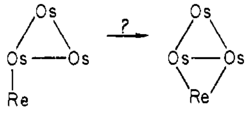
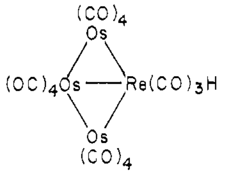
valence electrons = $18n - 2b$, where n is the number of metal atoms in the cluster and b is the number of metal–metal linkages). It is known[7] to lose a carbonyl ligand to form the species $H_2Os_3Re_2(CO)_{19}$; clearly a sixth metal–metal linkage has been formed; no unambiguous assignment as to its position can be made, although it is probable that further "triangulation" of the metal-atom framework has occurred. Similar problems exist with the closely related tetranuclear species $HOs_3Re(CO)_{16}$ (probably having the skeletal framework III —i.e., an equatorially monospiked triangular cluster or "tetrametallamethylcyclopropane" skeleton) and its conversion, upon carbonyl loss, to an $HOs_3Re(CO)_{15}$ molecule (possibly having the rhomboidal skeleton, IV). It should be noted that the $HOs_3Re(CO)_{15}$ molecule isolated via this decarbonylation reaction is apparently[7] different from the $HOs_3Re(CO)_{15}$ molecule synthesized from $Os_3(CO)_{12}$, $Re(CO)_5^-$, and H^+ (cf. ref 17) and previously shown by us[4] to have structure V. The general problem of possible isomerism based upon metal position is another area which has yet to receive significant attention. Work on these species is continuing and will be reported in subsequent articles.



III IV



V

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Registry No. I, 64885-82-1.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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Four-Coordinate Metal Nitrosyls. 2.[1] Structures of $NiX(NO)(P(C_6H_5)_3)_2$ Complexes[2]

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The crystal and molecular structure of (isothiocyanato)nitrosylbis(triphenylphosphine)nickel, $Ni(NCS)(NO)(P(C_6H_5)_3)_2$, has been determined by single-crystal X-ray diffraction. The complex crystallizes in the triclinic space group $P\bar{1}$ with two molecules in a unit cell of dimensions $a = 12.288$ (3) Å, $b = 13.496$ (3) Å, $c = 9.947$ (2) Å, $\alpha = 91.25$ (2)°, $\beta = 86.80$ (2)°, and $\gamma = 95.58$ (2)°. Full-matrix least-squares refinement of the structure based on 4420 unique reflections having $F_o^2 \geq 3\sigma(F_o^2)$ converged with a conventional R factor of 0.065. The structure consists of discrete $Ni(NCS)(NO)(P(C_6H_5)_3)_2$ molecules with pseudotetrahedral coordination geometry about the Ni atom. The P–Ni–P angle is 111.98 (6)°, the N–Ni–N angle is 116.82 (22)°, and the dihedral angle between the P–Ni–P and N–Ni–N planes is 81.73°. The distinctly nonlinear nitrosyl group has an Ni–N–O angle of 161.5 (5)°. The two Ni–P distances of 2.271 (2) and 2.328 (2) Å are significantly different. Chloronitrosylbis(triphenylphosphine)nickel, $NiCl(NO)(P(C_6H_5)_3)_2$, crystallizes in a monoclinic space group (Cc or $C2/c$) with unit cell dimensions of $a = 17.399$ (3) Å, $b = 13.136$ (3) Å, $c = 16.945$ (3) Å, and $\beta = 104.74$ (1)° and four molecules per unit cell. The $NiCl(NO)(P(C_6H_5)_3)_2$ molecules are pseudotetrahedral with an approximate P–Ni–P angle of 121°. The space group could not be unambiguously assigned nor could a satisfactory description of the N, O, and Cl positions be obtained from the several disordered and ordered models which were refined.

Introduction

It has been shown[3-5] that the geometries of $\{MNO\}^7$ and $\{MNO\}^8$ triatomic fragments[6] can be controlled by the stereochemistry of the other ligands coordinated to the metal. The properties of $\{MNO\}^{10}$ complexes should also be sensitive to the stereochemistry about the metal atom, and two limiting possibilities have been proposed[3,7] for four-coordinate complexes containing the $\{MNO\}^{10}$ moiety: (1) pseudotetrahedral geometry with a linear MNO group; (2) square-planar geometry with a strongly bent MNO group. These proposed limiting situations imply that distorted coordination geometries may have intermediate MNO angles.

Several years ago we showed[1] that the $\{NiNO\}^{10}$ complex $Ni(N_3)(NO)(P(C_6H_5)_3)_2$ has distorted tetrahedral coordi-

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nation geometry, inequivalent Ni–P distances, and an intermediate Ni–N–O angle of 153°. The structures of several cationic $\{NiNO\}^{10}$ complexes have been reported in which each nickel atom is also coordinated to three phosphorus atoms.[9-11] All are pseudotetrahedral and exhibit Ni–N–O angles in the range 168–180°. Intermediate M–N–O angles have recently been reported for two $\{RhNO\}^{10}$ complexes. In $Rh(NO)(SO_2)(P(C_6H_5)_3)_2$ the Rh–N–O angle is 140°, and the rhodium atom is considered to be four-coordinate even though the SO_2 ligand is attached to the metal through both the sulfur atom and one of the oxygen atoms.[8] In $Rh(NO)(P(C_6H_5)_3)_3$ a Rh–N–O angle of 157° is reported, but the interpretation is complicated by a threefold disorder.[33] Thus, $Ni(N_3)(NO)(P(C_6H_5)_3)_2$ remains one of the best characterized examples of a four-coordinate $\{MNO\}^{10}$ complex with an intermediate M–N–O angle. Moreover, the accessibility of complexes with a variety of X groups in addition to N_3^- makes the $NiX(NO)(P(C_6H_5)_3)_2$ series amenable to systematic structural investigation.

It was originally suggested[1] that the irregular stereochemistry of $Ni(N_3)(NO)(P(C_6H_5)_3)_2$ was due in part to the asymmetric nonbonded interactions between the phosphorus atoms and the bent azide ligand. In order to further explore the relationships among coordination geometry, the Ni–N–O angle, and the nature of X in $NiX(NO)(P(C_6H_5)_3)_2$ complexes, we have carried out structural studies of the complexes with X = Cl^- (spherical anion with ligand field strength similar to N_3^-) and with X = NCS^- (triatomic ligand with a nitrogen donor atom which coordinates linearly to the metal rather than angularly as does N_3^-). The results of these investigations are reported herein.

Experimental Section

Preparation of Compounds. Triphenylphosphine was obtained from Eastern Chemical Corp.; sodium nitrite and potassium thiocyanate were reagent grade; solvents were reagent grade and were dried by the use of Linde Molecular Sieves and degassed by bubbling dry nitrogen through them just prior to use. Since the complexes are sensitive to oxygen while in solution, all preparations and recrystallizations were carried out using standard Schlenk apparatus connected to a double-manifold vacuum/nitrogen line. A nitrogen atmosphere was maintained over all solutions.

$NiCl(NO)(P(C_6H_5)_3)_2$ was prepared according to the method published by Feltham.[12] Recrystallization of the product was effected by adding *n*-hexane to a benzene solution.

$Ni(NCS)(NO)(P(C_6H_5)_3)_2$. A suspension of $NiCl(NO)(P(C_6H_5)_3)_2$ (0.068 g, 0.105 mmol) in 25 mL of dried, degassed methanol was prepared. KSCN (0.022 g, 0.225 mmol) was added to the suspension, and the mixture was stirred for 20 h. The product (dark purple-blue powder) was filtered off, washed three times with water and twice with methanol, and dried under vacuum. The product was recrystallized from benzene/*n*-heptane (0.037 g, 53% yield).

Sample Preparation. Several previous attempts[13] to obtain single crystals of these complexes suitable for X-ray diffraction studies were unsuccessful. Methods utilized in the previous attempts included various solvent/nonsolvent systems for liquid diffusion, temperature gradient, and combined liquid diffusion–temperature gradient techniques. In all cases crystal growth was complete in 2–3 days. Longer growing times were not used because of problems with the formation of triphenylphosphine oxide. The crystals obtained were often visibly twinned or were shown to be badly split when examined on the diffractometer by the ω-scan technique.

Suitable crystals for X-ray structure determination were grown by vapor diffusion. Approximately 3 mL of a nearly saturated solution of the complex was placed in a small test tube which was then placed inside a Schlenk tube containing about 10 mL of nonsolvent. The Schlenk tube was purged with nitrogen and then was sealed and set aside in a quiet place at room temperature. After crystallization was complete (the solution became colorless), the crystals were collected on a frit and washed several times with diethyl ether and then dried in a stream of nitrogen. The complexes are quite stable to the atmosphere in the solid state and no special precautions were taken for handling the dry crystalline materials. The crystals used in the structural studies were obtained from benzene/*n*-hexane or benzene/*n*-heptane over a 4–5 day period.

Data Collection and Structural Work. $Ni(NCS)(NO)(P(C_6H_5)_3)_2$. Preliminary precession photographs (Cu Kα) indicated that the crystals were triclinic. The space group was assumed to be $P\bar{1}$ which was confirmed by subsequent successful solution and refinement of the structure. The crystal used for the preliminary precession photographs was mounted on a Picker FACS-1 four-circle diffractometer, and 5040 unique data were collected ($(\sin\theta)/\lambda \leq 0.565$ Å^{-1}) using Cu Kα radiation. Three standard reflections from diverse regions of reciprocal space were monitored every 100 reflections. The intensities of the standard reflections exhibited an average decline of 25% during the time required to collect the data. This decline may have been due to instrumental problems which were diagnosed shortly after completion of data collection or due to decomposition caused by Cu Kα X-rays. After successful solution of the structure, better data were obtained from another crystal under different experimental conditions (vide infra).

The structure was solved by direct methods using the MULTAN[16] package and the 400 reflections with the highest values of $|E|$. An E map based upon these reflections revealed the nickel, both phosphorus, both nitrogen, the sulfur, and 24 carbon atoms. A difference electron density map calculated after two cycles of refinement on the positions of the 30 atoms located by MULTAN revealed the rest of the carbon atom positions. The carbon atoms of the phenyl rings were then treated as rigid groups (C–C = 1.383 Å, D_{6h}-$6/mmm$ symmetry)[5] with individual isotropic thermal parameters. After three cycles of refinement varying the positions of the seven atoms and the six phenyl groups and the individual isotropic thermal parameters, a difference electron density map clearly revealed the position of the oxygen atom.

A second data set was collected from a new crystal of approximate dimensions 0.13 × 0.14 × 0.20 mm using a Syntex $P2_1$ diffractometer. The unit cell parameters determined from a least-squares refinement of the setting angles of 19 automatically centered reflections from diverse regions of reciprocal space having $2\theta < 23°$ (Mo K$\bar{\alpha}$, λ 0.71069 Å) are a = 12.288 (3) Å, b = 13.496 (3) Å, c = 9.947 (2) Å, α = 91.25 (2)°, β = 86.80 (2)°, and γ = 95.58 (2)°. The observed density of 1.36 g/cm^3, determined by flotation in carbon tetrachloride/*n*-heptane, agrees with the calculated density of 1.36 g/cm^3 for two formula units of $Ni(NCS)(NO)(P(C_6H_5)_3)_2$ per unit cell. A total of 7884 unique reflections having $(\sin\theta)/\lambda \leq 0.675$ Å^{-1} were collected. The diffractometer utilized an incident-beam monochromator equipped with a graphite crystal to obtain Mo Kα radiation. The reflections were collected using a θ–2θ step-scan technique (96 steps) with a scan range from 2θ(Mo Kα_1) − 0.7° to 2θ(Mo Kα_2) + 0.7° (λ(Mo Kα_1) 0.70926 Å; λ(Mo Kα_2) 0.71354 Å). Any step of the scan which exceeded 5000 counts was corrected for coincidence losses. The scan rate was variable and ranged from 2.0 to 29.3°/min and was based on the count of a 2 s prescan through the peak. Stationary-crystal, stationary-counter backgrounds were measured at both ends of the scan, each for half the time of the scan. Throughout data collection three standard reflections from diverse regions of reciprocal space were monitored every 100 reflections. The intensities of the standard reflections showed no systematic changes during the time required to collect the data.

Intensities were calculated by the formula $I = [C - (t_s/t_b)(B_H + B_L)](SR)$ where C is the total integrated peak count, t_s and t_b are the scan time and the total background time, B_H and B_L are the two background counts, and SR is the scan rate. Standard deviations were assigned by the formula $\sigma(I) = [C + (t_s/t_b)^2(B_H + B_L)]^{1/2}(SR)$. Lorentz and polarization[21] corrections were then applied to I and $\sigma(I)$ using $Lp = \{[(1 + \cos^2 2\theta_m \cos^2 2\theta)/(1 + \cos^2 2\theta_m)] + [(1 + |\cos 2\theta_m| \cos^2 2\theta)/(1 + |\cos 2\theta_m|)]\}/(2 \sin 2\theta)$ where θ_m is the Bragg angle of the monochromator crystal (6.1°) and θ is the Bragg angle of the reflection being observed. Since the linear absorption coefficient is only 7.83 cm^{-1} for Mo Kα radiation and the crystal was small and of fairly equant habit, no absorption corrections were applied to this data set.

Refinement of the complete structure was based on F_o with the function $\sum w(|F_o| - |F_c|)^2$ being minimized; the weights were taken as $w = 4F_o^2/[\sigma(F_o^2) + (pF_o^2)^2]$ with p = 0.03. Atomic scattering factors for the nonhydrogen atoms were taken from the tabulation of Cromer and Waber.[17] The effects of anomalous scattering for the nickel, phosphorus, and sulfur atoms were included in the calculated structure factors.[18] Refinement was carried out using the 4420

Table I. Final Atomic and Group Parameters for $Ni(NCS)(NO)(P(C_6H_5)_3)_2$

Atom[a]	x	y	z
Ni	0.82780(6)	0.83008(5)	0.81197(7)
P(1)	0.69210(11)	0.89311(10)	0.70467(13)
P(2)	0.89452(11)	0.69582(10)	0.69410(14)
S	0.64233(18)	0.64380(15)	1.16458(22)
C(1)	0.7087(5)	0.7090(4)	1.0455(6)
N(1)	0.7550(4)	0.7539(4)	0.9605(5)
N(2)	0.9071(4)	0.9308(4)	0.8516(5)
0	0.9387(5)	1.0136(4)	0.8689(6)

Group[b]	x_c	y_c	z_c	ϕ	θ	ρ
P1R1	0.45999(20)	0.76216(19)	0.69644(22)	0.4549(22)	2.6786(23)	0.0625(25)
P1R2	0.62182(20)	1.09168(20)	0.85583(26)	-2.756(5)	-2.0652(22)	-1.529(5)
P1R3	0.76546(20)	0.95947(18)	0.40268(24)	2.2366(27)	2.7165(20)	1.5879(25)
P2R1	1.00260(23)	0.72934(21)	0.47239(27)	0.9724(28)	2.7718(23)	2.0080(26)
P2R2	1.07260(22)	0.59446(22)	0.85374(26)	2.8745(29)	2.6342(26)	-0.5807(29)
P2R3	0.70069(21)	0.52529(19)	0.63833(26)	-0.8303(26)	2.8049(21)	1.4291(28)

Group	B_1	B_2	B_3	B_4	B_5	B_6
P1R1	3.12(10)	3.78(11)	4.79(13)	4.70(13)	4.40(12)	3.76(11)
P1R2	3.12(10)	4.42(12)	5.79(15)	5.53(15)	5.02(14)	3.86(11)
P1R3	2.94(9)	3.97(11)	4.54(13)	4.69(13)	4.68(13)	3.86(11)
P2R1	3.17(10)	4.57(13)	5.50(15)	5.64(15)	5.70(15)	4.45(12)
P2R2	3.81(11)	4.77(13)	6.23(17)	5.90(16)	5.80(16)	5.10(14)
P2R3	3.21(10)	4.09(12)	5.04(14)	5.50(15)	5.58(15)	4.58(13)

[a] x, y, and z are fractional triclinic coordinates. Anisotropic thermal parameters for the nongroup atoms are given in Table S1 in the supplementary material. [b] x_c, y_c, and z_c are the fractional coordinates of the group origins. The angles ϕ, θ, and ρ (in radians) are the rotations necessary to bring about alignment (except for translation) of the group internal-coordinate system with the fixed crystallographic coordinate system. B_i is the isotropic thermal parameter in square angstroms of atom i in a given group. The rings are numbered so that atom C_1 is attached to P and atom C_4 is para to C_1.

Table II. Derived Parameters for the Group Carbon Atoms for $Ni(NCS)(NO)(P(C_6H_5)_3)_2$[a]

group	atom	x	y	z
P1R1	C(1)	0.5601 (2)	0.8185 (2)	0.6976 (4)
	C(2)	0.5486 (2)	0.7232 (3)	0.7482 (4)
	C(3)	0.4485 (3)	0.6668 (2)	0.7471 (4)
	C(4)	0.3598 (2)	0.7058 (3)	0.6953 (4)
	C(5)	0.3713 (2)	0.8011 (3)	0.6446 (4)
	C(6)	0.4715 (3)	0.8575 (2)	0.6458 (4)
P1R2	C(1)	0.6549 (3)	1.0084 (2)	0.7877 (3)
	C(2)	0.6559 (3)	1.0142 (3)	0.9266 (3)
	C(3)	0.6228 (4)	1.0975 (3)	0.9948 (3)
	C(4)	0.5887 (4)	1.1750 (3)	0.9240 (4)
	C(5)	0.5878 (3)	1.1691 (2)	0.7850 (4)
	C(6)	0.6208 (3)	1.0858 (3)	0.7169 (3)
P1R3	C(1)	0.7299 (3)	0.9309 (3)	0.5317 (3)
	C(2)	0.6774 (2)	0.8883 (2)	0.4222 (4)
	C(3)	0.7129 (3)	0.9169 (3)	0.2931 (3)
	C(4)	0.8010 (3)	0.9880 (3)	0.2736 (3)
	C(5)	0.8535 (3)	1.0306 (3)	0.3832 (4)
	C(6)	0.8180 (3)	1.0021 (3)	0.5122 (3)
P2R1	C(1)	0.9738 (3)	0.7193 (3)	0.5330 (3)
	C(2)	0.9270 (2)	0.7687 (3)	0.4339 (4)
	C(3)	0.9847 (3)	0.7888 (3)	0.3126 (3)
	C(4)	1.0891 (3)	0.7595 (3)	0.2904 (3)
	C(5)	1.1358 (2)	0.7101 (3)	0.3896 (4)
	C(6)	1.0782 (3)	0.6900 (3)	0.5109 (4)
P2R2	C(1)	0.9892 (3)	0.6351 (3)	0.7926 (4)
	C(2)	1.0535 (4)	0.6925 (2)	0.8802 (4)
	C(3)	1.1369 (3)	0.6519 (3)	0.9414 (4)
	C(4)	1.1560 (3)	0.5539 (3)	0.9149 (4)
	C(5)	1.0917 (4)	0.4964 (2)	0.8273 (5)
	C(6)	1.0083 (3)	0.5370 (3)	0.7661 (4)
P2R3	C(1)	0.7881 (3)	0.5958 (3)	0.6577 (4)
	C(2)	0.7388 (3)	0.5426 (3)	0.7657 (3)
	C(3)	0.6514 (3)	0.4721 (3)	0.7464 (3)
	C(4)	0.6133 (3)	0.4547 (3)	0.6190 (4)
	C(5)	0.6626 (3)	0.5079 (3)	0.5109 (3)
	C(6)	0.7500 (3)	0.5785 (3)	0.5303 (3)

[a] x, y, and z are fractional triclinic coordinates. Estimated standard deviations (given in parentheses) are derived from those of the group parameters by NUCLS.

Table III. Fixed Hydrogen Atom Positions (in Fractional Triclinic Coordinates) for $Ni(NCS)(NO)(P(C_6H_5)_3)_2$

group	atom	x	y	z
P1R1	H(2)	0.6095	0.6965	0.7837
	H(3)	0.4406	0.6014	0.7818
	H(4)	0.2911	0.6670	0.6945
	H(5)	0.3105	0.8278	0.6091
	H(6)	0.4794	0.9229	0.6110
P1R2	H(2)	0.6793	0.9611	0.9752
	H(3)	0.6235	1.1016	1.0901
	H(4)	0.5661	1.2322	0.9707
	H(5)	0.5644	1.2223	0.7364
	H(6)	0.6202	1.0818	0.6215
P1R3	H(2)	0.6170	0.8394	0.4356
	H(3)	0.6769	0.8876	0.2179
	H(4)	0.8254	1.0076	0.1850
	H(5)	0.9140	1.0795	0.3698
	H(6)	0.8540	1.0313	0.5874
P2R1	H(2)	0.8553	0.7887	0.4491
	H(3)	0.9526	0.8227	0.2445
	H(4)	1.1287	0.7733	0.2071
	H(5)	1.2075	0.6901	0.3744
	H(6)	1.1103	0.6561	0.5791
P2R2	H(2)	1.0404	0.7598	0.8983
	H(3)	1.1811	0.6914	1.0015
	H(4)	1.2132	0.5260	0.9569
	H(5)	1.1048	0.4291	0.8091
	H(6)	0.9641	0.4976	0.7060
P2R3	H(2)	0.7650	0.5545	0.8533
	H(3)	0.6176	0.4356	0.8206
	H(4)	0.5532	0.4063	0.6056
	H(5)	0.6363	0.4960	0.4234
	H(6)	0.7838	0.6150	0.4561

reflections with $F_o^2 \geq 3\sigma(F_o^2)$. In the final cycles anisotropic thermal parameters were assumed for the eight nongroup atoms and individual isotropic thermal parameters for the group carbon atoms. Each of the 30 hydrogen atoms was included in an idealized position (C–H distance 0.95 Å)[19] and given an isotropic thermal parameter 1.0 Å^2 larger than that of the carbon atom to which it is attached. The hydrogen atom scattering factor curve was obtained from the calculation of Stewart, Davidson, and Simpson.[20] Refinement converged with $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.065$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2} = 0.069$. The standard deviation of an observation of unit weight was 2.06. For the final cycle of refinement the number of observations was 4420 and the number of variables was 145, giving an observation to variable ratio of 30.5:1.

During the final cycle of least-squares refinement all of the parameter shifts were less than 0.2σ. The largest peak in the final difference electron density map was 1.1 e/Å^3. All of the prominent peaks on the map were closely associated with the phenyl rings and would likely be removed by refining the rings as individual anisotropic carbon atoms. Analysis of the weighting scheme showed small dependencies of $w(|F_o| - |F_c|)^2$ on $(\sin \theta)/\lambda$ which could also be accounted for on the basis of the incomplete description of the phenyl carbon atoms. Possibly a better description of the phenyl rings could have been obtained by using a slightly longer C–C bond distance in the rigid groups.[1]

Lists of $10|F_o|$ and $10|F_c|$ (Table S1) and anisotropic thermal parameters for the nongroup atoms (Table S2) are available as supplementary material.[22] The final structural parameters are given in Table I, the derived carbon atom positions are given in Table II, and the positions of the fixed hydrogen atoms are given in Table III.

$NiCl(NO)(P(C_6H_5)_3)_2 \cdot C_6H_6$. The crystals of this complex contain benzene of crystallization which is slowly lost from unprotected crystals upon exposure to an X-ray beam; therefore the crystal used for precession photographs and data collection was sealed in a thin-walled glass capillary. Preliminary precession photographs (Mo Kα) of a multifaceted crystal of approximate dimensions 0.3 × 0.3 × 0.4 mm indicated that the crystals are monoclinic. The systematic absences of $h0l$ when $l = 2n + 1$ and hkl when $h + k = 2n + 1$ are consistent with the space groups Cc (No. 9) and $C2/c$ (No. 15). The unit cell parameters (at 23 ± 2 °C) are a = 17.399 (3) Å, b = 13.136 (3) Å, c = 16.954 (3) Å, and β = 104.74 (1)°. These parameters were determined from a least-squares refinement of the setting angles of 14 automatically centered reflections from diverse regions of reciprocal space having 2θ between 35 and 40°. The observed density of 1.32

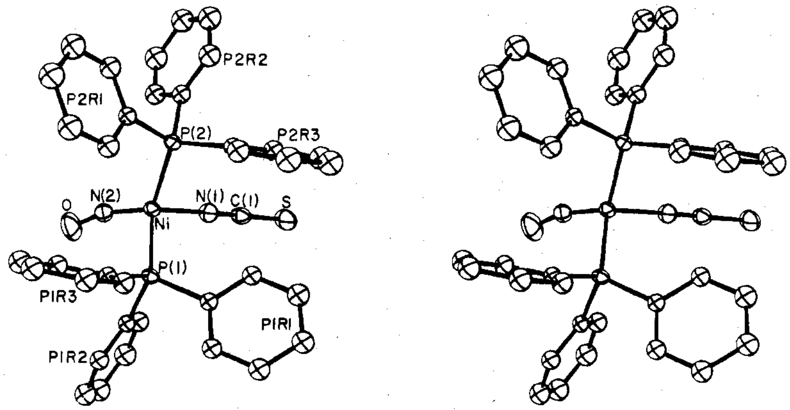

Figure 1. Stereopair showing a perspective view of $Ni(NCS)(NO)(P(C_6H_5)_3)_2$. H atoms have been omitted for clarity. The thermal ellipsoids are 30% probability envelopes.

g/cm^3, determined by flotation in carbon tetrachloride/*n*-heptane, and the calculated density of 1.29 g/cm^3 for four formula units of $NiCl(NO)(P(C_6H_5)_3)_2$ and four formula units of benzene per unit cell differ by 2.3%. Four molecules per unit cell corresponds to one molecule per asymmetric unit in space group *Cc* or to one-half molecule per asymmetric unit in space group *C*2/*c*. The crystal faces were indexed and are {100}, {001}, {110}, (111), (1,–1,1), (1,–1,–1), (–1,1,1), (–1,–1,1), and an irregular surface best approximated to be (1,1,–2).

The crystal used for preliminary precession photographs was mounted on a Picker FACS-1 four-circle diffractometer for data collection. The *b* axis was slightly offset from the ϕ axis to minimize the multiple-reflection problem. A total of 5773 unique reflections from the regions *hkl* and *–h*,*k*,*l* and 739 Friedel pair data from the regions *h*,*–k*,*–l* and *–h*,*–k*,*–l* were collected using an incident-beam monochromator equipped with a graphite crystal to obtain Mo Kα radiation. The takeoff angle was 1.5°, and the θ–2θ scan had a base width of 1.8° centered on 2θ–Mo K$\bar{\alpha}$, plus the dispersion correction. The scan rate was 1.0°/min, and stationary-crystal, stationary-counter background counts of 10 s were taken at both ends of the scan. The scintillation counter was 32.5 cm from the crystal with an aperature of 4 × 4 mm. The pulse height analyzer was set to admit ~90% of the Mo Kα peak. Metal foil attenuators having attenuator factors of ~1.7 were inserted into the diffracted beam whenever the counting rate exceeded ~7000 counts/s. Throughout data collection two standard reflections from diverse regions of reciprocal space were monitored every 50 reflections. Neither of the standard reflections gave evidence for decomposition of the crystal during the time required to collect the data.

The data were reduced to F^2 and $\sigma(F^2)$ by procedures similar to those previously described.[14] The value for *p* in the expression[14] for $\sigma(F^2)$ was taken as 0.04. The linear absorption coefficient for the compound for Mo Kα radiation is 7.25 cm^{-1}, and absorption corrections were calculated using the Gaussian method.[15b]

The space group was assumed to be the centrosymmetric choice, *C*2/*c*, and the structure was solved by direct methods using the MULTAN package and the 400 reflections with the highest values of $|E|$. An *E* map based upon these reflections revealed the nickel, the phosphorus, and three carbon atoms. A series of structure factor calculations, least-squares refinements, and difference electron density maps revealed the other nonhydrogen atoms. The three phenyl rings and the half benzene of crystallization were treated as rigid groups (C–C = 1.383 Å, D_{6h}-6/*mmm* symmetry) with individual isotropic thermal parameters. Occupancies of 0.5 were assigned to the crystallographically disordered N, O, and Cl atoms. After four cycles of least-squares refinement (positions and isotropic thermal parameters) the unreasonable pattern of distances and angles (Ni–N = 2.31, Ni–Cl = 1.90, N–O = 0.95, Cl–O = 1.05 Å; Ni–N–O = 106, Ni–Cl–O = 136°) suggested that the positions of the nitrogen and the chlorine half-atoms should be interchanged. However, interchanging the half-atoms followed by least-squares refinement did not improve the *R* factor and again produced chemically unreasonable distances and angles (Ni–N = 2.24, Ni–Cl = 2.02, N–O = 0.69, Cl–O = 1.08 Å; Ni–N–O = 153, Ni–Cl–O = 131°).

Several other disordered and ordered models were explored in both space groups *Cc* and *C*2/*c*, and the details are presented elsewhere.[23] The best model in space group *C*2/*c* gave *R* = 0.087 and was based upon nickel and phosphorus atoms with anisotropic thermal parameters, grouped phenyl rings with individual isotropic thermal parameters, benzene of crystallization with isotropic thermal parameters for individual atoms, and half-atoms of chlorine, nitrogen, and oxygen with individual isotropic thermal parameters. The final parameters for this model (Tables S3 and S4) and selected distances and angles (Table S5) are available.[22] The most suitable model for the noncentrosymmetric space group *Cc* was generated by applying the twofold operation to the atomic positions obtained from the "best" *C*2/*c* refinement. Both enantiomers were generated, and each was refined to convergence. The benzene carbon atoms were treated as individual isotropic atoms; the nickel and phosphorus atoms were assumed to vibrate anisotropically; anomalous contributions for the nickel, phosphorus, and chlorine atoms were included; the phenyl carbon atoms were treated as rigid groups. These refinements converged with conventional *R* values of 0.080 and 0.078. Final structure parameters for the latter enantiomer are available[22] in Tables S6 and S7, and selected distances and angles are given in Table S8. An *R* factor ratio test[24] showed that the centrosymmetric and noncentrosymmetric models were indistinguishable at the 95% confidence level. For all models several of the distances and angles involving the Cl, N, and O atoms appear chemically unreasonable (vide infra).

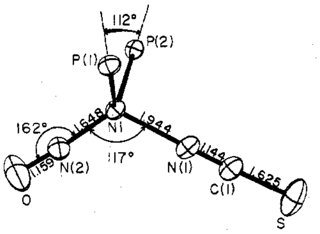

Figure 2. Perspective view of the inner coordination sphere of $Ni(NCS)(NO)(P(C_6H_5)_3)_2$. The thermal ellipsoids are 30% probability envelopes.

The major programs used in these studies were local modifications of the AGNOST general absorption correction program,[15] the MULTAN direct-methods program,[16] Ibers' NUCLS least-squares program, itself a modification of Busing, Martin, and Levy's ORFLS, Zalkin's FORDAP Fourier summation program, Busing and Levy's ORFEE function and error program, Johnson's ORTEP II plotting program, and Corfield's RANGER weighting analysis program. All major calculations were performed at the University of Arizona on a CDC 6400 computer.

Description

$Ni(NCS)(NO)(P(C_6H_5)_3)_2$. Selected interatomic distances and angles, together with some nonbonded intramolecular contacts are given in Table IV. The numbering scheme for the molecule and perspective views of the molecule and its inner coordination sphere are shown in Figures 1 and 2. Root-mean-square amplitudes of vibration along the principal axes are given in Table V for the anisotropic atoms.

The crystal structure consists of discrete well-separated $Ni(NCS)(NO)(P(C_6H_5)_3)_2$ molecules. The crystal packing

Table IV. Selected Interatomic Distances and Angles for $Ni(NCS)(NO)(P(C_6H_5)_3)_2$[a]

Distances

Ni-P(1)	2.271 (2)	P(1)-P1R1C1	1.827 (3)	N(1)-N(2)	3.06
Ni-P(2)	2.328 (2)	P(1)-P1R2C1	1.831 (4)	P(1)-N(1)	3.36
Ni-N(1)	1.944 (5)	P(1)-P1R3C1	1.827 (3)	P(1)-N(2)	3.08
Ni-N(2)	1.648 (5)	P(2)-P2R1C1	1.845 (3)	P(2)-N(1)	3.20
N(1)-C(1)	1.144 (7)	P(2)-P2R2C1	1.826 (4)	P(2)-N(2)	3.50
C(1)-S	1.625 (6)	P(2)-P2R3C1	1.830 (3)	P(1)-P(2)	3.81
N(2)-O	1.159 (6)				

Angles

P(1)-Ni-P(2)	111.98 (6)	Ni-P(1)-P1R3C1	114.41 (22)
P(1)-Ni-N(1)	105.59 (15)	Ni-P(2)-P2R1C1	118.62 (22)
P(1)-Ni-N(2)	102.65 (16)	Ni-P(2)-P2R2C1	111.36 (22)
P(2)-Ni-N(1)	96.61 (15)	Ni-P(2)-P2R3C1	113.44 (21)
P(2)-Ni-N(2)	122.47 (17)	P1R1C1-P(1)-P1R2C1	102.69 (22)
N(1)-Ni-N(2)	116.82 (22)	P1R1C1-P(1)-P1R3C1	105.69 (22)
Ni-N(1)-C(1)	177.5 (5)	P1R2C1-P(1)-P1R3C1	103.35 (24)
N(1)-C(1)-S	179.1 (6)	P2R1C1-P(2)-P2R2C1	102.69 (23)
Ni-N(2)-O	161.5 (5)	P2R1C1-P(2)-P2R3C1	105.46 (23)
Ni-P(1)-P1R1C1	118.42 (20)	P2R2C1-P(2)-P2R3C1	103.75 (23)
Ni-P(1)-P1R2C1	110.64 (22)	plane NiN_2-plane NiP_2	81.73 (13)

[a] Distances in angstroms and angles in degrees. Standard deviations (given in parentheses) for the distances and angles which involve the group carbon atoms were calculated using only variances. The estimated variances for the carbon atoms are those given in Table II.

Table V. Root-Mean-Square Amplitudes of Vibration (Å) for $Ni(NCS)(NO)(P(C_6H_5)_3)_2$

atom	min	intermed	max
Ni	0.164 (1)	0.202 (1)	0.216 (1)
P(1)	0.171 (2)	0.186 (2)	0.213 (2)
P(2)	0.172 (2)	0.201 (2)	0.213 (2)
S	0.197 (3)	0.259 (2)	0.414 (3)
C(1)	0.195 (8)	0.216 (8)	0.265 (8)
N(1)	0.195 (7)	0.232 (7)	0.261 (7)
N(2)	0.200 (7)	0.220 (7)	0.245 (7)
O	0.221 (7)	0.323 (7)	0.397 (7)

is dominated by the bulky triphenylphosphine ligands. The nonbonded intermolecular contacts are of the order of van der Waals distances or greater. All hydrogen–hydrogen interactions are 2.25 Å or greater.

The coordination geometry about the nickel atom is pseudotetrahedral with a P–Ni–P angle of 111.98 (6)° and a N–Ni–N angle of 116.82 (22)°. The dihedral angle between the plane defined by N(1), Ni, and N(2) and the plane defined by P(1), Ni, and P(2) is 81.73°. Table VI provides a comparison of the coordination geometry of this complex with several other structurally characterized pseudotetrahedral $\{MNO\}^{10}$ nitrosyl complexes.

The Ni–P bond lengths of 2.271 (2) and 2.328 (2) Å are 29σ different. Nonequivalent nickel–phosphorus bond lengths have been previously observed in two other $\{MNO\}^{10}$ complexes: $Ni(N_3)(NO)(P(C_6H_5)_3)_2$[1] (2.257 (2) and 2.306 (2) Å, 24σ different) and $Rh(NO)(SO_2)(P(C_6H_5)_3)_2$[8] (2.288 (2) and 2.410 (2) Å, 61σ different). The P–C bond lengths and the Ni–P–C and P–C–C angles are all well within the range of observed distances and angles for the triphenylphosphine ligand.

The nitrosyl group is coordinated in a nonlinear fashion with an Ni–N–O angle of 161.5 (5)°. This can be compared with values of 152.7 (7), 176.8 (2),[9] and 180 (0)°[26] reported for $Ni(N_3)(NO)(P(C_6H_5)_3)_2$, $[Ni(P(OCH_2)_3CCH_3)_3(NO)]^+$, and $[Ni(CH_3C(CH_2P(C_2H_5)_2)_3)(NO)]^+$, respectively. The Ni–NO distance of 1.648 (5) Å falls between 1.63 Å found for $[Ni(CH_3C(CH_2P(C_2H_5)_2)_3)(NO)]^+$ and 1.686 (7) Å found for $Ni(N_3)(NO)(P(C_6H_5)_3)_2$. The N–O distance is 1.159 (6) Å.

The isothiocyanate group coordinates linearly to the metal atom via the nitrogen atom. The coordination geometry is completely normal with an Ni–N–C angle of 177.5 (5)° and an N–C–S angle of 179.1 (6)°. The Ni–N distance of 1.944 (5) Å is slightly shorter than the 2.04 (2) Å found in the octahedral bis(isothiocyanato)bis(thiosemicarbazide)nickel(II) complex.[27] The N–C distance of 1.144 (7) Å and the C–S distance of 1.625 (6) Å are essentially the same as the 1.11 (3) and 1.60 (2) Å in the thiosemicarbazide complex.

$NiCl(NO)(P(C_6H_5)_3)_2$. The crystal structure consists of discrete molecules of $NiCl(NO)(P(C_6H_5)_3)_2$ and molecules of benzene. The $NiCl(NO)(P(C_6H_5)_3)_2$ molecule is pseudotetrahedral with a P–Ni–P angle of approximately 121.0°. In all of the models refined, the maximum deviation of the P–Ni–P angle from 121.0° was less than 0.2°. The bond distances and angles as well as the thermal parameters found for the $Ni(P(C_6H_5)_3)_2$ portion of the molecule are reasonable. The Ni–Cl, Ni–N, and N–O distances and the Ni–N–O angle are dependent upon the model refined. The ranges for the tabulated models[22] are as follows: Ni–Cl, 2.01–2.12 Å; Ni–N, 1.99–2.24 Å; N–O, 0.77–1.12 Å; Ni–N–O, 129–147°. There is no statistical basis for choosing one model over another (vide supra). The ambiguous results for this part of the molecule are not totally unexpected[1] because the NO group and the Cl atom have similar numbers of electrons (15 and 17, respec-

Table VI. Coordination Geometries of Selected Four-Coordinate Nitrosyl Complexes[a]

$\{MNO\}^{10}$ complexes	X	P–M–P	N–M–X	P–M–N	P–M–X	M–P	M–N	M–N–O	MP_2-MN_2
$Ni(NCS)(NO)(P(C_6H_5)_3)_2$[b]	NCS^-	111.98 (6)	116.82 (22)	122.47 (17)	96.61 (15)	2.271 (2)	1.648 (5)	161.5 (5)	81.7
				102.65 (16)	105.59 (15)	2.328 (2)			
$NiCl(NO)(P(C_6H_5)_3)_2$[b]	Cl^-	121.0							
$Ni(N_3)(NO)(P(C_6H_5)_3)_2$[c]	N_3^-	120.52 (8)	128.8 (3)	110.4 (2)	95.3 (2)	2.257 (2)	1.686 (7)	152.7 (7)	85.1
				101.1 (2)	102.4 (2)	2.306 (2)			
$Rh(NO)(SO_2)(P(C_6H_5)_3)_2$[d]	*e*	109.37 (6)	126.5	108.7 (2)	97.6	2.288 (2)	1.802 (6)	140.4 (6)	87.7
				101.8 (2)	110.8	2.410 (2)			
$Ir(NO)(CO)(P(C_6H_5)_3)_2$[f]	CO	103.9 (1)	128.7 (4)	118.7 (2)	93.3 (3)	2.323 (2)	1.787 (8)	174.1 (7)	84.3
				107.7 (2)	101.1 (3)	2.324 (2)			
$Ni(NO)[P(OCH_2)_3CCH_3]_3^+$[g]		107.3 (2)		113.5 (5)		2.191 (4)	1.581 (12)	176.8 (2)	87.4
		105.4 (1)		113.5 (5)		2.176 (5)			85.7
		99.8 (2)		116.0 (5)		2.191 (4)			88.3
$Rh(NO)(P(C_6H_5)_3)_3$[h]		102.57 (5)		115.71 (4)		2.351 (2)	1.795 (13)	156.7 (3)	
		101.51 (6)		116.58 (5)		2.347 (2)			
		102.51 (5)		115.77 (4)		2.353 (2)			

[a] Distances in angstroms and angles in degrees. Estimated standard deviations are given in parentheses where available. [b] This work. [c] Reference 1. [d] Reference 8. [e] The sulfur and one oxygen of SO_2 are coordinated to the rhodium atom. Moody and Ryan consider the complex as four-coordinate with the SO_2 moiety occupying one coordination site. The position used for X in this table is the midpoint of the sulfur-coordinated oxygen vector. [f] Reference 25. [g] Reference 9. [h] Reference 33.

Table VII. Nonbonded Intramolecular Contacts in Selected Four-Coordinate Nitrosyl Complexes[a]

complex	X	P_{short}-NO	P_{short}-X	P_{long}-NO	P_{long}-X	N-X	P-P
$Ni(NCS)(NO)(P(C_6H_5)_3)_2$[b]	NCS^-	3.08 (0.32)	3.36 (0.04)	3.50	3.20 (0.20)	3.06	3.81
$Ni(N_3)(NO)(P(C_6H_5)_3)_2$[c]	N_3^-	3.08 (0.32)	3.33 (0.07)	3.30 (0.10)	3.20 (0.20)	3.34	3.96
$Rh(NO)(SO_2)(P(C_6H_5)_3)_2$[d]	SO_2	3.19 (0.21)	3.31 (0.44)[e]	3.43	3.42[f]	[g]	3.83
$Ir(NO)(CO)(P(C_6H_5)_3)_2$[h]	CO	3.33 (0.07)	3.25	3.55	3.07	3.30	3.66 (0.14)
$Ni(NO)[P(OCH_2)_3CCH_3]_3^+$[i]		3.17 (0.23)					3.52 (0.28)
		3.15 (0.25)					3.49 (0.31)
		3.22 (0.18)					3.34 (0.46)
$Ru(NO)_2(P(C_6H_5)_3)_2$[j]	NO	3.25 (0.15)	3.02 (0.38)	3.14 (0.26)	3.27 (0.13)	3.23	3.72 (0.08)
$Ru(NO)_2(P(C_6H_5)_3)_2$[k]	NO	3.33 (0.07)	3.03 (0.37)	3.24 (0.16)	3.29 (0.11)	3.32	3.69 (0.11)
$Os(NO)_2(P(C_6H_5)_3)_2$[l]	NO	3.33 (0.07)	3.03 (0.37)	3.23 (0.17)	3.28 (0.12)	3.32	3.67 (0.13)

[a] Distances in angstroms. Numbers given in parentheses are calculated by taking the sum of the van der Waals radii minus the contact distance. The number is given only if the contact distance is less than the sum of the van der Waals radii. Only complexes which contain no crystallographically imposed symmetry are included in this table. [b] This work. [c] Reference 1. [d] Reference 8. [e] P_{short}-S. [f] P_{long}-O. [g] N-S = 3.42; N-O = 3.52 Å. [h] Reference 25. [i] Reference 9. [j] Reference 29b. [k] Reference 29a. [l] Reference 30.

tively) and because Ni–Cl, Ni–N, and N–O bond lengths are such that the midpoint of the N–O vector and the Cl atom position can be nearly superposed by the approximate twofold axis defined by the $Ni(P(C_6H_5)_3)_2$ portion of the molecule.[23]

Discussion

The primary interests in this and the earlier study of $NiX(NO)(PR_3)_2$ complexes are the relationships among the geometry of the $\{NiNO\}^{10}$ group, the stereochemistry about the metal atom, and the effective ligand field generated by the X^- and PR_3 ligands. Table VI compares the structure of $Ni(NCS)(NO)(P(C_6H_5)_3)_2$ with other four-coordinate complexes containing $\{MNO\}^{10}$ groups. Several differences can be noted in the structures of $NiX(NO)(P(C_6H_5)_3)_2$ complexes for $X^- = N_3^-$ and NCS^-: (1) the Ni–NO distance is shorter in the NCS^- complex (1.648 (5) vs. 1.686 (7) Å); (2) the Ni–N–O angle is larger in the NCS^- complex (161.5 (5) vs. 152.7 (7)°); (3) the P–Ni–P and N–Ni–X angles in the NCS^- complex are more nearly tetrahedral. Taken together these facts are consistent with the symmetry and bonding arguments presented previously[1,3] for four-coordinate complexes containing the $\{NiNO\}^{10}$ group. That is, as the stereochemistry of an $\{MNO\}^{10}$ complex changes from tetrahedral toward square planar, the M–N–O angle decreases. The square-planar limit should produce a complex with $M–N–O \approx 120°$ and a substantially longer M–NO bond than observed for pseudotetrahedral complexes.[3,7]

No definitive description of the coordinated NO group could be obtained for the complex with $X^- = Cl^-$. However, the P–Ni–P angle of 121° is similar to that for $X^- = N_3^-$, consistent with the general idea that N_3^- and Cl^- have similar ligand field strengths.[28]

An unexpected feature of the structure of $Ni(N_3)(NO)(P(C_6H_5)_3)_2$ was the inequivalent Ni–P distances (2.257 (2) and 2.306 (2) Å).[1] Initially these differences were ascribed to the asymmetric nonbonded interaction of the coordinated N atom of the azide ligand with the coordinated P atoms in the solid state due to the nonlinear geometry of coordinated azide. Anisotropic nonbonded repulsions between N(2) and the P atoms cannot occur in $Ni(NCS)(NO)(P(C_6H_5)_3)_2$ because the NCS^- ligand is linearly coordinated to the Ni atom. Even so, statistically different Ni–P distances (2.271 (2) and 2.328 (2) Å) are observed for the NCS^- complex. Table VI shows that similar differences have been found in other pseudotetrahedral complexes. Several possible explanations for these differences in M–P distances can be considered.

One possibility is that the differences arise from nonbonded intramolecular contacts between the donor atoms coordinated to the metal. Table VII summarizes these contacts, which are frequently less than the sum of the van der Waals radii[31] of the relevant atoms. In general, however, it will be noted that the shorter contacts are to the P atom with the shorter M–P bond length. Moreover, in $Ir(NO)(CO)(P(C_6H_5)_3)_2$[25] the two Ir–P distances are equivalent, but the nonbonded intramolecular contacts exhibit the same pattern of distances as in the other complexes. Thus, it seems unlikely that intramolecular nonbonded repulsions between donor atoms are responsible for the inequivalent M–P distances in the complexes of Table VI.

It has been suggested that the differences in Ni–P bonds in $Ni(N_3)(NO)(P(C_6H_5)_3)_2$ are due to vibronic distortions of the molecule to C_1 symmetry due to accidental degeneracy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in C_s symmetry (see Figure 13 of ref 3). Similar electronic effects can be postulated for $Ni(NCS)(NO)(P(C_6H_5)_3)_2$ and for the other complexes of Table VI.

Another possible explanation for the observed M–P distances is the intermolecular packing interactions of the phenyl groups of the phosphine ligands. This possibility cannot be ruled out for $Ni(NCS)(NO)(P(C_6H_5)_3)_2$ and $Ni(N_3)(NO)(P(C_6H_5)_3)_2$ even though they crystallize in different space groups and have different packing arrangements. The role of packing forces in stabilizing various structures of phenyl derivatives of group 5 elements is under investigation.[32]

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Registry No. $Ni(NCS)(NO)(P(C_6H_5)_3)_2$, 14056-76-9; $NiCl(NO)(P(C_6H_5)_3)_2 \cdot C_6H_6$, 67988-77-6.

Supplementary Material Available: Table S1 listing $10|F_o|$ and $10|F_c|$, Table S2 listing anisotropic thermal parameters for $Ni(NCS)(NO)(P(C_6H_5)_3)_2$, and Tables S3–S8 listing parameters and selected distances and angles for two of the refined models for $NiCl(NO)(P(C_6H_5)_3)_2$ (27 pages). Ordering information is given on any current masthead page.

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Structural Characterization of the Single Hydrogen Bridge Attachment of the Tetrahydroborate Group in Tris(methyldiphenylphosphine)(tetrahydroborato)copper

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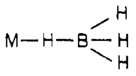
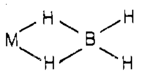
The crystal and molecular structure of $Cu[PPh_2Me]_3BH_4$ has been determined by single-crystal X-ray diffraction. The compound crystallizes in the orthorhombic space group $Pn2_1a$ with unit cell dimensions $a = 20.292$ (8) Å, $b = 17.435$ (7) Å, and $c = 10.419$ (5) Å, $Z = 4$. The copper atom resides in a quasi-tetrahedral environment consisting of the phosphorus atoms of the three PPh_2Me ligands and a single hydrogen atom of the tetrahydroborate group. This novel attachment of BH_4^- has a bridging Cu–H distance of 1.47 Å and a Cu–H–B angle of 170°. Upon dissolution of the compound in benzene, a phosphine dissociates and its coordination site is occupied by a second hydrogen atom from BH_4^-. This monodentate–bidentate conversion is readily discernible from a comparison of the solid-state and solution infrared spectra. The factors which influence the preferred coordination mode of the tetrahydroborate group in copper(I)–phosphine compounds are discussed.

Introduction

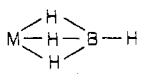
Covalent complexes containing the tetrahydroborate group, BH_4^-, have been reported for the majority of d and f transition metals.[2] Of the three possible modes of attachment, the double (II) and triple (III) hydrogen bridge structures have been characterized definitively by X-ray and neutron diffraction techniques.[2b] In contrast, evidence for the single hydrogen atom bridge (I) has been sparse and comprised entirely of spectroscopic observations. Holah and co-workers, for example, proposed that structure I obtains in $Co(PPh_3)_3BH_4$[3] and some five- and six-coordinate Ru(II) complexes[4] on the basis of electronic, infrared, and NMR data. More recently, Bommer and Morse presented infrared and NMR evidence in support of a singly bridged BH_4^- in $Cu[PPh_2Me]_3BH_4$.[5] Independent studies (vide infra) of this Cu(I) complex conducted by us resulted in a similar conclusion.[6]



I



II



III

The novel structural features associated with the single-bridge attachment of BH_4^-, coupled with the considerable interest in the stereochemistry of tetracoordinate copper(I)–phosphine complexes,[7-10] prompted us to determine the detailed structure of $Cu[PPh_2Me]_3BH_4$ by single-crystal X-ray diffraction. Our results, which have been summarized in a preliminary communication,[6] are reported in full here.

Table I. Crystal Data

compd	$Cu[P(C_6H_5)_2CH_3]_3BH_4$
mol wt	679.0
linear abs coeff, cm^{-1}	7.71
calcd density,[a] g cm^{-3}	1.22
max crystal dimensions, mm	0.20 × 0.20 × 0.20
space group	$Pn2_1a$
molecules/unit cell	4
cell constants,[b] Å	
a	20.292 (8)
b	17.435 (7)
c	10.419 (5)
cell vol, $Å^3$	3686.2

[a] Experimental density was not determined. [b] Mo Kα radiation, λ 0.710 69 Å. Ambient temperature of 22 °C.

Experimental Section

A. Preparation and Characterization of $Cu[PPh_2Me]_3BH_4$. Cuprous chloride[11] and diphenylmethylphosphine[12] were obtained by literature methods. $Cu[PPh_2Me]_3BH_4$ was prepared by the general method of Lippard and Ucko,[13] using either a 2:1 or the recommended 4:1 mole ratio of phosphine to CuCl. Anal. Calcd: C, 68.98; H, 6.38; P, 13.68; Cu, 9.36; mol wt 679. Found: C, 68.70; H, 6.17; P, 13.84; Cu, 8.95; mol wt (0.011–0.016 M complex in benzene) 381; mp 123–123.5 °C (uncorrected). Analyses were performed by Galbraith

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