bisecting pairs of *cis* C and *cis* P atoms on the approximately square-planar metal centers. The symmetrical C_{2h} twist-chair conformation of the eight-membered ring [internal ring torsion angles are 107·9 (2)–115·5 (2)° at Pd—P bonds and 38·3 (3)–48·6 (3)° at P—CH_2 bonds, angles involving the same P atom being of opposite sign] compares favorably to that found in $[Pt_2Me_4(Me_2PCH_2PMe_2)]$ (internal ring torsion angles of 109–114° at Pt—P bonds and 42–54° at P—CH_2 bonds) (Ling & Puddephatt, 1983). The bond angles within the eight-membered $Pd_2P_4C_2$ ring are slightly distorted from the ideal values of 90° at palladium and 109·5° at phosphorus and carbon. The P—Pd—P angle is 100·67 (5)° with the P—C—P angle being 119·3 (3)°. There are three sets of Pd—P—C angles. This is not just due to the presence of both methyl and methylene C atoms but also due to steric effects analogous to those found in $[Pt_2Me_4(Me_2PCH_2PMe_2)]$ (Manojlović-Muir, Muir, Frew, Ling, Thomson & Puddephatt, 1984). The average Pd—P—C angle involving the two methylene C atoms is 111·7 (2)°. The average Pd—P—C angle involving the axial methyl groups, C(2) and C(4), is 124·0 (2)° and the average Pd—P—C angle involving the equatorial methyl groups, C(3) and C(5), is 112·3 (2)°. The Pd—Cl bond distances of 2·360 (1) and 2·353 (1) Å are comparable to the average Pd—Cl bond distance in analogous compounds: 2·362 (3) Å in *cis*-$[PdCl_2\{P(CH_3)_2C_6H_5\}_2]$ (Martin & Jacobson, 1971), 2·357 Å in *cis*-$[PdCl_2\{(C_6H_5)_2PCH_2P(C_6H_5)_2\}]$ (Steffen & Palenik, 1976), 2·359 Å in *cis*-$[PdCl_2\{(C_6H_5)_2PC_2H_4P(C_6H_5)_2\}]$ (Steffen & Palenik, 1976), 2·354 Å in *cis*-$[PdCl_2\{(C_6H_5)_2PC_3H_6P(C_6H_5)_2\}]$ (Steffen & Palenik, 1976) and 2·341 Å found in *cis*-$[PdCl_2\{P(CH_3)(C_6H_5)_2\}_2]$ (Alcock & Nelson, 1985). The Pd—P distances of 2·264 (1) and 2·265 (1) Å are slightly less than the median Pd—P bond distance of 2·281 (8) Å found in palladium trimethylphosphine complexes (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1989).

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Structures of $[CoCl(C_{18}H_{15}P)_3]$ and $[NiCl(C_{18}H_{15}P)_3].C_7H_8$

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Abstract. Chlorotris(triphenylphosphine)cobalt, $M_r = 881·26$, trigonal, $P3$, $a = 19·151\ (4)$, $c = 10·543\ (2)$ Å, $V = 3349\ (1)$ Å^3, $Z = 3$, $D_x = 1·31$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 5·84$ cm^{-1}, $F(000) = 1374$, $T = 296$ K, $R = 0·040$, $wR = 0·049$ for 3860 unique reflections with $I > 3\sigma(I)$. The molecule $CoCl[P(C_6H_5)_3]_3$ consists of three triphenylphosphine ligands and one chlorine atom bonded to cobalt in a distorted tetrahedral coordination geometry. Three independent molecules are found in the unit cell with each Co—Cl bond situated on a crystallographic threefold rotation axis. Chlorotris(triphenylphosphine)nickel–toluene (1/1), $M_r = 973·11$, triclinic, $P\bar{1}$, $a = 13·161\ (2)$, $b = 20·026\ (5)$, $c = 10·110\ (2)$ Å, $\alpha =$

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95·56 (2), $\beta = 101{\cdot}98$ (2), $\gamma = 102{\cdot}25$ (2)°, $V = 2519{\cdot}4$ (9) Å^3, $Z = 2$, $D_x = 1{\cdot}28$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 5{\cdot}71$ cm^{-1}, $F(000) = 1018$, $T = 296$ K, $R = 0{\cdot}039$, $wR = 0{\cdot}046$ for 7014 unique reflections with $I > 3\sigma(I)$.

Introduction. Monovalent $CoCl[P(C_6H_5)_3]_3$ and $NiCl[P(C_6H_5)_3]_3$ have been studied extensively for use as catalysts. The nickel compound is reported to catalyze the isomerization of 1-pentene (Kanai, Kushi, Sakanone & Kishimoto, 1980) and but-l-ene (Kanai, 1972) through formation of a nickel hydride complex (D'Aniello & Barefield, 1978). Chlorotris(triphenylphosphine)cobalt acts as a catalyst for the cyclic dimerization of butadiene (Cairns & Nixon, 1974). In addition, the cobalt complexes, $CoX[P(C_6H_5)_3]_3$ (where X = Cl, Br or I), are known to selectively dimerize and hydrogenate olefin compounds when complexed with Lewis acids (Kawakami, Mizoroki & Ozaki, 1978; Kanai, Watanabe & Nakayama, 1986; Kawakami, Mizoroki & Ozaki, 1979).

The halogenotris(triphenylphosphine)nickel compounds have been synthesized by reaction of π-allyl-Ni-X with excess $P(C_6H_5)_3$ and norbornene in a benzene/diethyl ether solution (Porri, Gallazzi & Vitulli, 1967), although alternative synthetic methods are available (Barnett, 1974). The chlorotris(triphenylphosphine)cobalt compound can be synthesized from $CoCl_2.6H_2O$ and $P(C_6H_5)_3$ in the presence of a reducing agent (Arresta, Rossi & Sacco, 1969). The electronic spectra and magnetic moments of $CoCl[P(C_6H_5)_3]_3$ suggest that it has a tetrahedral configuration in both the solid and solution state.

From reactions of $CoCl_2$ or $NiCl_2$ with $Bi(SiMe_3)_3$ in the presence of $P(C_6H_5)_3$, $MCl[P(C_6H_5)_3]_3$ compounds were obtained. The crystal structures of these two compounds are reported herein.

Experimental. $CoCl[P(C_6H_5)_3]_3$ (I) was produced upon addition of $Bi(SiMe_3)_3$ (1·1 cm^3) to anhydrous $CoCl_2$ (0·75 g, 5·8 mmol) in the presence of $P(C_6H_5)_3$ (3·03 g, 6·88 mmol) in tetrahydrofuran solution. The corresponding nickel complex was prepared similarly and isolated as its toluene solvate (II). Blue crystals of $CoCl_2[P(C_6H_5)_3]_2$ were also obtained from the former reaction as was determined by comparison of preliminary cell constants with the X-ray powder cell parameters of the isomorphous $NiCl_2[P(C_6H_5)_3]_2$ complex (Goodgame & Goodgame, 1965; Garton, Henn, Powell & Venanzi, 1963).

A green crystal of (I) suitable for a single crystal X-ray study (0·5 × 0·4 × 0·5 mm, cut prism) was obtained from a toluene solution of the product and mounted on a glass fiber with epoxy cement. Crystal data were collected using 2θ–ω scans on a Rigaku AFC5S four-circle diffractometer [Rigaku *CONTROL* (4:0:0) *Automatic Data Collection Series* (Molecular Structure Corporation, 1988*a*)]. The primitive unit cell was determined from a least-squares fit of 25 random reflections ($7{\cdot}36 \leq 2\theta \leq 11{\cdot}76°$). These data indicated a primitive trigonal cell which was supported by examination of equivalent reflections for this Laue symmetry. Three standard reflections were chosen ($\bar{1}40$, $\bar{3}40$, 030) and remeasured after every 150 reflections to check for crystal decay and/or reorientation. Final average decay of the standard intensities was 2·5%. Excluding standards, 5665 reflections were measured with 5152 independent reflections ($R_{\rm int}$ = 1·8%) and 3860 reflections were observed [$I > 3\sigma(I)$] for the quadrant $\pm h$, $+k$, $+l$, ranging from h: −25 to 25, k: 0 to 25, l: 0 to 14 with $2\theta_{\max} = 55°$ and $[(\sin\theta)/\lambda]_{\max} = 0{\cdot}65$ Å^{-1}. Lack of systematic absences and intensity statistics indicated that the space group was noncentrosymmetric $P3$ (No. 143) which was subsequently shown to be correct from successful refinement of the structure.

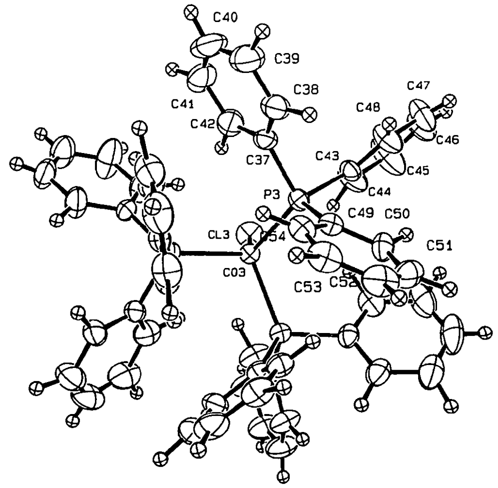

Fig. 1. *ORTEP*II (Johnson, 1976) diagram of one molecule of $CoCl[P(C_6H_5)_3]_3$. Selected bond distances and angles are found in Table 2.

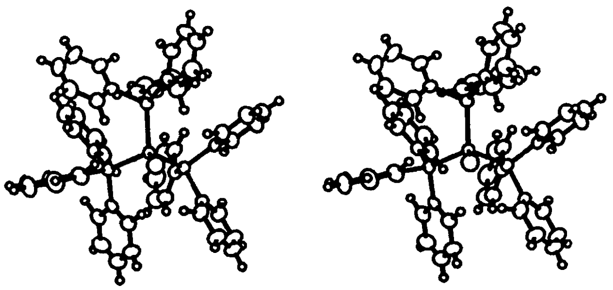

Fig. 2. *ORTEP*II (Johnson, 1976) stereoview of one molecule of $CoCl[P(C_6H_5)_3]_3$.

The structure was solved by using the program *MITHRIL* (Gilmore, 1983) which located three unique cobalt atoms situated on three crystallographically independent threefold axes. Subsequent least-squares cycles and Fourier syntheses utilizing the *TEXSAN* (Version 2.1) structure analysis package (Molecular Structure Corporation, 1988*b*) gave the remaining non-hydrogen atoms. The hydrogens on the phenyl groups were included in calculated positions but were not refined. Full-matrix least-squares refinement minimized $\sum w(|F_o| - |F_c|)^2$, where $w = (\sigma^2|F_o|)^{-1}$ (σ^2 = variance) with all non-hydrogen atoms refined anisotropically (number of variables = 531). The data were corrected for absorption (ψ scans, transmission range 0·9740–1·0000), decay and Lorentz/polarization effects. Final least-squares refinement converged with $R = 0{\cdot}040$, $wR = 0{\cdot}049$, $(\Delta\rho)_{\max} = 0{\cdot}42$ e Å^{-3}, $(\Delta/\sigma)_{\max} = 0{\cdot}06$ and $S = 1{\cdot}26$. To determine the correct enantiomorph, least-squares refinement was carried to convergence on both enantiomorphs without anomalous dispersion. Anomalous dispersion and the Friedel pairs were then included and each enantiomorph re-refined. The resulting weighted *R* factors were compared (0·0487 and 0·0493, respectively) and the model with the lower value was chosen to be the correct enantiomorph.

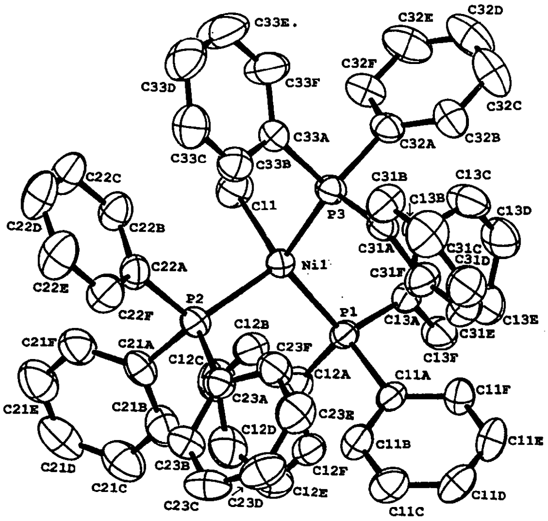

Fig. 3. *ORTEP*II (Johnson, 1976) diagram of NiCl[P($C_6H_5)_3$]$_3$. Selected bond distances and angles are found in Table 4.

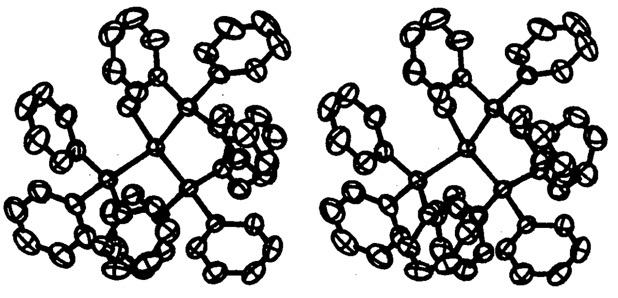

Fig. 4. *ORTEP*II (Johnson, 1976) stereoview of NiCl[P($C_6H_5)_3$]$_3$.

Table 1. *Positional parameters and* B_{eq} *values for the non-hydrogen atoms of* CoCl(PPh$_3$)$_3$

$$B_{\rm eq} = 8\pi^2/3(U_{11}aa^{*2} + U_{22}bb^{*2} + U_{33}cc^{*2} - U_{12}aba^*b^*).$$

	x	y	z	$B_{\rm eq}$ (Å^2)
Co(1)	$\frac{1}{3}$	$\frac{2}{3}$	0·2951	2·52 (3)
Co(2)	$\frac{2}{3}$	$\frac{1}{3}$	0·5003 (1)	2·42 (3)
Co(3)	1	0	0·7937 (1)	2·16 (3)
Cl(1)	$\frac{1}{3}$	$\frac{2}{3}$	0·5074 (2)	4·36 (7)
Cl(2)	$\frac{2}{3}$	$\frac{1}{3}$	0·2871 (2)	4·01 (7)
Cl(3)	1	0	0·5795 (2)	3·93 (6)
P(1)	0·20752 (8)	0·57903 (8)	0·2060 (2)	2·73 (5)
P(2)	0·69791 (8)	0·45602 (8)	0·5906 (2)	2·63 (4)
P(3)	0·89818 (8)	0·01676 (8)	0·8822 (2)	2·40 (4)
C(1)	0·1425 (3)	0·6244 (3)	0·1988 (6)	3·1 (2)
C(2)	0·1538 (4)	0·6776 (4)	0·2940 (6)	3·9 (2)
C(3)	0·1079 (5)	0·7173 (4)	0·2961 (7)	5·1 (3)
C(4)	0·0497 (4)	0·6986 (5)	0·2062 (8)	5·2 (3)
C(5)	0·0359 (4)	0·6432 (5)	0·1161 (8)	5·2 (3)
C(6)	0·0824 (4)	0·6052 (4)	0·1099 (6)	4·4 (3)
C(7)	0·1382 (3)	0·4862 (3)	0·2945 (6)	3·2 (2)
C(8)	0·0647 (4)	0·4297 (4)	0·2451 (6)	4·4 (2)
C(9)	0·0116 (4)	0·3626 (4)	0·3131 (9)	5·7 (3)
C(10)	0·0333 (5)	0·3506 (4)	0·4335 (8)	5·6 (3)
C(11)	0·1046 (5)	0·4078 (5)	0·4850 (7)	6·0 (3)
C(12)	0·1573 (4)	0·4747 (4)	0·4161 (6)	4·2 (2)
C(13)	0·2023 (3)	0·5397 (3)	0·0445 (5)	3·1 (2)
C(14)	0·1972 (4)	0·4658 (4)	0·0267 (6)	3·9 (2)
C(15)	0·2019 (5)	0·4404 (4)	−0·0957 (8)	5·5 (3)
C(16)	0·2122 (5)	0·4896 (5)	−0·1990 (6)	5·6 (3)
C(17)	0·2170 (4)	0·5621 (5)	−0·1816 (6)	5·1 (3)
C(18)	0·2128 (4)	0·5880 (4)	−0·0577 (6)	3·8 (2)
C(19)	0·6100 (3)	0·4712 (3)	0·5949 (5)	3·0 (2)
C(20)	0·5577 (4)	0·4405 (4)	0·4947 (7)	4·3 (3)
C(21)	0·4909 (4)	0·4526 (5)	0·4871 (8)	5·6 (3)
C(22)	0·4786 (4)	0·4952 (5)	0·581 (1)	5·9 (4)
C(23)	0·5316 (5)	0·5272 (5)	0·678 (1)	5·9 (4)
C(24)	0·5972 (4)	0·5156 (4)	0·6881 (7)	4·3 (3)
C(25)	0·7675 (3)	0·5496 (3)	0·5054 (5)	3·0 (2)
C(26)	0·8010 (4)	0·6246 (4)	0·5631 (6)	4·1 (2)
C(27)	0·8494 (4)	0·6936 (4)	0·4941 (7)	5·0 (3)
C(28)	0·8628 (4)	0·6899 (4)	0·3678 (8)	5·4 (3)
C(29)	0·8297 (5)	0·6164 (5)	0·3097 (7)	5·5 (3)
C(30)	0·7810 (4)	0·5445 (4)	0·3763 (6)	4·1 (2)
C(31)	0·7399 (3)	0·4788 (3)	0·7513 (5)	3·1 (2)
C(32)	0·6913 (4)	0·4487 (4)	0·8587 (6)	3·9 (2)
C(33)	0·7240 (5)	0·4579 (4)	0·9784 (6)	4·9 (3)
C(34)	0·8071 (5)	0·4983 (5)	0·9940 (6)	5·5 (3)
C(35)	0·8556 (4)	0·5273 (4)	0·8881 (7)	5·2 (3)
C(36)	0·8245 (4)	0·5184 (4)	0·7682 (6)	4·1 (2)
C(37)	0·9244 (3)	0·1230 (3)	0·8953 (5)	3·0 (2)
C(38)	0·8957 (4)	0·1534 (4)	0·9882 (6)	4·0 (2)
C(39)	0·9182 (5)	0·2338 (5)	0·9915 (8)	5·5 (3)
C(40)	0·9702 (6)	0·2846 (4)	0·898 (1)	6·3 (4)
C(41)	0·9979 (5)	0·2566 (4)	0·8036 (8)	5·3 (3)
C(42)	0·9731 (4)	0·1743 (4)	0·8014 (6)	4·3 (3)
C(43)	0·8061 (3)	−0·0193 (3)	0·7878 (5)	2·7 (2)
C(44)	0·8022 (4)	−0·0456 (5)	0·6649 (6)	4·6 (3)
C(45)	0·7327 (5)	−0·0701 (7)	0·5937 (7)	7·0 (4)
C(46)	0·6684 (4)	−0·0673 (5)	0·6380 (7)	5·3 (3)
C(47)	0·6718 (4)	−0·0402 (5)	0·7586 (8)	5·3 (3)
C(48)	0·7383 (4)	−0·0183 (4)	0·8342 (6)	4·4 (3)
C(49)	0·8599 (3)	−0·0262 (3)	1·0385 (5)	2·7 (2)
C(50)	0·7939 (3)	−0·1045 (3)	1·0522 (6)	3·4 (2)
C(51)	0·7723 (4)	−0·1398 (4)	1·1705 (6)	4·4 (3)
C(52)	0·8157 (5)	−0·0996 (5)	1·2767 (6)	4·7 (3)
C(53)	0·8809 (4)	−0·0226 (4)	1·2665 (5)	4·0 (2)
C(54)	0·9027 (3)	0·0136 (3)	1·1492 (5)	3·2 (2)

Diffraction data for (II) were collected on an orange crystal (0·5 × 0·5 × 0·5 mm) grown by slow cooling of the compound dissolved in toluene. It was mounted on a glass fiber with epoxy cement. Crystal data were collected as above using 2θ–ω scans. The

Table 2. *Selected intramolecular distances* (Å) *and angles* (°) *for* $\mathrm{CoCl[P(C_6H_5)_3]_3}$

Co(1)—Cl(1)	2·237 (3)	P(1)—C(7)	1·853 (6)
Co(1)—P(1)	2·337 (2)	P(2)—C(31)	1·832 (5)
Co(2)—Cl(2)	2·248 (3)	P(2)—C(25)	1·846 (5)
Co(2)—P(2)	2·319 (1)	P(2)—C(19)	1·847 (6)
Co(3)—Cl(3)	2·258 (3)	P(3)—C(49)	1·824 (5)
Co(3)—P(3)	2·324 (1)	P(3)—C(43)	1·833 (5)
P(1)—C(1)	1·843 (6)	P(3)—C(37)	1·840 (5)
P(1)—C(13)	1·845 (6)		

Cl(1)—Co(1)—P(1)	113·71 (4)	C(31)—P(2)—Co(2)	118·7 (2)
P(1)—Co(1)—P(1)	104·92 (5)	C(25)—P(2)—C(19)	97·5 (2)
Cl(2)—Co(2)—P(2)	114·23 (4)	C(25)—P(2)—Co(2)	118·6 (2)
P(2)—Co(2)—P(2)	104·32 (5)	C(19)—P(2)—Co(2)	112·1 (2)
Cl(3)—Co(3)—P(3)	113·66 (4)	C(49)—P(3)—C(43)	103·1 (2)
P(3)—Co(3)—P(3)	104·97 (4)	C(49)—P(3)—C(37)	104·9 (3)
C(1)—P(1)—C(7)	98·3 (2)	C(49)—P(3)—Co(3)	118·4 (2)
C(1)—P(1)—Co(1)	112·0 (2)	C(43)—P(3)—C(37)	97·8 (2)
C(13)—P(1)—C(7)	101·9 (3)	C(43)—P(3)—Co(3)	116·5 (2)
C(13)—P(1)—Co(1)	119·4 (2)	C(37)—P(3)—Co(3)	113·5 (2)
C(7)—P(1)—Co(1)	118·3 (2)	C(2)—C(1)—P(1)	115·3 (4)
C(31)—P(2)—C(25)	101·6 (2)	C(6)—C(1)—P(1)	124·8 (5)
C(31)—P(2)—C(19)	105·4 (3)	C(1)—P(1)—C(13)	104·1 (3)
C(8)—C(7)—P(1)	121·5 (5)	C(26)—C(25)—P(2)	121·9 (4)
C(12)—C(7)—P(1)	120·0 (4)	C(30)—C(25)—P(2)	118·3 (4)
C(20)—C(19)—P(2)	116·2 (4)	C(42)—C(37)—P(3)	116·7 (4)
C(24)—C(19)—P(2)	124·4 (5)	C(38)—C(37)—P(3)	124·8 (5)
C(18)—C(13)—P(1)	119·4 (4)	C(32)—C(31)—P(2)	121·9 (4)
C(14)—C(13)—P(1)	120·3 (5)	C(36)—C(31)—P(2)	119·6 (4)
C(54)—C(49)—P(3)	120·7 (4)	C(48)—C(43)—P(3)	122·0 (4)
C(44)—C(43)—P(3)	120·9 (4)	C(50)—C(49)—P(3)	121·2 (4)

Table 3. *Positional parameters and* B_{eq} *values for the non-hydrogen atoms of* $\mathrm{Ni(PPh_3)_3Cl.C_7H_8}$

$$B_{\rm eq} = 8\pi^2/3(U_{11}aa^{*2} + U_{22}bb^{*2} + U_{33}cc^{*2} - U_{12}aba^*b^*).$$

	x	y	z	$B_{\rm eq}$ (Å^2)
Ni(1)	0·36503 (3)	0·23666 (2)	0·21254 (3)	2·73 (1)
Cl(1)	0·43330 (7)	0·24600 (5)	0·44174 (7)	4·56 (3)
P(1)	0·42760 (6)	0·34297 (4)	0·15203 (7)	2·83 (2)
P(2)	0·18230 (6)	0·21633 (4)	0·17914 (8)	3·20 (3)
P(3)	0·42548 (6)	0·14281 (4)	0·13690 (7)	2·97 (3)
C(11*A*)	0·3916 (2)	0·3499 (1)	−0·0299 (3)	3·0 (1)
C(11*B*)	0·2846 (2)	0·3382 (2)	−0·0933 (3)	3·9 (1)
C(11*C*)	0·2507 (3)	0·3346 (2)	−0·2330 (3)	4·5 (1)
C(11*D*)	0·3244 (3)	0·3427 (2)	−0·3127 (3)	4·7 (1)
C(11*E*)	0·4313 (3)	0·3550 (2)	−0·2513 (3)	4·9 (1)
C(11*F*)	0·4649 (2)	0·3588 (2)	−0·1113 (3)	3·8 (1)
C(12*A*)	0·3847 (2)	0·4141 (1).	0·2348 (3)	3·1 (1)
C(12*B*)	0·3896 (3)	0·4162 (2)	0·3733 (3)	4·0 (1)
C(12*C*)	0·3641 (3)	0·4697 (2)	0·4453 (3)	5·0 (1)
C(12*D*)	0·3314 (3)	0·5212 (2)	0·3791 (4)	5·1 (1)
C(12*E*)	0·3251 (3)	0·5197 (2)	0·2425 (4)	5·0 (1)
C(12*F*)	0·3520 (3)	0·4664 (2)	0·1696 (3)	3·9 (1)
C(13*A*)	0·5726 (2)	0·3785 (1)	0·1981 (3)	3·0 (1)
C(13*B*)	0·6391 (3)	0·3367 (2)	0·2445 (3)	4·3 (1)
C(13*C*)	0·7498 (3)	0·3625 (2)	0·2785 (4)	5·4 (2)
C(13*D*)	0·7929 (3)	0·4292 (2)	0·2679 (4)	5·3 (2)
C(13*E*)	0·7274 (3)	0·4712 (2)	0·2233 (4)	5·3 (1)
C(13*F*)	0·6186 (2)	0·4463 (2)	0·1893 (3)	4·2 (1)
C(21*A*)	0·1263 (2)	0·2797 (2)	0·2662 (3)	3·7 (1)
C(21*B*)	0·1275 (3)	0·3430 (2)	0·2217 (4)	4·8 (1)
C(21*C*)	0·0901 (3)	0·3931 (2)	0·2882 (4)	5·8 (2)
C(21*D*)	0·0508 (3)	0·3800 (2)	0·4020 (4)	6·0 (2)
C(21*E*)	0·0484 (3)	0·3178 (2)	0·4469 (4)	6·1 (2)
C(21*F*)	0·0860 (3)	0·2680 (2)	0·3803 (3)	5·0 (1)
C(22*A*)	0·1196 (2)	0·1378 (2)	0·2385 (3)	3·6 (1)
C(22*B*)	0·1699 (3)	0·1202 (2)	0·3604 (3)	4·3 (1)
C(22*C*)	0·1231 (3)	0·0631 (2)	0·4115 (3)	5·3 (1)
C(22*D*)	0·0256 (3)	0·0217 (2)	0·3391 (4)	5·7 (2)
C(22*E*)	−0·0243 (3)	0·0379 (2)	0·2173 (4)	6·0 (2)
C(22*F*)	0·0217 (3)	0·0956 (2)	0·1672 (3)	4·7 (1)
C(23*A*)	0·1076 (2)	0·2045 (1)	0·0007 (3)	3·3 (1)
C(23*B*)	0·0110 (2)	0·2224 (2)	−0·0432 (3)	4·2 (1)
C(23*C*)	−0·0390 (3)	0·2111 (2)	−0·1799 (4)	5·1 (1)
C(23*D*)	0·0057 (3)	0·1822 (2)	−0·2749 (3)	5·3 (1)
C(23*E*)	0·1001 (3)	0·1634 (2)	−0·2336 (3)	5·2 (1)
C(23*F*)	0·1512 (2)	0·1752 (2)	−0·0969 (3)	4·2 (1)
C(31*A*)	0·4008 (2)	0·1195 (1)	−0·0486 (3)	3·2 (1)
C(31*B*)	0·3711 (3)	0·0526 (2)	−0·1164 (3)	4·5 (1)
C(31*C*)	0·3557 (3)	0·0403 (2)	−0·2569 (4)	5·9 (2)
C(31*D*)	0·3715 (3)	0·0941 (2)	−0·3304 (3)	5·6 (2)
C(31*E*)	0·4011 (3)	0·1602 (2)	−0·2653 (3)	5·0 (1)
C(31*F*)	0·4146 (3)	0·1729 (2)	−0·1254 (3)	4·2 (1)
C(32*A*)	0·5703 (2)	0·1488 (1)	0·1915 (3)	3·4 (1)
C(32*B*)	0·6207 (3)	0·1682 (2)	0·3295 (3)	4·4 (1)
C(32*C*)	0·7295 (3)	0·1739 (2)	0·3731 (4)	5·8 (2)
C(32*D*)	0·7891 (3)	0·1623 (2)	0·2811 (5)	6·5 (2)
C(32*E*)	0·7405 (3)	0·1439 (2)	0·1457 (5)	6·4 (2)
C(32*F*)	0·6314 (3)	0·1369 (2)	0·1000 (3)	4·5 (1)
C(33*A*)	0·3675 (2)	0·0610 (1)	0·1909 (3)	3·3 (1)
C(33*B*)	0·2608 (3)	0·0298 (2)	0·1372 (3)	4·1 (1)
C(33*C*)	0·2133 (3)	−0·0316 (2)	0·1745 (4)	5·1 (1)
C(33*D*)	0·2722 (3)	−0·0620 (2)	0·2683 (4)	6·2 (2)
C(33*E*)	0·3768 (4)	−0·0315 (2)	0·3238 (5)	7·8 (2)
C(33*F*)	0·4245 (3)	0·0293 (2)	0·2854 (4)	6·0 (2)
C(1)	0·1119 (5)	0·6280 (3)	0·1816 (8)	8·6 (3)
C(2)	0·1714 (7)	0·6493 (4)	0·3104 (6)	9·9 (3)
C(3)	0·2670 (8)	0·6919 (5)	0·3313 (8)	11·7 (4)
C(4)	0·3078 (6)	0·7171 (4)	0·223 (1)	11·8 (4)
C(5)	0·2464 (8)	0·6930 (5)	0·0943 (8)	11·8 (5)
C(6)	0·1488 (5)	0·6483 (3)	0·0763 (5)	7·8 (3)
C(7)	0·0083 (6)	0·5816 (4)	0·160 (1)	18·0 (6)

primitive unit cell was determined from a least-squares fit of 25 random reflections ($7{\cdot}5 \le 2\theta \le 11{\cdot}75°$) and later refined with 25 reflections of higher angle ($38 \le 2\theta \le 42°$). These data indicated a triclinic unit cell. Three standard reflections (2$0\bar{1}$, 0$4\bar{1}$, 0$0\bar{2}$) were chosen and measured as above. Final average decay was 3%. Excluding standards, 11 000 reflections were collected with 10 496 independent reflections ($R_{\rm int} = 2{\cdot}2\%$) and 7013 reflections observed $[I > 3\sigma(I)]$ for $+h$, $\pm k$, $\pm l$: ranging from h: 0 to 15, k: -25 to 25, l: -12 to 12 with $2\theta_{\max} = 55°$ and $[(\sin\theta)/\lambda]_{\max} = 0{\cdot}65$ Å^{-1}. The choice of the more common centrosymmetric setting $P\bar{1}$ was made and shown to be correct by successful structure solution and refinement.

The structure was solved using the Patterson solution routine of the program *SHELXS*86 (Sheldrick, 1986) which located all non-hydrogen atoms of both the nickel compound and the solvent molecule. The structure was refined as above. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions but not refined. Attempts to refine the occupancy of the toluene solvent showed that it was fully present. The data were corrected for Lorentz–polarization effects but not for absorption or decay. Final least-squares refinement converged with $R = 0{\cdot}039$ and $wR = 0{\cdot}046$, $(\Delta\rho)_{\max} = 0{\cdot}40$ e Å^{-3}, $(\Delta/\sigma)_{\max} = 0{\cdot}002$ and $S = 1{\cdot}62$. Scattering factors were from *International Tables for X-ray Crystallography* (Cromer & Waber, 1974).

Discussion. The structure of $\mathrm{NiCl[P(C_6H_5)_3]_3.C_7H_8}$ consists of a discrete $\mathrm{NiCl[P(C_6H_5)_3]_3}$ molecule and a solvent toluene molecule while $\mathrm{CoCl[P(C_6H_5)_3]_3}$ has three distinct molecules situated on independent threefold axes and is isomorphous with $\mathrm{NiBr[P(C_6H_5)_3]_3}$ (Mealli, Dapporto, Sriyunyongwat & Albright, 1983). It is interesting that both sets of crystals are grown from toluene solvent but only one crystallizes with a solvent molecule in the lattice. All cobalt and chlorine atoms are situated on crystallographic threefold axes of rotation. Accordingly it

Table 4. *Selected intramolecular bond distances* (Å) *and angles* (°) *for* $Ni(PPh_3)_3Cl.C_7H_8$

Ni(1)—Cl(1)	2·2785 (9)	Ni(1)—P(1)	2·3029 (9)
Ni(1)—P(2)	2·2987 (9)	Ni(1)—P(3)	2·3148 (9)
P(1)—C(11*A*)	1·828 (3)	P(1)—C(12*A*)	1·831 (3)
P(1)—C(13*A*)	1·832 (3)	P(2)—C(21*A*)	1·838 (3)
P(2)—C(22*A*)	1·831 (3)	P(2)—C(23*A*)	1·833 (3)
P(3)—C(31*A*)	1·832 (3)	P(3)—C(32*A*)	1·846 (3)
P(3)—C(33*A*)	1·839 (3)		

Cl(1)—Ni(1)—P(1)	106·24 (4)	Cl(1)—Ni(1)—P(2)	106·97 (4)
Cl(1)—Ni(1)—P(3)	99·67 (4)	P(1)—Ni(1)—P(2)	108·56 (3)
P(1)—Ni(1)—P(3)	119·58 (3)	P(2)—Ni(1)—P(3)	114·40 (4)
Ni(1)—P(1)—C(11*A*)	116·27 (9)	Ni(1)—P(1)—C(12*A*)	114·64 (9)
Ni(1)—P(1)—C(13*A*)	117·12 (9)	C(11*A*)—P(1)—C(12*A*)	103·9 (1)
C(11*A*)—P(1)—C(13*A*)	103·0 (1)	C(12*A*)—P(1)—C(13*A*)	99·7 (1)
Ni(1)—P(2)—C(21*A*)	118·4 (1)	Ni(1)—P(2)—C(22*A*)	114·8 (1)
Ni(1)—P(2)—C(23*A*)	115·5 (1)	P(1)—C(13*A*)—C(13*B*)	119·3 (2)
C(21*A*)—P(2)—C(22*A*)	99·9 (1)	P(1)—C(13*A*)—C(13*F*)	122·4 (2)
C(21*A*)—P(2)—C(23*A*)	103·5 (1)	C(22*A*)—P(2)—C(23*A*)	102·3 (1)
Ni(1)—P(3)—C(31*A*)	116·41 (9)	Ni(1)—P(3)—C(32*A*)	116·9 (1)
Ni(1)—P(3)—C(33*A*)	114·90 (9)	C(31*A*)—P(3)—C(32*A*)	101·7 (1)
C(31*A*)—P(3)—C(33*A*)	102·6 (1)	P(2)—C(21*A*)—C(21*B*)	120·0 (2)
C(32*A*)—P(3)—C(33*A*)	102·2 (1)	P(2)—C(21*A*)—C(21*F*)	122·4 (3)
P(1)—C(11*A*)—C(11*B*)	118·4 (2)	P(1)—C(11*A*)—C(11*F*)	123·5 (2)
P(3)—C(32*A*)—C(32*B*)	118·9 (2)	P(3)—C(32*A*)—C(32*F*)	122·4 (4)
P(2)—C(22*A*)—C(22*B*)	119·3 (2)	P(2)—C(22*A*)—C(22*F*)	122·3 (2)
P(3)—C(33*A*)—C(33*B*)	119·1 (2)	P(3)—C(33*A*)—C(33*F*)	123·5 (2)
P(2)—C(23*A*)—C(23*B*)	125·0 (2)	P(2)—C(23*A*)—C(23*F*)	116·9 (2)
P(3)—C(31*A*)—C(31*B*)	124·6 (2)	P(3)—C(31*A*)—C(31*F*)	117·4 (2)

was necessary to find only one triphenylphosphine ligand per cobalt/chlorine pair to complete the structure solution. *ORTEP*II (Johnson, 1976) diagrams of one molecule of (I) and of (II) are shown in Figs. 1 and 2 with stereoviews given in Figs. 3 and 4. Selected positional parameters and intramolecular distances and angles are located in Tables 1–4.*

The nickel and cobalt atoms exhibit distorted tetrahedral coordination geometries, as anticipated from earlier studies (Arresta, Rossi & Sacco, 1969). The average Co—P distance is 2·327 (9) Å {e.s.d.'s of average values are calculated with the scatter formula: $\sigma = [\sum(d_i - d)^2/(N - 1)^{1/2}\}$ and the Co—Cl bond lengths range from 2·237 (3) to 2·258 (3) Å. The Co—P distances are not unusual when compared with the mean Co—P length in the Co^I complex *trans*-$HCo(CO)[P(C_6H_5)_3]_3$ [*d*Co—P(av.) = 2·188 (8) Å] (Whitfield, Watkins, Tupper & Bradley, 1977) and with the Co—P bond distances in $Co(CO)(NO)[P(C_6H_5)_3]_3$ [*d*Co—P = 2·224 (3) Å] and $Co(CO)_2(NO)[P(C_6H_5)_3]_2$ [*d*Co—P = 2·230 (3) Å] (Albano, Bellon & Ciani, 1972). The Co—P and Co—Cl distances in $CoCl_2[P(C_6H_5)_3][\eta\text{-}C_5(CH_3)_4\text{-}C_2H_5]C_7H_8$ are 2·289 (2), 2·263 (2) and 2·288 (2) Å, respectively (Couldwell & Husain, 1978). The angles around the cobalt atom deviate slightly from tetrahedral values with P—Co—P(av.) = 104·7 (4)° and Cl—Co—P(av.) = 113·9 (3)°.

The metricals for the nickel complex are considerably different from the chlorine to bromine compounds. For X = Br (Mealli *et al.*, 1983), the X—Ni—P averages 110·5 (5)° in a narrow spread while for X = Cl these angles range from 99·67 (4) to 106·97 (4)° with an average value of 104·3 (4·0)°. The smaller angles may reflect the smaller steric requirements of the chlorine ligand *versus* bromine. The P—Ni—P angles complement this by opening in the chlorine case to an average value of 114·2 (5·5)° as compared to the X = Br value of 108·4 (5)°.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54239 (128 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.