(PMe_3)$ is consistent with the ^1H NMR spectroscopy. We have found that the magnitude of the coupling constant for the phosphorus atom and the methyl protons is sensitive to the coordination site of the phosphine. Free PMe_3 has a value of $^2J_{PH}$ of 2.7 Hz. Coordination to a metal atom raises the value to 5–10 Hz, but PMe_3 derivatives involving complete use of the phosphorus atom lone pair of electrons have $^2J_{PH}$ values greater than 13 Hz (see Table VII). The coupling constant for Me_3PCS_2 of 13.4 Hz falls in the range expected. The ^1H NMR spectrum of $Ni(C_2S_4PMe_3)(PMe_3)$ consists of two doublets at room temperature, $^2J_{PH_1}$ = 13.4 Hz and $^2J_{PH_2}$ = 8.5 Hz, consistent with one PMe_3 molecule ligated to the nickel atom and one attached to a CS_2 molecule to form a phosphoniodithiocarboxylato type ligand. In the ^{31}P NMR spectrum (coupled to ^1H) the downfield resonance is split into 8 lines of an expected 10-line pattern, $^2J_{PH}$ = 13.4 Hz, and is assigned to the $Me_3PC_2S_4Ni$ resonance, while the upfield peak assigned to Me_3PNi is broadened but not resolved because of the smaller value of $^2J_{PH}$. Enrichment of $Ni(C_2S_4PMe_3)(PMe_3)$ in $^{13}CS_2$ (45%) results in the appearance of ^{13}C satellites on the downfield resonance ($^1J_{PC}$ = 73.3 Hz), further proof that this signal arises from a phosphoniodithiocarboxylato type linkage.

Table VIII. $^{13}C\{^1H\}$ NMR Spectral Data for CS_2 Complexes

compd	δ_{CS_2}[a]	ref
$Pt(CS_2)(PPh_3)_2$	253.2 (ddd, $J_{P_{cis}-C}$ = 4.3 Hz, $J_{P_{trans}-C}$ = 80.3 Hz, J_{Pt-C} = 565.5 Hz)	46
$Fe(CO)_2(CS_2)(PMe_3)_2$	288.0 (t, J_{P-C} = 15.6 Hz)	27
$Fe(CO)_2(PMe_3)_2(\mu\text{-}CS_2)\text{-}Mn(\eta^5\text{-}C_5H_5)(CO)_2$	283 (t, J_{P-C} = 14.0 Hz)	27
$Fe(CO)_2(PMe_3)_2(\mu\text{-}CS_2)Mo(CO)_5$	301.9 (J_{PC} = 17.3 Hz)	27
$[Fe(CO)_2(PMe_3)_2\text{-}(CS_2CH_2Ph)][PF_6]$	293.4 (J_{PC} = 16.5 Hz)	47
$Mn(\eta^5\text{-}C_5H_5)(CO)_2(CS_2)$	254.1	14
$[Mn(\eta^5\text{-}C_5H_5)(CO)_2]_2(\mu\text{-}CS_2)$	251.5	14
$[Pd(PMe_3)_2(S_2CHPMe_3)][BPh_4]$	45.27 (d, J_{PC} = 53.7 Hz)	21
$Ni(C_2S_4PMe_3)(PMe_3)$	42.4 (dd, J_{PC} = 74.4 Hz, J_{PC} = 28.1 Hz) 250.9 (d, J_{PC} = 26.9 Hz)	*b*

[a] Relative to Me_4Si. [b] This work.

The NMR spectral results for $Ni(C_2S_4PEt_3)(PEt_3)$ can be interpreted in a similar manner. The $^{31}P\{^1H\}$ NMR spectrum consists of two singlets at 47.2 and 30.0 ppm. The upfield peak, assignable to a nickel-bound PEt_3 ligand, is broadened. Cooling the sample results in the two peaks being split into doublets, $^2J_{PP}$ = 6.1 Hz. This suggests that the loss of P–P coupling is caused by associative exchange of the nickel-coordinated phosphine molecule. This process is slowed upon cooling the sample, and coupling is observed.

The $^{13}C\{^1H\}$ NMR spectrum of $Ni(C_2S_4PMe_3)(PMe_3)$ (45% enriched in $^{13}CS_2$) at room temperature contains two resonances arising from $^{13}CS_2$, a singlet at 251.2 ppm (δ_{C_2}) and a doublet at 42.6 ppm (δ_{C_1}, J_{PC} = 73.3 Hz). The splitting of the high-field peak is caused by coupling to a phosphorus atom, as confirmed by the $^{31}P\{^1H\}$ NMR spectrum (vide supra). Cooling the sample to −80 °C results in additional splitting of the $^{13}C\{^1H\}$ NMR spectrum because of coupling to the second phosphine molecule, which is no longer involved in an associative-exchange process. The spectrum now consists of a doublet at 250.9 ppm (δ_{C_2}, $J_{P_2C_2}$ = 26.9 Hz) and a doublet of doublets centered at 42.4 ppm (δ_{C_1}, $J_{P_1C_1}$ = 74.4 Hz, $J_{P_2C_1}$ = 28.1 Hz) (Figure 2). Limited $^{13}C\{^1H\}$ NMR spectral data have been reported for CS_2 complexes.[14,21,27,46,47] These are summarized in Table VIII.

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(38) Margulis, T. N.; Templeton, D. H. *J. Am. Chem. Soc.* **1961**, *83*, 995–996.

(39) Boniface, S. M.; Clark, G. R. *J. Organomet. Chem.* **1980**, *188*, 263–275.

(40) Armit, P. W.; Sime, W. J.; Stephenson, T. A.; Scott, L. *J. Organomet. Chem.* **1978**, *161*, 391–406.

(41) Baker, P. K.; Broadley, K.; Connelly, N. G. *J. Chem. Soc., Chem. Commun.* **1980**, 775.

(42) Bianchini, C.; Meli, A.; Orlandini, A.; Scapacci, G. *J. Organomet. Chem.* **1981**, *215*, C59–C62.

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(44) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Midollini, S.; Orlandini, A. *J. Organomet. Chem.* **1981**, *219*, C13–C15.

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(47) Touchard, D.; Le Bozec, H.; Dixneuf, P. H.; Carty, A. J.; Taylor, N. J. *Inorg. Chem.* **1981**, *20*, 1811–1817.

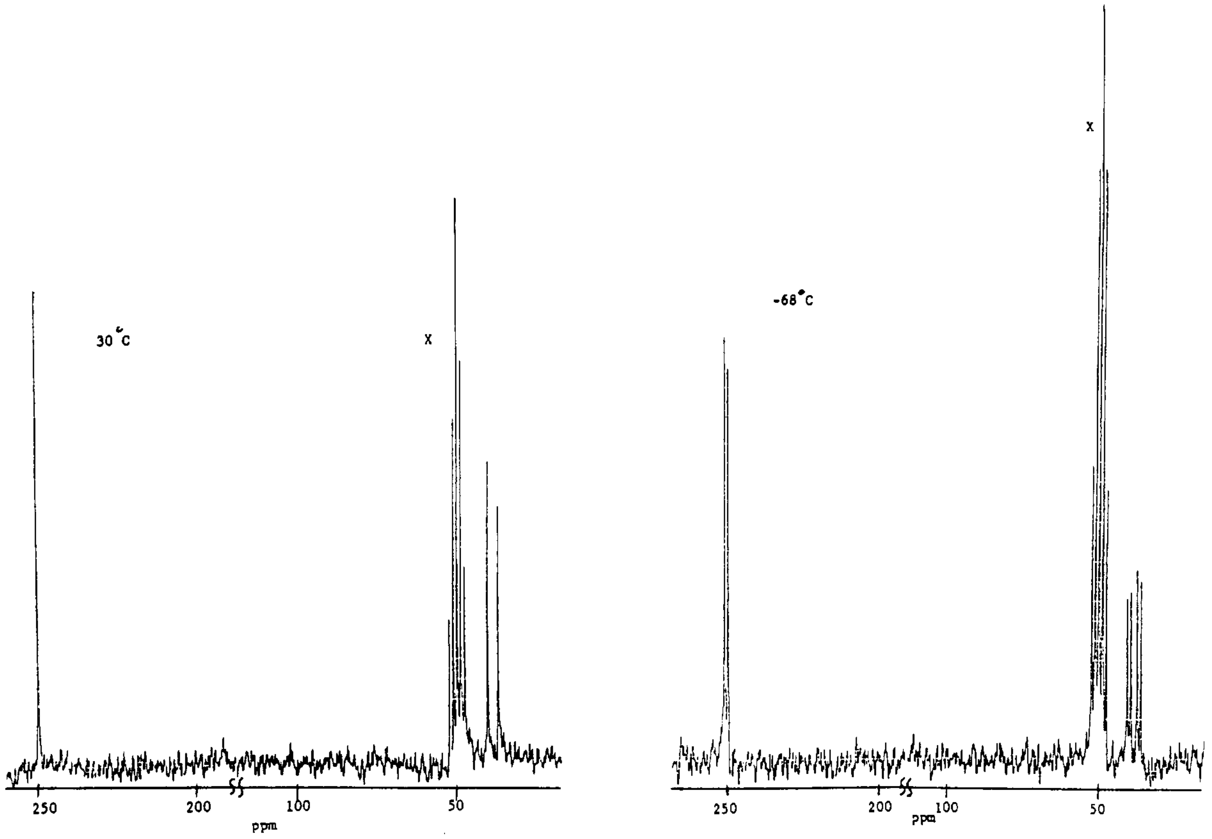

Figure 2. $^{13}C\{^1H\}$ NMR spectra of 45% $^{13}CS_2$-enriched Ni(SC(S)SC(PMe$_3$)S)(PMe$_3$) displaying bands enhanced by enrichment (peak X is the CD_2Cl_2 signal).

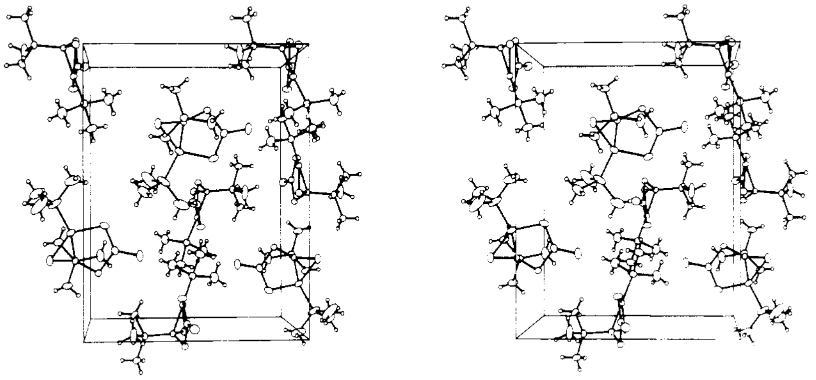

Figure 3. Stereoscopic packing diagram for Ni(SC(S)SC(PMe$_3$)S)(PMe$_3$) viewed down the *b* axis. Thermal ellipsoids are drawn at the 50% probability level except for hydrogen atoms, which have been drawn artificially small.

Bond distances given in Figure 1 are average values for the two independent molecules.[48] Selected bond lengths and bond angles are given in Tables IX and X. Unless otherwise noted, metrical parameters quoted in the text will be averaged values. The Cambridge Crystallographic Database[49] was used for the location and tabulation of comparative molecular parameters.

The crystal packing for Ni(SC(S)SC(PMe$_3$)S)(PMe$_3$) is displayed in Figure 3. The molecules are well separated with all contacts of the non-hydrogen atoms being greater than 3.50 Å, except for S(2)···S(2)′ (3.46 Å). In the immediate coordination sphere the two independent molecules are almost

Table IX. Selected Bond Distances (Å) for Ni(SC(S)SC(PMe$_3$)S)(PMe$_3$)

atoms	molecule 1	molecule 2
Ni-S(1)	2.156 (1)	2.164 (1)
Ni-C(1)	1.926 (3)	1.911 (3)
Ni-S(4)	2.152 (1)	2.154 (1)
Ni-P(2)	2.170 (1)	2.160 (1)
S(1)-C(1)	1.757 (3)	1.745 (3)
S(2)-C(1)	1.789 (3)	1.797 (3)
P(1)-C(1)	1.785 (3)	1.783 (3)
S(2)-C(2)	1.764 (3)	1.758 (3)
S(3)-C(2)	1.657 (3)	1.667 (3)
S(4)-C(2)	1.717 (3)	1.709 (3)
P(1)-C(3)	1.785 (3)	1.788 (4)
P(1)-C(4)	1.788 (4)	1.785 (4)
P(1)-C(5)	1.788 (5)	1.784 (4)
P(2)-C(6)	1.804 (4)	1.830 (6)
P(2)-C(8)	1.821 (5)	1.775 (6)
P(2)-C(7)	1.822 (4)	1.817 (5)

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(48) An estimated standard deviation in parentheses is the larger of that estimated for a single observation from the inverse matrix or from the values averaged.

(49) "Cambridge Crystallographic Database"; Cambridge Crystallographic Data Center, University Chemical Laboratory: Cambridge CB2 1EW, England, 1981.

Table X. Selected Bond Angles (deg) for Ni(SC(S)SC(PMe$_3$)S)(PMe$_3$)

atoms	molecule 1	molecule 2
C(1)-Ni-S(1)	50.59 (9)	50.22 (9)
C(1)-Ni-S(4)	92.44 (9)	93.30 (9)
C(1)-Ni-P(2)	161.84 (9)	161.6 (1)
S(1)-Ni-S(4)	139.02 (3)	138.70 (4)
S(1)-Ni-P(2)	112.45 (4)	112.70 (5)
S(4)-Ni-P(2)	105.68 (4)	105.10 (5)
C(1)-S(1)-Ni	57.93 (9)	57.3 (1)
C(1)-S(2)-C(2)	100.8 (1)	101.0 (1)
C(2)-S(4)-Ni	101.6 (1)	101.0 (1)
S(1)-C(1)-Ni	71.5 (1)	72.4 (1)
S(1)-C(1)-P(1)	114.7 (2)	114.8 (2)
S(1)-C(1)-S(2)	125.2 (2)	124.7 (2)
S(2)-C(1)-P(1)	113.3 (2)	113.2 (2)
S(2)-C(1)-Ni	111.3 (1)	111.4 (1)
P(1)-C(1)-Ni	113.2 (1)	113.1 (2)
S(2)-C(2)-S(3)	117.1 (2)	115.8 (2)
S(2)-C(2)-S(4)	118.5 (2)	119.2 (2)
S(3)-C(2)-S(4)	124.3 (2)	124.9 (2)
C(1)-P(1)-C(3)	109.2 (2)	110.0 (1)
C(1)-P(1)-C(4)	111.5 (2)	111.0 (2)
C(1)-P(1)-C(5)	110.0 (2)	110.5 (2)
C(3)-P(1)-C(4)	108.4 (2)	108.8 (2)
C(3)-P(1)-C(5)	108.8 (2)	107.7 (2)
C(4)-P(1)-C(5)	108.9 (3)	108.8 (2)
C(6)-P(2)-Ni	116.4 (1)	116.2 (2)
C(7)-P(2)-Ni	112.6 (1)	113.4 (2)
C(8)-P(2)-Ni	117.1 (2)	115.6 (2)
C(6)-P(2)-C(7)	103.7 (2)	102.9 (3)
C(6)-P(2)-C(8)	102.3 (2)	101.9 (4)
C(7)-P(2)-C(8)	102.9 (2)	105.2 (3)

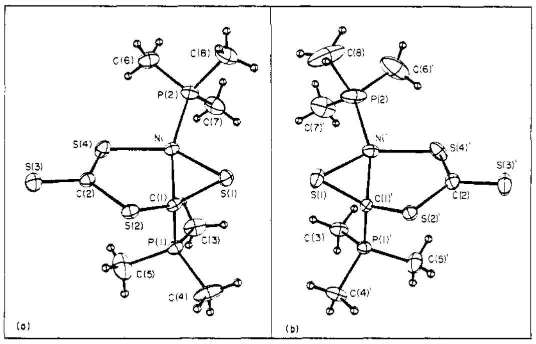

Figure 4. Enantiomeric relationship between (a) molecule 1 and (b) molecule 2.

identical, although the agreement between corresponding distances and angles in the two molecules is not as good as one might expect. Figure 4 displays the enantiomorphic relationship between the two crystallographically independent molecules. The largest structural differences between them involve methyl group rotations. The S(1)-Ni-P(2)-C$_{Me}$ and Ni-C(1)-P(1)-C$_{Me}$ torsion angles in molecule 1 differ by an average of 7 (1) and 7.4 (4)°, respectively, from the corresponding angles in molecule 2.

The Ni atom is coordinated to the phosphorus atom of a PMe$_3$ ligand, to a sulfur atom at one end of the SC(S)SC(PMe$_3$)S ligand, and to a S⋯C bond (in an η^2 fashion) at the other end of the linkage. The Ni-S(4) bond length of 2.153 (1) Å falls within the range of Ni-S distances previously reported (range 2.094-2.814 Å) for Ni-S-C bonding fragments.[50] The Ni-S(4) bond length and the Ni-S(4)-C(2) angle (101.3 (4)°) are comparable with the corresponding parameters in the $[Ni(S_2C_2(CN)_2)_2]^{2-}$[51] anion (mean Ni-S 2.160 (5) Å; mean Ni-S-C 103.0 (5)°). In the present structure the Ni-P bond length of 2.165 (7) Å is shorter than the mean Ni-P distance (mean Ni-P 2.22 (3) Å; range 2.194-2.290 Å) derived from known Ni-PMe$_3$ fragments,[49,52] while the Ni-P-C angle of 115 (2)° is normal (mean Ni-P-C 116 (3)°; range 107.6-123.5°). The mean P(2)-C(Me) distance of 1.81 (2) Å lies within the range (mean P-C 1.84(3) Å; range 1.787-1.887 Å) of observed P-C distances in Ni-PMe$_3$ units as does the C-P(2)-C bond angle of 103 (1)° (mean C-P-C 102°; range 97.2-107.0°). An η^2 bonding mode for the S(1)-C(1) linkage may be inferred from a comparison of the Ni-S(1) and Ni-C(1) bond lengths (2.159 (6) and 1.92(1) Å, respectively) with M-S and M-C distances found in η^2-CS$_2$ transition-metal complexes: in [Co(η^2-CS$_2$)(triphos)][24] the Co-S distance is 2.206 (4) Å and the Co-C distances is 1.88 (1) Å; in [Fe(CO)$_2$(η^2-CS$_2$)(PMe$_3$)(PPh$_3$)][17] the Fe-S and Fe-C(CS$_2$) distances are 2.334 (2) and 1.983 (8) Å, respectively. Of course, all of the M-(η^2-CS$_2$) linkages may alternatively be viewed as substituted cyclopropanes. But if one assumes that the midpoint of the S(1)-C(1) bond (Q = bond midpoint) occupies one coordination site of a trigonal complex, then the geometry of the coordination sphere is as follows: Ni-Q = 1.846 Å, P(2)-Ni-Q = 135.9°, S(4)-Ni-Q = 117.8°, P(2)-Ni-S(4) = 105.4 (4)°. The Ni atom lies 0.1 Å from a plane defined by Q and atoms S(4) and P(2). The S(1)-C(1) bond axis is tilted by 72° with respect to the normal to this plane.

The SC(S)SC(PMe$_3$)S linkage can be formally described as a condensation product of two molecules of CS$_2$ with one molecule of PMe$_3$. Previous examples of phosphoniodithiocarboxylato linkages in monometallic complexes have involved coordination of both sulfur atoms to the metal atom. In Ni(C$_2$S$_4$PMe$_3$)(PMe$_3$) one sulfur atm of the phosphonio dithiocarboxylato ligand has migrated to the carbon atom of a CS$_2$ molecule. The -S(4)C(2)[S(3)]S(2)- fragment is essentially planar with the largest deviation being 0.026 (3) Å for atom C(2). The sulfur-carbon bond lengths in this portion of the ligand have a range of 1.662 (7)-1.761 (4) Å compared with the value of S—C = 1.81 Å and S═C = 1.71 Å.[53] These parameters are indicative of delocalized bonding within this planar fragment of the ligand. Atom C(1) lies 0.265 (6) Å out of a plane defined by the four-atom fragment S(1)C(1)[P(1)]S(2). However, the C(1)⋯S(1) bond distance of 1.751 (9) Å is longer than corresponding carbon-sulfur bond distances observed in η^2-CS$_2$ transition-metal complexes: 1.676 (7) Å in [Fe(CO)$_2$(η^2-CS$_2$)(PMe$_3$)(PPh$_3$)][17] and 1.68 (1) Å in [(triphos)Co(η^2-CS$_2$)].[24] The bond length pattern is consistent with the spectroscopic results. The delocalized bonding around atom C(2) provides a pathway for coupling between the metal-bound phosphine (P(2)) and C(2). The single bond between atoms C(1) and S(2) blocks communication between atoms P(1) and C(2), and no coupling is seen in the $^{13}C\{^1H\}$ NMR spectrum. The CS stretching frequencies observed at 1010 and 850 cm^{-1} are comparable with those seen for [N(CH$_3$)$_4$]$_2$[Ni(CS$_3$)$_2$][54] at 1015 and 855 cm^{-1}. These are assigned to the exocyclic ν_{CS} and the endocyclic ν_{CS} vibrations, respectively.

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(50) A search of the Cambridge Database produced 160 structures possessing a Ni-S-C structural fragment.

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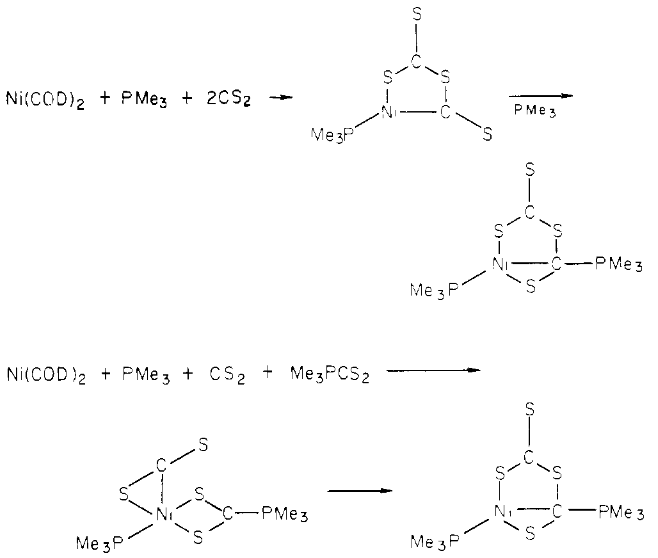
Scheme I



Three examples of transition-metal complexes containing C_2S_4 linkages have been reported recently.[25,32,36] But as can be deduced from Table VI, the SC(S)SC(PMe_3)S linkage in the present structure is the first example of a CS_2 condensation linkage that has an incorporated phosphine. Two possible routes to this compound are proposed in Scheme I.

Attempts to prepare additional nickel complexes that contain R_3PCS_2 ligands were unsuccessful. Addition of R_3PCS_2 (R = Et, Bu) to preformed Ni(COD)(dppe) (from $Ni(COD)_2$ and dppe; dppe = 1,2-bis(diphenylphosphino)ethane) upon prolonged mixing yielded no reaction. Generation of Ni(COD)(dppe) in situ by a Zn reduction of $NiCl_2$(dppe) in the presence of COD[55] followed by addition of R_3PCS_2 resulted in the formation of orange compounds of unknown structure.

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Registry No. $[Ni(CS_2)(PPh_3)]_2$, 55891-51-5; $[Ni(CS_2)(P(p\text{-tol})_3)]_2$, 82999-54-0; $[Ni(CS_2)(PCy_3)]_2$, 82999-55-1; $Ni(C_2S_4PMe_3)(PMe_3)$, 82999-59-5; $Ni(C_2S_4PEt_3)(PEt_3)$, 82999-60-8; $Ni(COD)_2$, 1295-35-8; Cy_3PCS_2, 70165-72-9; Et_3PCS_2, 3736-69-4; Me_3PCS_2, 83334-89-8; PEt_3, 554-70-1; PMe_3, 594-09-2; CS_2, 75-15-0.

Supplementary Material Available: Anisotropic thermal parameters (Table IV) and observed and calculated structure amplitudes (Table V) (22 pages). Ordering information is given on any current masthead page.

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Structure and Reactivity of $M^+[Fe(CO)_3(NO)]^-$

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The solid and solution structures of $M^+[Fe(CO)_3(NO)]^-$ have been investigated with use of a combination of IR and NMR spectroscopy and X-ray crystallography. Ion pairing has been shown to be important, and tight ion pairs involving a cation–nitrosyl interaction have been observed. The chemical reactivity of the salt has been investigated, with MeI as a substrate, and product variations have been noted as a function of solvent and cation variations. A kinetic study of the above reaction shows relatively small rate variations as a function of ion pairing but does clearly illustrate that the solvent-separated ion pairs are more kinetically reactive. A study using the metalate system to evaluate the cation-complexing capacities of crown ethers is included. The crystal and molecular structures were determined from 3656 data (Mo Kα) for which $I > 3\sigma(I)$. The space group is $P2_1/c$. Cell constants are a = 17.533 (6) Å, b = 9.202 (17) Å, c = 22.026 (11) Å, and β = 96.15 (3)°, with V = 3533.17 Å. The structure consists of isolated PPN cations and $Fe(CO)_3(NO)$ anions, and while the former are fully ordered and bent (P–N–P angle 140.5 (3)°) the latter are disordered in such a way that the NO ligand occupies each of the four tetrahedral sites nearly one-fourth of the time. Thus, there is not sufficient anchoring of the anion by the cation, which would prevent lattice disorder of CO's and NO, but the disorder is not perfect. The average Fe–X (X = C, N) bond length is 1.71 Å, which is a little longer than the values found for *ordered* Fe–NO bonds but comparable with other cases of disordered iron carbonyl nitrosyls. The average value of the P–N bonds is 1.58 (1) Å, which is normal. The phenyl rings are well-behaved insofar as distances and angles are concerned.

Introduction

The use of transition-metal metalates as reactive intermediates in the formation of metal–carbon bonds is well established.[2] Detailed studies on the solution structures of these intermediates and their mode of reactivity have only recently begun to attract attention. Initial studies by Edgell and coworkers illustrated that $M^+[Co(CO)_4]^-$ existed in solution as a mixture of tight and solvent-separated ion pairs in which the former contained a cation–carbonyl oxygen interaction.[3] Related cation–carbonyl oxygen interactions have been subsequently reported, e.g., $[Mn(CO)_5]^-$,[4,5] $[HFe(CO)_4]^-$,[6] and $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(L)]^-$,[7] while cation–ketonic carbonyl tight ion pairs have been observed in the $[LFe(CO)_3COPh]^-Li^+$ system[8] and cation–cyanide interactions reported for $[Fe(CO)_4(CN)]^-Na^+$ and $[Mo(CO)_5(CN)]^-Na^+$.[21] In addition to cation–carbonyl tight ion pairs, the widely used $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ system has been shown to exhibit a further,

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(1) (a) The University of Texas at El Paso. (b) The University of Houston.

(2) For an early review of this topic, see R. B. King, *Adv. Organomet. Chem.*, **2**, 157 (1964); for a later review, see J. Ellis, *J. Organomet. Chem.*, **86**, 1 (1975).

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