Structure and Properties of *cis*-Bis(dicyclohexylphosphine)dihalogenonickel(II) Complexes

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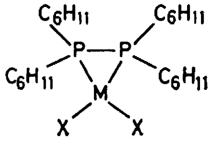
Dicyclohexylphosphine and tetracyclohexyldiphosphane both react with anhydrous nickel(II) chloride and bromide to form the same type of complex in either case, namely *cis*-[$NiX_2\{P(C_6H_{11})_2H\}_2$] (X = Cl or Br). This has been confirmed in the solid state by *X*-ray diffraction and in solution by ^1H and ^{31}P n.m.r. spectroscopy. Other spectroscopic data, as well as melting points, molecular weights, and elemental analyses, are also compatible with this conclusion. Evidence for a *trans* isomer of the bromide in solution is also observed. No evidence for the formation of a three-membered chelate ring in the reactions with the diphosphane could be detected. The ^{31}P chemical shifts in CH_2Cl_2 are 36.4 (20 °C, 0.2 mol dm^{-3}) and −46.1 and −30.5 p.p.m. (0 °C, 0.2 mol dm^{-3}) for *cis*-[$NiCl_2\{P(C_6H_{11})_2H\}_2$], *cis*-[$NiBr_2\{P(C_6H_{11})_2H\}_2$], and *trans*-[$NiBr_2\{P(C_6H_{11})_2H\}_2$] respectively, relative to 85% H_3PO_4. The complexes exhibit strong P–H coupling due to the secondary phosphine proton. *X*-Ray diffraction shows that *cis*-[$NiCl_2\{P(C_6H_{11})_2H\}_2$] crystallizes in the tetragonal space group $I4_1/a$ (No. 88) with a = 20.69(1) and b = 25.15(2) Å, and Z = 16. The structure was solved, using Weissenberg methods and the heavy-atom technique from 1400 independent reflections using Cu-K_α radiation, to R' 0.118. The nickel atom is 0.05 Å from the plane formed by the chlorine and phosphorus atoms. The average Ni—Cl distance is 2.20(1) Å and the average Ni—P distance is 2.15(1) Å.

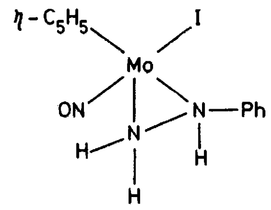
THE reactions of tetracyclohexyldiphosphane, $(C_6H_{11})_2P$–$P(C_6H_{11})_2$, with anhydrous nickel(II) chloride and bromide and palladium(II) chloride were reported by Issleib and Schwager[1] to yield complexes which are monomeric, diamagnetic, and polar. Consistent with these results and with the presumption that the P–P bond remains intact in the complexes, the structure proposed was *cis* planar, containing a bidentate diphosphane forming a three-membered chelate ring (1).



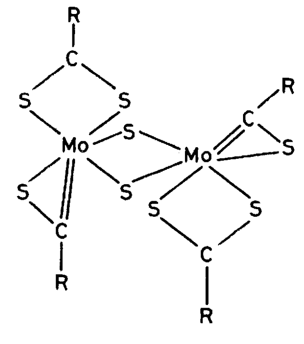
(1)

Similar results were obtained for cobalt halides, although a tetrahedral as well as a planar form was postulated for cobalt bromide.

Instances of well characterized *bona fide* three-membered *chelate* rings (in which two atoms bonded to each other are individually bonded to the same metal atom exclusive of any other bond between the ligand and metal) are rare. The most suitable ligands for forming such structures appear to be the $R_2\ddot{E}$–$\ddot{E}R_2$ compounds (E is a Group 5A element) that is hydrazine, diphosphane, diarsane, *etc.*, and their derivatives. In these compounds the E–E bonding is essentially a pure σ bond and the lone pairs on each atom E are available to form separate σ bonds with the metal.[2,3] In fact, many compounds of hydrazines, ketazines, aldazines, and phosphanes are known.[2,4-13] However, the insolubility (without decomposition) of most of the ketazine and aldazine complexes strongly suggests that the bidentate =N–N= groups are bridging two metals. One possible exception is $Co(N_2H_4{\cdot}HCl)_3Cl_2$,[5] although the crystal structure has not yet appeared. Very recently the first verified example of a true three-membered hydrazine chelate ring (2) has been reported.[9] In this structure both the Mo–N and N–N bond lengths are typical of single bonds, and the nitrogens appear to be essentially sp^3 hybridized. Another *bona fide* three-membered chelate ring (3), which involves both a double and single bond to the metal, has been found by Ricard *et al.*[14]



(2)



(3) R = NPr_2

Complexes formed by reaction of diphosphanes with metal salts and compounds might also be expected, at

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[1] K. Issleib and G. Schwager, *Z. anorg. Chem.*, 1961, **311**, 83.

[2] L. F. Audrieth and B. A. Ogg, ' The Chemistry of Hydrazine,' Wiley, New York, 1951.

[3] ' Compounds Containing Phosphorus–Phosphorus Bonds,' ed. A. H. Cowley, Dowden, Hutchinson, and Ross, Stroudsburg, Pennsylvania, 1973.

[4] D. Nicholls and R. Swindells, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2211.

[5] C. H. Stapfer and R. W. D'Andrea, *Inorg. Chem.*, 1971, **10**, 1224.

[6] C. H. Stapfer, R. W. D'Andrea, and R. H. Herber, *Inorg. Chem.*, 1972, **11**, 204.

[7] N. A. Aliev, G. K. Abdullaev, R. Ya. Aliev, N. M. Guseinov, and A. D. Kuliev, *Zhur. neorg. Khim.*, 1973, **18**, 844.

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[10] K. Issleib and G. Schwager, *Z. anorg. Chem.*, 1961, **310**, 43.

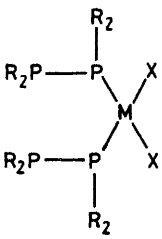
[11] K. Issleib and D. Jacob, *Chem. Ber.*, 1961, **94**, 107.

[12] K. Issleib and A. Tzschach, *Chem. Ber.*, 1959, **92**, 1397.

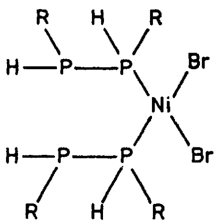
[13] K. Issleib and M. Keil, *Z. anorg. Chem.*, 1964, **333**, 10.

[14] L. Ricard, J. Estienne, and R. Weiss, *Inorg. Chem.*, 1973, **12**, 2182.

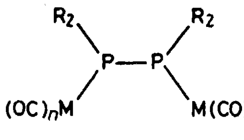
least in some instances, to involve three-membered rings. However, except for the series reported by Issleib and Schwager,[1] unidentate [10-12] (4), (5), or bridging diphosphanes [13,15] (6), or cleavage of the P–P bond [15,16] (7) are invariably observed (see also below). The properties of the complexes formed from tetracyclohexyldiphosphane and metal halides [1] clearly distinguish them from complexes formed by these closely analogous diphosphanes. This is particularly true of the apparent *cis* monomeric structure of the nickel complexes. Because of the bulkiness of the cyclohexyl groups, cleavage of the P–P bond might be expected to lead to a *trans* complex. Thus, the *cis* configuration (indicated by the dipole moment) [1] suggests that the P–P bond may, in fact, have survived. These considerations seem to support the postulated three-membered chelate-ring structure.



(4) R = Ph, MX_2 = $CoBr_2$, CoI_2, $PdCl_2$, or $NiBr_2$



(5) R = Ph



(6) R = C_6H_{11} or Me, M = Ni (n = 3) or Fe (n = 4)
R = Ph, Me, C_6H_{11}, or Et, M = Ni (n = 3)

We have repeated the preparation of the reported nickel chloride and bromide complexes of $(C_6H_{11})_2P-P(C_6H_{11})_2$,[1] intending to characterize them more completely, and have determined the crystal structure of the $NiCl_2$ complex. The results of these investigations, which show conclusively that the complexes are in fact *cis*-$[NiX_2\{P(C_6H_{11})_2H\}_2]$ both in solution and the solid state and thus contain no three-membered chelate rings, are presented.

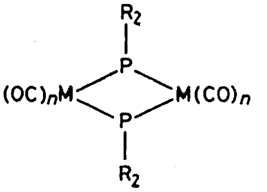
EXPERIMENTAL

Preparation of Compounds.—The preparations of the phosphine ligands were carried out following literature procedures [1,17,18] utilizing carefully dried, degassed, solvents. All the work was performed under dry nitrogen to avoid oxidation and/or hydrolysis of the phosphorus(III) intermediates. (It should be noted, however, that the crystalline metal complexes are indefinitely stable in air.)

Dicyclohexylphosphine, $P(C_6H_{11})_2H$, was prepared by reducing $P(C_6H_{11})_2Cl$ [19] with $Li[AlH_4]$ (using *ca.* 50% excess) in diethyl ether under reflux for 1 h. After quenching the excess of $Li[AlH_4]$ with wet diethyl ether, the $P(C_6H_{11})_2H$ was distilled at 95—105 °C at 0.8 mmHg* to give, on average, 90% yields (b.p. 281—283 °C at 760 mmHg).[19] The ^{31}P n.m.r. spectra of the neat liquid shows δ 28.4 p.p.m. relative to 85% H_3PO_4 at 30 °C and $^1J(P-H)$ 191 Hz. Tetracyclohexyldiphosphane was obtained by coupling $P(C_6H_{11})_2Cl$ with sodium in dioxan following the method of Issleib and his co-workers.[17] Best yields were obtained (*ca.* 60%) by allowing all the sodium to be consumed in the reaction, which took *ca.* 4 h. Recrystallization from toluene gave white crystals which, after powdering and drying *in vacuo*, melted at 173.5—175.5 °C; δ 21.1 p.p.m. (m.p. 173 °C, δ 21.5 p.p.m. in toluene [17]).

The reactions of tetracyclohexyldiphosphane with anhydrous nickel(II) chloride and bromide were carried out in refluxing toluene as described by Issleib and Schwager.[1] The deep red-brown bromo- and orange chloro-complexes were recrystallized from hot toluene with the addition of acetone (after cooling) to give *ca.* 50 and 30% yields, respectively.

Dicyclohexylphosphine was allowed to react with anhydrous nickel(II) chloride and bromide according to the procedure reported by Issleib and Tzschach [18] for preparation of the bromo-complex. Recrystallization from absolute ethanol–benzene (*ca.* 1 : 3) gave red-brown crystals for the bromide and orange crystals for the chloride. The crystals of both complexes were morphologically indistinguishable from the corresponding products of the reactions of the diphosphane with NiX_2.



(7) R = Ph, Et, or Me, n = 2-4, M = Ni, Fe, Cr, Mo, or W

Instrumentation.—Hydrogen-1 n.m.r. spectra were recorded on a JEOL 100 MHz spectrometer. Liquid samples were run neat and solids as saturated C_6D_6 solutions (at *ca.* 23 °C; 5.9×10^{-2} mol dm^{-3} for X = Cl and 1.9×10^{-1} mol dm^{-3} for X = Br). All the samples contained $SiMe_4$ as internal standard. Phosphorus-31 n.m.r. spectra were recorded at 36.43 MHz using, when appropriate, proton decoupling at 90 MHz with a Bruker HFX 10 spectrometer equipped for both continuous-wave frequency sweep (c.w.) and pulsed Fourier-transform (f.t.) operations. Solutions were examined in 5-mm tubes using the fluorine signal from hexafluorobenzene as a lock. Chemical shifts were measured relative to 85% H_3PO_4 by coaxial exchange techniques. Liquids were run as neat samples and solids as saturated toluene solutions (at *ca.* 23 °C; 4.0×10^{-2} mol

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 cal = 4.184 J.

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dm^{-3} for X = Cl and 2.0×10^{-1} mol dm^{-3} for X = Br). The probe temperature for most experiments was *ca.* 35 °C. Low-temperature spectra were recorded in methylene chloride since the solubility was much greater (at 25 °C; 0.48 mol dm^{-3} for X = Cl, 0.68 mol dm^{-3} for X = Br) using the fluorine signal in 1,2-dibromotetrafluoroethane as a stabilizing lock. Room-temperature spectra were not obtained in halogenated solvents due to slow decomposition of the complexes at higher temperatures in these solvents.

Infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer. Solutions were run in sealed KBr cells (0.044 mm). Solids were run either as KBr pellets or as Nujol mulls between KBr disks. Mass spectra were obtained on a Bell and Howell 21–490 mass spectrometer with the inlet temperature kept below the thermal-decomposition points of the complexes. Magnetic-susceptibility measurements were made at room temperature using standard Faraday techniques. Molecular weights were determined cryoscopically in benzene using a Normag apparatus with a calibrated Beckman thermometer.

Crystals of the chloro-complex of suitable size for a molecular-structure determination were grown by slow evaporation of solutions in either toluene or acetonitrile–tetrahydrofuran (30 : 70) under a nitrogen atmosphere. The crystal used in the structure determination had dimensions $0.20 \times 0.22 \times 0.35$ mm, with an average μr value of 0.50 for Cu-K_α radiation (μ 39.1 cm^{-1}). On rotating this crystal about the 0.35-mm axis the maximum change in the absorption correction factor, A^*, was from 2.18 to 3.19, indicating a variation of 19% to either side of a mean value. However, since the principle purpose of the structure determination could be served without it, the absorption correction was not made.

Preliminary X-ray diffraction data from rotation and equi-inclination Weissenberg photographs, $hk0$—2, indicated that the chloro-complex crystallized in a tetragonal space group with $a = 20.69 \pm 0.01$, $c = 25.15 \pm 0.02$ Å, $Z = 16$, and $M = 526.4$ g mol^{-1}. The observed and calculated densities are 1.28 (measured by flotation in a mixture of iodomethane and n-bromopentane) and 1.298 g cm^{-3}, respectively. Based on systematic absences $h + k + l = 2n$ for hkl data and $h(k) = 2n$ for $hk0$ data, the space group was determined as $I4_1/a$ (no. 88).[20]

Fifteen levels of equi-inclination Weissenberg intensity data, $hk0$—14, were collected on multiple-film packets consisting of five Ilford G films separated from each other by a piece of paper (to attenuate the X-ray beam so that the most intense reflections could be judged at least twice). Exposure time varied from 48 to 72 h depending on the intrinsic intensity of the level (odd levels were weak due to the location of the heavy atoms) and the value of μ. The levels were scaled together as a function of exposure time. The resulting 1 400 independent reflections were judged visually against a set of standard spots prepared from the 10 2 0 reflection. Corrections for spot shape, $\alpha_1 - \alpha_2$ separation, and Lorentz and polarization effects were made. (Lorentz and polarization corrections and the $\alpha_1 - \alpha_2$ separation were corrected with the program FORDAP.[21]) Computations were carried out on the IBM-370-135 computer at Triangle Universities Computation Center.

RESULTS

The Reaction of $(C_6H_{11})_2P–P(C_6H_{11})_2$ *and* $P(C_6H_{11})_2H$ *with Nickel Halides.*—The products of reaction of anhydrous nickel chloride with either of the cyclohexyl compounds are identical. The same is true of nickel bromide. This is borne out by the following data.

Elemental analysis. The analytical data for the complexes prepared by us are compared in Table 1 with those originally reported by Issleib and Schwager.[1] Although consistent with the conclusion stated above, these data in themselves do not prove the identity of the products or distinguish between the diphosphane and bis(secondary phosphine) structures since the difference in analysis caused by the two phosphine hydrogens is within the error limits of the technique.

TABLE 1

Melting-point and elemental-analysis data for $C_{24}H_{46}NiP_2X_2$ [a]

		Analysis (%)			
X	M.p. (θ_c/°C)	X	P	C	H
Cl		13.5	11.8	55.0	8.40 [b]
	195—200	13.35	11.7	55.1	8.55 [c]
	201—205		12.05		*d*
	Not reported [e]				
	196.8—204.0	13.7	12.05	55.0	8.90 [f]
		13.45	11.75	54.75	8.75 [g]
Br		26.05	10.1	47.0	7.25 [b]
	194.5—195.5	26.3	9.95	46.95	7.45 [c]
	192—194	25.15	10.0		*d*
	195—198	26.0	10.15		*e*
	192.5—196.4	26.25	9.90	46.95	7.50 [f]
		26.0	10.05	46.85	7.45 [g]

[a] Analyses by MHW Laboratories, Garden City, Michigan. [b] Calc. for $[NiX_2\{(C_6H_{11})_2P–P(C_6H_{11})_2\}]$. [c] Found in this work for $[NiX_2\{P(C_6H_{11})_2H\}_2]$; preparation from $(C_6H_{11})_2P–P(C_6H_{11})_2$. [d] Found for ‘$NiX_2\{(C_6H_{11})_2P–P(C_6H_{11})_2\}$.[1] [e] Found for $[NiX_2\{P(C_6H_{11})_2H\}_2]$.[12] [f] Found in this work for $[NiX_2\{P(C_6H_{11})_2H\}_2]$; preparation from $P(C_6H_{11})_2H$. [g] Calc. for $[NiX_2\{P(C_6H_{11})_2H\}_2]$.

Molecular weights. The molecular weights of the chloro- and bromo-complexes were determined as 540 and 580 g mol^{-1} compared to 526 and 614 g mol^{-1}, respectively, calculated for the monomers.

X*-Ray Diffraction.* The photographs for oscillation about the needle (c) axis of crystals from either preparation are completely identical as to spacings and intensity patterns for either the chloride or bromide. The crystal data are summarized in Table 2. The complete crystal structure of the nickel chloride complex is described below. The crystal structure of the bromo-complex appears to be similar to that of the chloride but with a unit cell *ca.* twice as large. The molecular structure of the chloride clearly

TABLE 2

Crystal-structure data for $[NiX_2\{P(C_6H_{11})_2H\}_2]$

	X	
	Cl	Br
Space group	$I4_1/a$	$I4_1a$?
a/Å	20.69(1)	20.8(1)
c/Å	25.15(2)	53.4(2)
Z	16	32
D_c/g cm^{-3}	1.298	1.47
D_m/g cm^{-3}	1.28	1.47

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[20] ‘International Tables for X-Ray Crystallography,’ Kynoch Press, Birmingham, 1952, vol. 1, p. 178.

[21] A. Zalkin, FORDAP—Crystallographic Fourier Program, University of California, Berkeley.

involves *cis* phosphorus atoms, but the P–P distance [3.05(1) Å], although less than the sum of the van der Waals radii, is far greater than the 2.20—2.27 Å observed for P–P bonds.[5] Since no hydrogens could be located, either on the carbon or phosphorus atoms, the diffraction data in themselves may be said only to indicate strongly that the P–P bond has been broken. However, the fact that the structure is the same regardless of whether the complex is made from tetracyclohexyldiphosphane or dicyclohexylphosphine clearly provides the necessary proof of the P–P bond scission.

Infrared spectra. The data are summarized in Table 3. Spectra of products from reactions of the same halide with either the diphosphane or secondary phosphine are indistinguishable. The spectra of the bromo- and chloro-complexes differ from each other only in the bands associated with Ni–X and P–H vibrations. Not all the bands in the i.r. spectrum are listed in Table 3 since assignments of the many cyclohexyl bands seemed superfluous and uninformative. The bands assigned to the P–H stretch in the complex spectra were weak and somewhat broad. However, a strong P–H band was clearly present in spectra of samples of the free $P(C_6H_{11})_2H$ ligand and absent in those of the free diphosphane. A band assignable to the P–P stretch could be seen only in the spectrum of the free diphosphane, as expected.

TABLE 3

Infrared spectral assignments (cm^{-1})

Compound		
$[NiBr_2\{P(C_6H_{11})_2H\}_2]$	*ca.* 2 350br	P–H
	300	Ni–Br
$[NiCl_2\{P(C_6H_{11})_2H\}_2]$	318, 294	Ni–Cl
	2 351m	P–H
$P(C_6H_{11})_2H$	2 464s	P–H

Mass spectra. The most intense and pertinent peaks in the electron-ionization spectra are listed and assigned in Table 4. Again, spectra of products from reaction with either ligand were identical. Parent ions were observed for both free ligands but not for the complexes. No peaks involving the NiX_2 moieties were observed. In the spectra of the complexes a $[P(C_6H_{11})_2H]^+$ peak is clearly seen, but no $[(C_6H_{11})_2P-P(C_6H_{11})_2]^+$ peak was ever found. However, many peaks due to three-co-ordinate phosphorus species resulting from rearrangements are observed, making the lack of the diphosphane peak somewhat inconclusive. Mass spectra using $[CH_3]^+$ ionization provided no additional insight.

Hydrogen-1 *and phosphorus*-31 *n.m.r.* The n.m.r. data are also independent of the ligand used in the reaction. But most importantly, both ^1H and ^{31}P spectra show unambiguously the effects of strong P–H coupling due to a secondary phosphine. The ^1H n.m.r. consists of complex cyclohexyl proton structure in the 0.7—2.4 p.p.m. region, the P–C–H proton doublet (broad) at 2.70 p.p.m., and a weak set of broad peaks, some of which are apparently obscured by the P–C–H band, that can only be due to a P–H proton coupled to the phosphorus. The ratio of intensities of C_6H_{11} : P–C–H : P–H is expected to be 20 : 2 : 1 and has been found to be *ca.* 17 : 2 : 1 for both halides. The ^1H-undecoupled ^{31}P n.m.r. spectra of both halides consist of quartets, the phosphorus resonances collapsing to singlets with broad-band ^1H decoupling. Both ^1H and ^{31}P spectra exhibit an $(AMX_2)_2$ [22] pattern, from which the relevant coupling constants may be obtained. These are listed in Table 5 together with the chemical shifts. Such strong P–H coupling is characteristic of hydrogens *directly* attached to phosphorus atoms only.[23,24] The small value of $^2J(P-P)$ for the chloro-complex and one of the bromide signals is consistent with normally observed small $^2J(P-P)$ for *cis* complexes relative to the large values for the *trans* complexes.[23-25] It is also consistent with the observed *cis* structure of the chloride in the solid state (see below). The bromo-complex is apparently predominantly *trans* at ambient temperature in toluene solution, but becomes predominantly *cis* at lower temperatures. However, the similarity of the rotation photographs of the bromide crystals to those of the chloride suggests that the isomer that crystallizes from benzene–toluene solution is *cis*. A detailed analysis of the n.m.r. spectra is beyond the scope of this paper and will be published separately.[26]

TABLE 4

Mass spectral assignments

Compound	*m/e*	Assignment
$[NiCl_2\{P(C_6H_{11})_2H\}_2]$	198	$[P(C_6H_{11})_2H]^+$, base peak
	116	$[P(C_6H_{11})H_2]^+$
	83	$[C_6H_{11}]^+$
$[NiBr_2\{P(C_6H_{11})_2H\}_2]$	198	$[P(C_6H_{11})_2H]^+$
	116	$[P(C_6H_{11})H_2]^+$
	83	$[C_6H_{11}]^+$, base peak
$(C_6H_{11})_2P-P(C_6H_{11})_2$	394	$[(C_6H_{11})_2P-P(C_6H_{11})_2]^+$, parent ion
	312	$[(C_6H_{11})_2P-P(C_6H_{11})H]^+$
	230	$[(C_6H_{11})_2P-PH_2]^+$ or $[H(C_6H_{11})P-P(C_6H_{11})H]^+$
	198	$[P(C_6H_{11})_2H]^+$
	148	$[H(C_6H_{11})P-PH_2]^+$
	116	$[P(C_6H_{11})H_2]^+$
	83	$[C_6H_{11}]^+$, base peak
	66	$[H_2P-PH_2]^+$
$P(C_6H_{11})_2H$	198	$[P(C_6H_{11})_2H]^+$, parent ion
	116	$[P(C_6H_{11})H_2]^+$
	83	$[C_6H_{11}]^+$, base peak

TABLE 5

Phosphorus-31 n.m.r. parameters for $[NiX_2\{P(C_6H_{11})_2H\}_2]$ (0.2 mol dm^{-3})

	$^2J(P-P)$	$^1J(P-H)$	$^3J(P-H')$	δ *	θ_c
X		Hz		p.p.m.	°C
Cl (*cis*)	65(10)	330(10)	40(10)	−36.4	20
Br (*cis*)	65(10)	330(10)	40(10)	−46.1	0
Br (*trans*)	380(10)	340(10)	10(10)	−30.5	0

* Relative to 85% H_3PO_4; in CH_2Cl_2.

The Crystal and Molecular Structure of cis-$[NiCl_2\{P(C_6H_{11})_2H\}_2]$.—The crystal structure was solved by the heavy-atom technique. From the Patterson function the nickel atom was located in the 16-fold general position near the 4_1 axis. Calculation of the structure factors based on the nickel position with program UCLS,[27] followed by a three-dimensional Fourier synthesis, resulted in the location

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of the chlorine and phosphorus atoms. All the carbon atoms were located by repeated structure-factor calculations followed by three-dimensional Fourier maps. The structure was refined isotropically by full-matrix least squares using structure factors by Hanson *et al.*[28] (zero oxidation state for all atoms) to a conventional R value of 0.14 after three cycles. The function minimized was S_qF. Inclusion of anomalous scattering factors [29] for nickel, rejudging several reflections exhibiting poor agreement between F_o and F_c, and removing the intense reflections (200, 220, 240, 422, 204, and 314, which appeared to be seriously affected by secondary extinction), lowered the R value to 0.120 after two additional cycles. A weighting scheme similar to that proposed by Hughes [30] was used in the final refinement: $w^{\frac{1}{2}} = 1$ for $F_o \geqslant 8$; $w^{\frac{1}{2}} = 8/F_o$ for $F_o < 8$. This yielded an R' value $\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ of 0.118 after three cycles. Due to the increased number of parameters in an anisotropic refinement and the limited amount of data, anisotropic refinement was not justified. A final three-dimensional Fourier-difference map on the isotropically refined parameters revealed no additional peaks. The largest peak at a distance comparable to a bond length from a given atom is 0.3 e Å^{-3}. No attempt was made to locate either the cyclohexyl or phosphine hydrogens in this background.

Final observed and calculated structure factors, except those affected by secondary extinctions, and thermal parameters, are in Supplementary Publication No. SUP 22340 (9 pp.).* The final positional parameters are given in Table 6 with their standard deviations in parentheses. In the final refinement cycle the maximum changes in nickel, chlorine, and phosphorus atomic co-ordinates were 4 × 10^{-5} (y co-ordinate), 4 × 10^{-4} [y co-ordinate of Cl(1)], and 2 × 10^{-4} Å [z co-ordinate of P(2)], respectively, while the changes in the thermal parameters were 1 × 10^{-3}, 5 × 10^{-3}, and 2 × 10^{-3}, respectively. The maximum change in any carbon atomic co-ordinate was 8 × 10^{-4} Å [x co-ordinate of C(14)] while the maximum change in the isotropic thermal parameter was 1.6 × 10^{-2} on atom C(15).

TABLE 6

Positional parameters with standard deviations in parentheses

Atom	x	y	z
Ni	0.746 1(2)	0.496 3(2)	0.489 8(2)
Cl(1)	0.672 8(4)	0.470 9(4)	0.429 8(4)
Cl(2)	0.824 6(3)	0.506 3(3)	0.432 0(4)
P(1)	0.670 8(3)	0.483 3(3)	0.547 1(4)
P(2)	0.814 1(3)	0.517 0(3)	0.552 8(4)
C(1)	0.639(1)	0.400(1)	0.545(1)
C(2)	0.597(1)	0.536(1)	0.541(1)
C(3)	0.838(1)	0.600(1)	0.561(1)
C(4)	0.889(1)	0.469(1)	0.550(1)
C(5)	0.699(1)	0.356(1)	0.540(1)
C(6)	0.670(1)	0.283(1)	0.542(2)
C(7)	0.633(1)	0.268(1)	0.594(2)
C(8)	0.575(1)	0.315(1)	0.596(1)
C(9)	0.601(1)	0.387(1)	0.598(1)
C(10)	0.614(1)	0.596(1)	0.510(2)
C(11)	0.548(1)	0.636(1)	0.506(2)
C(12)	0.521(1)	0.649(1)	0.560(2)
C(13)	0.508(2)	0.591(2)	0.592(2)
C(14)	0.576(1)	0.549(2)	0.598(2)
C(15)	0.774(1)	0.642(1)	0.553(1)
C(16)	0.795(1)	0.714(1)	0.565(1)
C(17)	0.846(1)	0.738(1)	0.526(2)
C(18)	0.910(1)	0.694(1)	0.537(1)
C(19)	0.889(1)	0.621(1)	0.522(1)
C(20)	0.873(1)	0.397(1)	0.548(1)
C(21)	0.937(1)	0.361(1)	0.544(2)
C(22)	0.976(1)	0.369(1)	0.597(2)
C(23)	0.993(1)	0.447(1)	0.600(1)
C(24)	0.927(1)	0.485(1)	0.604(1)

Figure 1 (plotted by the program ORTEP [31]) shows the approximately square-planar geometry about the central nickel atom and the orientation of the cyclohexane rings relative to the phosphorus atoms. All the four cyclohexane rings are in the chair configuration with the phosphorus bonded to the ring in an equatorial position. Tables 7 and 8 give the bond distances and angles, respectively, with their estimated standard deviations. Figure 2 shows the molecular packing of the nickel co-ordination sphere and carbon atoms C(1)—(4).

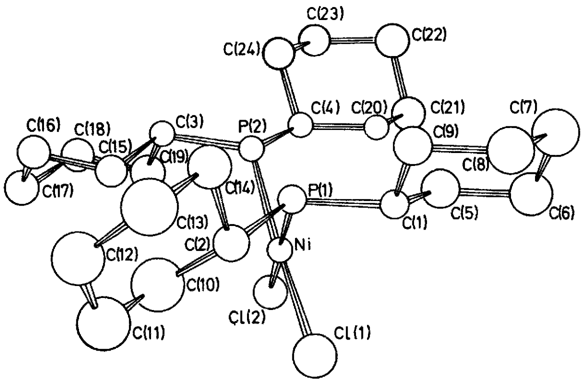

FIGURE 1 Molecular structure of *cis*-$[NiCl_2\{P(C_6H_{11})_2H\}_2]$

TABLE 7

Bond distances (Å) with standard deviations in parentheses

Ni–Cl(1)	2.20(1)	C(11)–C(12)	1.48(5)
Ni–Cl(2)	2.19(1)	C(12)–C(13)	1.46(4)
Ni–P(1)	2.14(1)	C(13)–C(14)	1.66(4)
Ni–P(2)	2.16(1)	C(14)–C(2)	1.53(4)
P(1)–C(1)	1.85(2)	C(3)–C(15)	1.61(3)
P(1)–C(2)	1.88(2)	C(15)–C(16)	1.58(3)
P(2)–C(3)	1.79(2)	C(16)–C(17)	1.52(4)
P(2)–C(4)	1.85(2)	C(17)–C(18)	1.65(4)
C(1)–C(5)	1.54(3)	C(18)–C(19)	1.62(3)
C(1)–C(9)	1.58(4)	C(19)–C(3)	1.50(3)
C(5)–C(6)	1.63(4)	C(4)–C(20)	1.53(3)
C(6)–C(7)	1.53(4)	C(20)–C(21)	1.53(3)
C(7)–C(8)	1.54(4)	C(21)–C(22)	1.58(4)
C(8)–C(9)	1.59(3)	C(22)–C(23)	1.66(3)
C(2)–C(10)	1.51(4)	C(23)–C(24)	1.57(3)
C(10)–C(11)	1.62(4)	C(24)–C(4)	1.60(3)

The average Ni–Cl bond distance [2.20(1) Å] is slightly longer than those reported by Smith [32] for $[NiCl_2\{PPh(C_6H_{11})H\}_2]$ (2.116 Å). The average Ni–P bond distance [2.15(1) Å] is approximately the same as that (2.159 Å) found in $[NiMe(pd)\{P(C_6H_{11})_3\}]$ (pd = pentane-2,4-dion-

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* See Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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[29] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1952, vol. 3, p. 162.

[30] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

[31] C. K. Johnson, ORTEP—A Fortran Thermal-Ellipsoid Plot Program, ORNL–3794, Oak Ridge National Laboratories, 1965.

[32] A. E. Smith, *Inorg. Chem.*, 1972, **11**, 3017.

ate).[33] However, these distances are the shortest Ni–P distances presently known. Other Ni–P distances in four-co-ordinate nickel(II) complexes are: 2.175 Å in *trans*-$[Ni(C{\equiv}CPh)_2(PEt_3)_2]$,[34,35] 2.227 Å in bis(9-phenyl-9-phosphabicyclo[3.3.1]nonane)nickel(II) chloride,[32] 2.26 Å in $[NiBr_2(PEt_3)_2]$,[36] 2.257 and 2.306 Å in $[Ni(N_3)(NO)(PPh_3)_2]$,[37] 2.323 and 2.343 Å in $[NiBr_2(PPh_3)_2]$,[38] and 2.263 Å in square-planar and 2.316 Å in tetrahedral $[NiBr_2\{PPh_2(CH_2Ph)\}_2]$.[39] The expected Ni–P single bond length in square-planar nickel(II) complexes is 2.28 Å.[34] Electrostatic and steric repulsion energies are greater in square-planar nickel(II) complexes than in the corresponding tetrahedral complexes. Thus, the energy necessary to stabilize a square-planar complex results from the increased overlap of the σ- or π-bonding orbitals with the metal orbitals. As a consequence the bond lengths are generally shorter in a square-planar than in the analogous tetrahedral complex.[40]

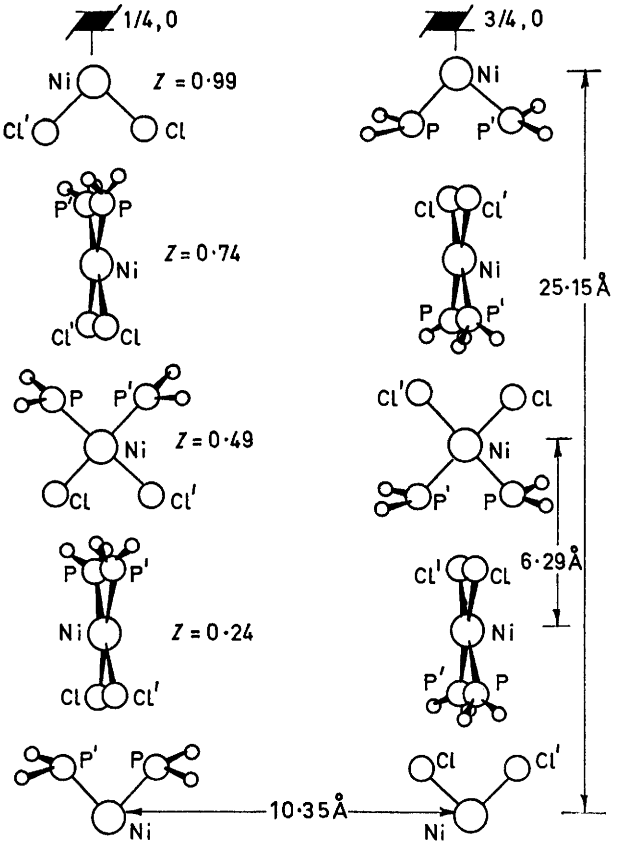

FIGURE 2 Molecular packing in *cis*-$[NiCl_2\{P(C_6H_{11})_2H\}_2]$

The mean P–C bond distance [1.84(4) Å] is in good agreement with those reported in the literature. In other four-co-ordinate nickel(II) complexes, which involve a cyclohexyl group bound directly to a phosphorus atom, the P–C bond lengths range from 1.843 to 1.902 Å.[33,41-43] It is worthwhile to note, however, that the P–C distances in the present complex are slightly shorter than normally observed. The average C–C bond length found is 1.56(6) Å. The significant non-bonded distances are: P(1)–P(2) 3.05(1), P(1)–Cl(1) 2.96(1), P(2)–Cl(2) 3.05(1), and Cl(1)–Cl(2) 3.22(1) Å.

Except for the P–Ni–P angle [90.3(3)°], all the angles about the central metal atom deviate from 90°, although their sum (360°) indicates the high degree of planarity of the co-ordination sphere. The maximum deviation of any atom from this plane is 0.05 Å (Ni). Interestingly, P(1), P(2), and C(1)—C(4) lie in a plane [maximum deviation 0.22 Å by C(4)] virtually orthogonal to the plane of the co-ordination sphere. The Cl–Ni–Cl angle [94.6(4)°] results in an unusually short average distance between adjacent chlorine and phosphorus atoms of 3.00(1) Å, which is less than the sum of van der Waals radii (3.7 Å). The average of the other bond angles observed is as follows: C–P–C 105(2), C–P–Ni 115(3), C–C–P 108(3), and C–C–C 108(3)°.

TABLE 8

Bond angles (°) with standard deviations

P(1)–Ni–P(2)	90.3(3)	C(11)–C(10)–C(2)	105(2)
P(1)–Ni–Cl(1)	85.9(4)	C(12)–C(11)–C(10)	111(3)
P(2)–Ni–Cl(2)	89.2(4)	C(13)–C(12)–C(11)	116(3)
Cl(1)–Ni–Cl(2)	94.6(4)	C(14)–C(13)–C(12)	108(3)
C(1)–P(1)–Ni	111.1(9)	C(2)–C(14)–C(13)	105(3)
C(2)–P(1)–Ni	117(1)	C(15)–C(3)–P(2)	106(1)
C(1)–P(1)–C(2)	104(1)	C(19)–C(3)–P(2)	114(2)
C(3)–P(2)–Ni	116.8(9)	C(20)–C(4)–P(2)	110(1)
C(4)–P(2)–Ni	114.1(9)	C(24)–C(4)–P(2)	105(2)
C(3)–P(2)–C(4)	106.3(9)	C(15)–C(3)–C(19)	110(2)
C(9)–C(1)–P(1)	108(2)	C(16)–C(15)–C(3)	105(2)
C(5)–C(1)–P(1)	105(1)	C(17)–C(16)–C(15)	112(2)
C(10)–C(2)–P(1)	109(2)	C(18)–C(17)–C(16)	105(2)
C(14)–C(2)–P(1)	105(2)	C(19)–C(18)–C(17)	105(2)
C(9)–C(1)–C(5)	112(2)	C(3)–C(19)–C(18)	108(2)
C(6)–C(5)–C(1)	104(2)	C(20)–C(4)–C(24)	109(2)
C(7)–C(6)–C(5)	114(3)	C(21)–C(20)–C(4)	107(2)
C(8)–C(7)–C(6)	107(3)	C(22)–C(21)–C(20)	109(3)
C(9)–C(8)–C(7)	110(2)	C(23)–C(22)–C(21)	104(2)
C(1)–C(9)–C(8)	107(2)	C(24)–C(23)–C(22)	108(2)
C(10)–C(2)–C(14)	114(2)	C(4)–C(24)–C(23)	106(2)

DISCUSSION

The results cited above show clearly that the reaction of tetracyclohexyldiphosphane with nickel chloride and bromide causes scission of the P–P bond with formation of bis(secondary phosphine) complexes. The formation of identical products from the reaction of each of the halides with dicyclohexylphosphine confirms this conclusion. The *X*-ray diffraction data show that the solid-state structure of the chloride is *cis*. Analysis of the n.m.r. spectra of both halides is consistent with the presence of the *cis* structure in solution as well, although the bromo-complex shows evidence of a *trans* isomer at higher temperatures.[26]

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The fact that these complexes do not contain the reported three-membered ring is disappointing, but should not be too surprising considering the structures of other complexes resulting from reaction of tetrasubstituted diphosphanes with metal salts. The tetraphenyldiphosphane ligand, for example, is found to be either unidentate [10,12] (4) or bridging bidentate [13,15] (6). With nickel(II) halides, P_2Ph_4 forms *cis* planar complexes, but these are 2 : 1 complexes with apparently unidentate diphosphanes [14] (4). The inherent steric problems of a diphosphane ligand containing either cyclohexyl or phenyl substituents should be very similar. Thus, on the basis of steric considerations, both ligands would be expected to give rise to similarly structured complexes. However, it should be noted that, although the two ligands complex in different modes the sterically hindered co-ordinating phosphorus atoms are *cis* to each other in both cases. The steric strain cannot, therefore, be the deciding factor in the mechanism of complexation. This is further supported by the fact the 1,2-diphenyldiphosphane ligand complexes similarly to P_2Ph_4 [11] (5). One might argue that the presence of the electron-withdrawing phenyl rings significantly lowers the phosphorus electron density available for bonding. If the electron-withdrawing effect is large enough only one phosphorus might then be able to co-ordinate. However, this argument is weakened by the existence of a number of bidentate tetraphenyldiphosphane complexes [13,15,16] as illustrated, for example, by (6). Furthermore, the known structures of complexes involving other tetra-alkyldiphosphanes do not have three-membered rings. Tetramethyl- or tetraethyl-diphosphane give either diphosphane-bridged [13,15] (6) or, perhaps more significantly, alkylphosphide-bridged complexes resulting from ready cleavage of the P–P bond [15,16] (7).

The point in the reaction of $(C_6H_{11})_2P-P(C_6H_{11})_2$ with nickel halides at which the P–P bond is cleaved is not yet known. Since the diphosphane is recrystallized from boiling toluene and the complexes are prepared from the same solvent, the nickel salt may act as a template promoting cleavage by stretching the bond to its breaking point, at which time it is protonated by reaction with solvent (or cyclohexyl groups). Thus, the possibility of a transient existence for the three-membered chelate ring cannot be ruled out conclusively. Once the P–P bond is cleaved, the large bulky ligands might be expected to rearrange to *trans* positions in the complex. Complexes containing mutually *cis* phosphine ligands, however, are generally more stable than the analogous *trans* complexes by *ca.* 10 kcal mol^{-1}.[44] This is apparently due to larger *s*-orbital character in the *cis* phosphorus ligands than in the *trans*, as measured by ^{31}P n.m.r. spectroscopy.[45] The equilibrium between *cis* and *trans* structures has also been found to depend on the halide.[44]

It is interesting to note that of all the potentially bidentate ligands ($R_2\ddot{E}-\ddot{E}R_2$) only one has been shown to form a true chelate ring (2).[9] The binuclear molybdenum complex (3) apparently forms the single other example of a three-membered chelate ring.[14] Do other three-membered chelate rings exist? The evidence clearly shows that they do not in the case of the reaction of tetracyclohexyldiphosphane with $NiCl_2$ or $NiBr_2$. We have not yet concluded our investigations of the other members of the series of complexes formed from this diphosphane originally reported as also containing the three-membered chelate ring (complexes with $CoCl_2$, $CoBr_2$, CoI_2, and $PdCl_2$). Additional work on the structures and properties of these complexes is in progress.

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[7/1730 *Received, 30th September*, 1977]

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