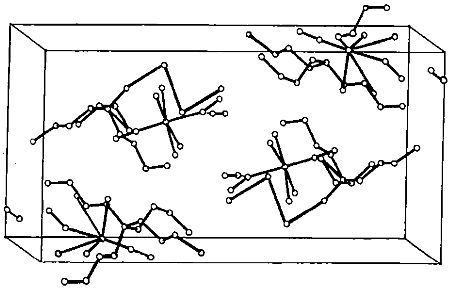

Fig. 2. A view of the unit-cell contents.

(Radonovich & Hoard, 1984) and $Tc(NO)Br_2(CNCMe_3)_3$ (Linder, Davison, Dewan, Costello & Maleknia, 1986) similar distortions have been observed. The Tc—N—O bond angle of 175·5 (10)° confirms that the ligand should be considered as NO^+ rather than NO^-. The Tc—N bond length of 1·689 (11) Å appears shorter than in the two complexes above which are 1·716 (4) and 1·726 (15) Å respectively (though this is barely statistically significant) while the N—O bond is intermediate between the other two, 1·203 (6) and 1·136 (17) Å. The Tc—O bond is probably elongated owing to the *trans* effect of the nitrosyl, although a lack of comparable Tc complexes prevents a quantitative assessment of the effect. However a long axial bond has been observed in the analogous rhenium complex (Ciano, Guisto, Manassero & Sansoni, 1975). The contact distance of 2·610 (2) Å for O(2)—O(3) is attributed to hydrogen bonding between coordinated and solvated methanols.

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cis-Dichloro[trimethylenebis(diphenylphosphine)]platinum(II)

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Abstract. $[PtCl_2\{P_2(C_3H_6)(C_6H_5)_4\}]$, $M_r = 678·4$, triclinic, $P\bar{1}$, $a = 14·424$ (1), $b = 10·686$ (1), $c = 8·580$ (1) Å, $\alpha = 72·61$ (1), $\beta = 79·80$ (1), $\gamma = 88·31$ (1)°, $U = 1241·6$ Å^3, $Z = 2$, $D_m = 1·80$ (1), $D_x = 1·81$ g cm^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0·71069$ Å, $\mu = 63·0$ cm^{-1}, $F(000) = 660$, $T = 294$ (1) K, $R = 0·025$, $wR = 0·029$ for 6195 unique reflections [$I \geq 3\sigma(I)$]. Crystals are isomorphous with those of their palladium analogue and molecular dimensions differ only in detail. The Pt—P bond distances are equivalent to within experimental error [av. 2·2321 (6) Å] but the Pt—Cl distances are inequivalent [2·3559 (8) and 2·3687 (8) Å]. The alkyl backbone of the phospine ligand exhibits substantial angular strain.

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Introduction. The title compound was obtained, as the only crystalline product formed, while attempting to recrystallize *cis*-$[PtCl(COC_6H_9)\{(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2\}]$ (Bennett & Rokicki, 1983). Data collection and structure solution were commenced on the basis of apparently satisfactory density agreement found, later, to be due to a numerical error. Nevertheless, precise molecular dimensions for the title compound are of interest, both for comparison with related molecules and because it provides a further example of length differences between chemically equivalent Pt—Cl bonds.

Experimental. Tabular colourless crystals from dichloromethane solution of *cis*-$[PtCl(OCC_6H_9)\{(C_6$-

$H_5)_2P(CH_2)_3P(C_6H_5)_2\}]$. D_m by flotation in aq. $ZnBr_2$. Sample crystal (cleaved) $0{\cdot}125 \times 0{\cdot}19 \times 0{\cdot}16$ mm perpendicular to bounding forms {100}, {010} and {001}; Philips PW 1100/20 diffractometer, θ–2θ continuous-scan mode [3° min^{-1} 2θ, 2 × 7s background counts at extremes, $3 < 2\theta < 60°$, Mo $K\bar{\alpha}$, graphite-crystal monochromator, forms recorded $\pm h$, $\pm k$, $+l$, $20 \geq h \geq -20$, $15 \geq k \geq -15$, $12 \geq l \geq 0$, 7644 reflections including standards (3 every hour, 902, 060 and 005, total degradation 1·7, 1·1 and 2·0% respectively)]; data corrected for absorption (de Meulenaer & Tompa, 1965) [transmission factors: 0·563 (max.), 0·384 (min.)] and for crystal degradation (rate = $2{\cdot}103 \times 10^{-6}$ per measured reflection; three-standards average); sorting and averaging yield 6195 reflections with $I \geq 3\sigma(I)$; $R_s[=\sum\sigma(F_o)/\sum|F_o|]$ for this data set = 0·020; R_{int} for 705 terms = 0·011; cell dimensions from 25 well dispersed reflections with $49 < 2\theta < 57°$ [Mo $K\alpha_1$ radiation, $T = 294$ (2) K]; structure solved by conventional Patterson and Fourier techniques; full-matrix least-squares refinement on F with weights $w = [\sigma^2(F_o) + 0{\cdot}0003|F_o|^2]^{-1}$ (Busing & Levy, 1957; Corfield, Doedens & Ibers, 1967), anisotropic thermal parameters for C, Cl, P and Pt, isotropic thermal parameters for H (located by calculation, C—H = 0·95 Å, $B_H = 1{\cdot}1B_C$), correction for extinction (Zachariasen, 1963), $R = 0{\cdot}025$, $wR = 0{\cdot}029$, $S = 1{\cdot}135$, extinction coefficent = 0·8 (2) $\times 10^{-5}$, $-1{\cdot}3 < (\rho_o - \rho_c) < 2{\cdot}0$ e Å^{-3}, max. $\Delta/\sigma = 0{\cdot}08$; scattering factors, with dispersion corrections for all non-H, from *International Tables for X-ray Crystallography* (1974); calculations performed with *ANUCRYS* programs (McLaughlin, Taylor & Whimp, 1977) and the Australian National University Univac 1100/82 computer.

Discussion. Atomic coordinates are listed in Table 1* and selected bond lengths and bond angles in Table 2. The atom nomenclature is defined in Fig. 1 (*ORTEP*II; Johnson, 1976).

Crystals of the title compound (I) are isomorphous with those of the palladium analogue *cis*-$[PdCl_2\{(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2\}]$ (II)† (Steffen & Palenik, 1976) and molecules are dimensionally similar.

The Pt atom has slightly distorted square-planar coordination geometry with the chlorine ligands displaced by 0·278 (1) [Cl(2)] and −0·045 (1) Å [Cl(1)] from the Pt, P(1), P(2) plane. Corresponding values for (II) are 0·324 (1) and −0·065 (1) Å. A similar deformation [0·264 (7), −0·050 (7) Å] in *cis*-$[PtCl_2\{(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2\}]$ (III) (Farrar & Ferguson, 1982) has been attributed to an unfavourable intramolecular non-bonding interaction (H···Cl 2·51 Å). No such interaction occurs for (I). Cl(2) does make two marginally short intermolecular contacts [Cl(2)···H(26) (x, $1+y$, $1+z$) 2·81 Å, Cl(2)···H(12) (x, y, $1-z$) 2·89 Å] but neither appears so directed as to result in the observed deformation. Rather, it probably

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = \tfrac{1}{3}\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Pt	0·245167 (8)	0·337807 (11)	0·101508 (14)	2·1
Cl(1)	0·27267 (7)	0·17962 (8)	−0·04369 (11)	3·3
Cl(2)	0·23006 (9)	0·49570 (9)	−0·15106 (11)	4·1
P(1)	0·21637 (6)	0·48560 (8)	0·23991 (11)	2·5
P(2)	0·27920 (6)	0·18633 (8)	0·32542 (11)	2·5
C(1)	0·1483 (2)	0·6240 (3)	0·1453 (5)	2·9
C(2)	0·0572 (3)	0·6006 (4)	0·1235 (6)	4·0
C(3)	0·0038 (3)	0·7042 (5)	0·0503 (7)	4·7
C(4)	0·0404 (4)	0·8290 (5)	−0·0032 (6)	5·0
C(5)	0·1293 (4)	0·8539 (4)	0·0177 (7)	4·9
C(6)	0·1838 (3)	0·7518 (4)	0·0918 (5)	3·8
C(7)	0·3244 (2)	0·5541 (3)	0·2639 (4)	2·7
C(8)	0·4012 (3)	0·5742 (5)	0·1359 (5)	4·3
C(9)	0·4863 (3)	0·6229 (5)	0·1516 (7)	5·2
C(10)	0·4962 (4)	0·6512 (5)	0·2899 (7)	5·3
C(11)	0·4215 (4)	0·6333 (7)	0·4156 (7)	7·1
C(12)	0·3346 (4)	0·5851 (6)	0·4027 (6)	5·6
C(13)	0·1461 (3)	0·4220 (4)	0·4489 (5)	3·6
C(14)	0·1707 (3)	0·2891 (4)	0·5571 (5)	4·0
C(15)	0·2675 (3)	0·2383 (4)	0·5117 (4)	3·4
C(16)	0·4011 (2)	0·1391 (4)	0·2866 (4)	3·0
C(17)	0·4723 (3)	0·2202 (4)	0·2946 (6)	4·2
C(18)	0·5661 (3)	0·1906 (6)	0·2518 (7)	5·4
C(19)	0·5890 (3)	0·0815 (5)	0·2019 (6)	4·7
C(20)	0·5195 (4)	0·0020 (5)	0·1934 (6)	4·9
C(21)	0·4252 (3)	0·0297 (4)	0·2360 (6)	4·0
C(22)	0·2076 (3)	0·0367 (3)	0·3967 (4)	3·0
C(23)	0·1286 (3)	0·0267 (4)	0·3309 (5)	4·1
C(24)	0·0733 (4)	−0·0866 (6)	0·3932 (7)	5·9
C(25)	0·0945 (4)	−0·1876 (5)	0·5181 (7)	5·8
C(26)	0·1723 (4)	−0·1784 (4)	0·5870 (7)	5·7
C(27)	0·2300 (4)	−0·0676 (4)	0·5238 (6)	4·7

Table 2. *Selected lengths* (Å) *and angles* (°)

Pt—Cl(1)	2·3687 (8)	Pt—P(1)	2·2325 (8)
Pt—Cl(2)	2·3559 (8)	Pt—P(2)	2·2317 (8)
P(1)—C(1)	1·814 (4)	P(2)—C(15)	1·822 (4)
P(1)—C(7)	1·810 (3)	P(2)—C(16)	1·816 (4)
P(1)—C(13)	1·836 (4)	P(2)—C(22)	1·812 (4)
Cl(1)—Pt—Cl(2)	88·41 (3)	Cl(2)—Pt—P(1)	91·73 (3)
Cl(1)—Pt—P(1)	178·90 (3)	Cl(2)—Pt—P(2)	172·44 (4)
Cl(1)—Pt—P(2)	88·34 (3)	P(1)—Pt—P(2)	91·63 (3)
Pt—P(1)—C(1)	115·0 (1)	Pt—P(2)—C(15)	115·2 (1)
Pt—P(1)—C(7)	111·6 (1)	Pt—P(2)—C(16)	110·0 (1)
Pt—P(1)—C(13)	114·5 (1)	Pt—P(2)—C(22)	116·0 (1)
C(1)—P(1)—C(7)	106·2 (2)	C(15)—P(2)—C(16)	105·2 (2)
C(1)—P(1)—C(13)	102·1 (2)	C(15)—P(2)—C(22)	102·6 (2)
C(7)—P(1)—C(13)	106·6 (2)	C(16)—P(2)—C(22)	107·0 (2)
P(1)—C(1)—C(2)	118·8 (3)	P(2)—C(15)—C(14)	112·5 (3)
P(1)—C(1)—C(6)	122·3 (3)	P(2)—C(16)—C(17)	119·5 (3)
P(1)—C(7)—C(8)	118·6 (3)	P(2)—C(16)—C(21)	121·4 (3)
P(1)—C(7)—C(12)	123·3 (3)	P(2)—C(22)—C(23)	121·1 (3)
P(1)—C(13)—C(14)	117·9 (3)	P(2)—C(22)—C(27)	119·8 (3)

* Lists of structure-factor amplitudes, anisotropic thermal parameters, H-atom coordinates and all bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43767 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Transformed (shortest edge) cell: $a = 14{\cdot}461$ (5), $b = 10{\cdot}633$ (3), $c = 8{\cdot}537$ (2) Å, $\alpha = 72{\cdot}99$ (2), $\beta = 80{\cdot}28$ (3), $\gamma = 88{\cdot}69$ (3)°.

reflects the near eclipsed disposition of the P(1)—C(1) and Pt—Cl(2) bonds about Pt—P(1) [torsion angle 25·1 (1) (I), 26·8 (2)° (II)]. The same feature is undoubtedly responsible for the 3·40 (4)° difference between the Cl(2)—Pt—P(1) and Cl(1)—Pt—P(2) angles [3·36 (7)° for (II)].

Pt—P distances are equivalent to within experimental error [av. 2·2321 (6) Å] but Pt—Cl distances are inequivalent [2·3559 (8), 2·3687 (8) Å]. A similar result holds for (II) [Δ/σ(Pd—Cl) = 3·13] and for one of two isomers of *cis*-$[PtCl_2(PMePh_2)_2]$ ($\Delta/\sigma = 10$) (Ho, McLaughlin, McPartlin & Robertson, 1982). Pt—Cl inequivalence, but accompanied by Pt—P inequivalence, has also been reported for *cis*-$[PtCl_2(PPh_3)_2]$ (Anderson, Clark, Davies, Ferguson & Parvez, 1982). Weighted averages of the *M–L* bond lengths in (I) [Pt—*L* = 2·297 Å] and (II) [Pd—*L* = 2·298 Å] are in excellent agreement, consistent with the expectation of near identical covalent radii for Pt^{II} and Pd^{II}. However, the pattern of distances differs. *M*—P distances in (I) are shorter [av. 0·013 (1) Å] and *M*—Cl distances are longer [av. 0·008 (1) Å] than those in (II), probably reflecting the greater affinity of Pt *cf.* Pd for phosphine ligands. It is also noteworthy that the longer *M*—Cl bonds in both (I) and (II) are those associated with the most linear P—*M*—Cl moieties [178·9 *cf.* 172·4°, (I); 177·7 *cf.* 171·9°, (II)]. We have remarked previously, in relation to bond-length variations in *cis*-$[PtCl_2(PMePh_2)_2]$ (Ho, McLaughlin, McPartlin & Robertson, 1982), that such a result might well flow from the high *trans* influences of the phosphine ligands. The present result appears to provide some support for that contention. So too does the (pairwise) equivalence of the *M*—Cl distances in *cis*-$[PtCl_2\{Ph_2P(CH_2)_2PPh_2\}]$ (III) (Farrar & Ferguson, 1982), *cis*-$[PdCl_2\{Ph_2P(CH_2)_2PPh_2\}]$ (IV) (Steffen & Palenik, 1976), *cis*-$[PtCl_2\{(t\text{-Bu})_2P(CH_2)_2P(t\text{-Bu})_2\}]$ (V) (Harada, Kai, Yasuoka & Kasai, 1976) and *cis*-$[PtCl_2\{(t\text{-Bu})_2P(CH_2)_3P(t\text{-Bu})_2\}]$ (VI) (Harada, Kai, Yasuoka & Kasai, 1979), in each of which the P—*M*—Cl angles are not (pairwise) very different [Δ(max.) = 0·9°]. The correlation observed in the isomers of *cis*-$[PtCl_2(PMePh_2)_2]$, between *M*—Cl bond length and deviation of the *cis* P—*M*—Cl angle from 90°, is not evident in the chelate complexes (I)–(VI).

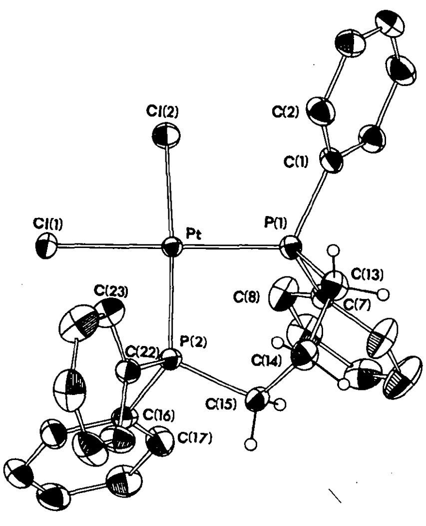

Fig. 1. Molecular conformation and atom nomenclature for (I). Vibration ellipsoids depict 30% probability surfaces; phenyl H atoms are omitted.

Comparison of (I) and (III) shows the Pt—P distances in the six-membered platinacycle to be significantly greater than those in the five-membered ring [av. 2·2321 (4) (I), 2·208 (4) Å (III)]. Similar results hold for (V) and (VI) [av. Pt—P 2·281 (2) (VI), 2·263 (2) Å (V)] and for the Pd complexes (II) and (IV) [av. Pd—P 2·246 (1) (II), 2·229 (1) Å (IV)]. The result for the Pd complexes has been attributed convincingly to distributed ring strain in the six-membered chelate ring (Steffen & Palenik, 1976). In (I) and (II) the strain is such as to cause angle deformations in the alkyl chains of up to *ca* 8° from regular tetrahedral. Pt—P distances in (V) and (VI) are appreciably greater (*ca* 0·05 Å) than those in (I) and (III), apparently as a result of substantially increased strain with the more bulky *t*-Bu-substituted ligands.

Distances and angles in the phenyl rings in (I) are unexceptional and *M*—P—C—C torsion angles are uniformly within 2·6° of those in (II). P—C(phenyl) distances average 1·813 (2) Å and P—C(alkyl) distances average 1·829 (3) Å. The difference is closely compatible with that between sp^2 and sp^3 carbon σ-orbital radii. There are no unusually short Pt···*o*-H interactions [min. 3·06 Å, Pt···H(8); 3·08 Å, Pt···H(23)].

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Structure of *trans*-Carbonylchlorobis(tri-*p*-tolylphosphine)iridium(I)

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Abstract. $[IrCl(CO)\{P(C_7H_7)_3\}_2]$, $M_r = 864{\cdot}5$, orthorhombic, $Pna2_1$, $a = 21{\cdot}586$ (2), $b = 10{\cdot}603$ (1), $c = 16{\cdot}814$ (2) Å, $V = 3848{\cdot}3$ (8) Å^3, $Z = 4$, $D_x = 1{\cdot}49$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·710 730 Å, μ(Mo $K\alpha$) = 38·7 cm^{-1}, $F(000) = 1728$, $T = 297$ K, $R(F) = 3{\cdot}5$, $R(wF) = 3{\cdot}1$% for all 5323 reflections (hkl and $hk\bar{l}$). The central Ir^{I} atom has a square-planar coordination environment in which Ir—P(1) = 2·330 (2), Ir—P(2) = 2·332 (2), Ir—Cl = 2·364 (2) and Ir—CO = 1·817 (8) Å. The tetrahedral bonding to the P atoms is distorted towards C_{3v} from T_d and the phenyl rings are distorted from D_{6h} to C_{2v} symmetry by the electronegative P atoms.

Introduction. We have been involved in the structural characterization of a variety of simple alkyl and alkoxy complexes of Ir^{I}, including *trans*-$[Ir(PPh_3)_2(CO)CH_3]$ (Rees, Churchill, Li & Atwood, 1985), *trans*-$[Ir(PPh_3)_2(CO)(OC_6H_5)]$ (Rees, Churchill, Fettinger & Atwood, 1985), *trans*-$[Ir(PPh_3)_2(CO)(OC_6F_5)]$ (Churchill, Fettinger, Rees & Atwood, 1986*c*), $[Ir(PPh_3)_2(CO)_2\{C(=O)OCH_3\}]$ (Churchill, Fettinger, Rees & Atwood, 1986*b*), $[Ir(PPh_3)_2(CO)(CH_3)(CH_3CO_2CH=CHCO_2CH_3)]$ (Churchill, Fettinger, Rees & Atwood, 1986*a*) and $[Ir(PPh_3)_2(CO)(CH_3)(CH_3CO_2C\equiv CCO_2CH_3)]$ (Rees, Churchill, Fettinger & Atwood, 1987); the species *trans*-$[Ir(PPh_3)_2(CO)(C_6F_5)]$ has also been studied (Clearfield, Gopal, Bernal, Moser & Rausch, 1975). We have recently turned our attention to the related derivatives of the tri-*p*-tolylphosphine ligand and have discovered the tetrahedral Ir^{I} complex $[Ir\{P(C_6H_4\text{-}p\text{-}CH_3)_3\}_2\{C(=O)CH_2C(CH_3)_3\}\{CH_3CO_2C\equiv CCO_2CH_3\}]$ (Rappoli, Churchill, Janik, Rees & Atwood, 1987). We now report the results of an X-ray diffraction study on the simple parent molecule of this system, $[Ir\{P(C_6H_4\text{-}p\text{-}CH_3)_3\}_2(CO)Cl]$.

Experimental. A canary-yellow colored crystal with approximate orthogonal dimensions of 0·30 × 0·30 × 0·40 mm was sealed into a thin-walled glass capillary in an inert (Ar) atmosphere and was mounted and aligned accurately on a Syntex $P2_1$ automated four-circle diffractometer. Determination of unit-cell parameters and the crystal orientation matrix and data collection [Mo $K\alpha$; $2\theta = 4{\cdot}5$–$45{\cdot}0°$; $[(\sin\theta)/\lambda]_{max} = 0{\cdot}539$ Å^{-1}] were performed as has previously been described in detail (Churchill, Lashewycz & Rotella, 1977). Three standard reflections (in approximately mutually orthogonal directions in space) were measured before each batch of 97 data; no fluctuations nor decay were observed. Diffraction data were corrected for absorption (by interpolation in 2θ and φ between a set of close-to-axial ψ scans in which $T_{max}/T_{min} = 1{\cdot}09$–$1{\cdot}14$). The systematic absences $0kl$ for $k + l = 2n + 1$ and $h0l$ for $h = 2n + 1$ ($00l$ for $l = 2n + 1$) are consistent with the non-centrosymmetric space group $Pna2_1$ or the centrosymmetric space group $Pnam$. Data for the octants hkl and $hk\bar{l}$ were collected ($h\,0\to 23$, $k\,0\to 12$, $l\,-20\to 20$), corrected for Lorentz and polarization factors and reduced to observed structure-factor amplitudes. Any reflection with a net intensity less than zero was assigned an $|F_o|$ value of zero. Intensity statistics favored the non-centrosymmetric case; this was confirmed by the successful solution and refinement of the structure in the non-centrosymmetric space group.

The coordinates of the Ir atom were determined from a three-dimensional Patterson map. The positions of all remaining non-H atoms were located from a series of difference-Fourier syntheses. H atoms on the methyl groups of the *p*-tolyl ligands were located directly and input in idealized positions; H atoms of the aromatic rings were input in calculated trigonal positions based upon externally bisecting geometry with d(C—H) = 0·95 Å (Churchill, 1973). All H atoms were assigned a thermal parameter of $U = 0{\cdot}076$ Å^2. Full-matrix least-squares refinement of positional parameters for all non-H atoms, anisotropic thermal parameters for the $IrP_2(CO)Cl$ fragment and isotropic thermal parameters

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