parallelograms form ribbons by sharing common Cu—Cl(1) edges, which lie in crystallographic mirror planes. The dihedral angle between two adjacent parallelograms is insignificantly different from zero, 0·6 (5)°. Alternatively, the structure may be regarded as containing nearly linear Cu—Cl—Cu chains with a Cu′—Cl(1)—Cu″ angle of 173·1 (1)° and equal Cu—Cl separations, 3·139 (3) Å. The Cl(1′)—Cu—Cl(1″) angle is also 173·1 (1)°. Further geometrical information is included in Fig. 2.

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# Structure of (*tert*-Butyl isocyanide)carbonyl(chloro)bis[dimethyl(phenyl)phosphine]phenylruthenium(II), $[Ru(C_6H_5)(C_5H_9N)(C_8H_{11}P)_2(CO)Cl]$

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**Abstract.** $M_r = 601·15$, orthorhombic, *Pnma*, $a = 22·250$ (7), $b = 13·706$ (4), $c = 9·963$ (3) Å, $V = 3038·3$ Å$^3$, $F(000) = 1239·5$, $T = 290 \pm 1$ K, $Z = 4$, $D_x = 1·31$ Mg m$^{-3}$, $\lambda$(Cu $K\alpha$) = 1·54178 Å, $\mu$(Cu $K\alpha$) = 62·6 cm$^{-1}$, $R = 0·047$ for 1613 observed reflections. The complex consists of discrete monomeric units, with octahedral coordination for the Ru atom. The chloride, carbonyl, phenyl and isocyanide ligands lie on a crystallographic mirror plane. The mutually *trans* chloride and carbonyl ligands are disordered. The Ru—P distance is 2·366 (2) Å. The isocyanide and phenyl ligands lie *trans* to one another with Ru—C distances of 2·013 (9) and 2·141 (9) Å respectively. The isocyanide is slightly non-linear [C—N—CMe$_3$ 169·7 (9)°].

**Introduction.** Complexes $[Ru(CO)_2RCl(PMe_2Ph)_2]$ ($R = C_6H_5$, $p$-$MeC_6H_4$, $p$-$MeOC_6H_4$, *etc.*) react with the isocyanide $Me_3CNC$ in two quite different ways. One mode of reaction involves substitution of a carbonyl ligand and formation of $[Ru(CO)RCl(CNCMe_3)(PMe_2Ph)_2]$, while the other yields benzoyl complexes $[Ru(CO)(COR)(CNCMe_3)_2(PMe_2Ph)_2]^+$. The relative yields of the two types of product are markedly affected by the nature of the group $R$ and by the conditions used for the reactions.

Beyond establishing that the two $PMe_2Ph$ ligands were mutually *trans*, it was not possible to use spectroscopic methods to determine the ligand arrangement in substitution products $[Ru(CO)RCl(CNCMe_3)(PMe_2Ph)_2]$. In addition, the exact orientation of the aryl ligand and the lengths of the various Ru—C bonds were of particular interest following the recent determination of the structure of the complex $[Ru(CO)(COPh)Ph(CNCMe_3)(PMe_2Ph)_2]$ (Chawdhury, Dauter, Mawby, Reynolds, Saunders & Stephenson, 1983). For these reasons, the crystal structure of $[Ru(CO)PhCl(CNCMe_3)(PMe_2Ph)_2]$ was determined.

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**Experimental.** Complex prepared from [$Ru(CO)_2$-$PhCl(PMe_2Ph)_2$] and slight excess of $Me_3CNC$ in $CHCl_3$ at 333 K, using a stream of $N_2$ to purge the solution of CO. Recrystallization of crude product from propanone/ethanol gave colourless needles, elongated along **b**. Unit-cell and space-group data from Weissenberg photographs (lattice parameters from 26 reflections). Systematic absences $0kl$ $k + l$ odd and $hk0$ $h$ odd indicated space groups $Pn2_1a$ or $Pnma$.

Hilger & Watts Y290 computer-controlled four-circle diffractometer, $\omega$–$2\theta$ scanning technique, crystal ~0·10 × 0·70 × 0·08 mm, count time per step 1 s, range of each scan 0·9°, $\theta_{max} = 56°$ ($0 \le h \le 23$, $0 \le k \le 14$, $0 \le l \le 10$), $R_{int} = 0{\cdot}011$ for 2412 reflections, 461 of which, with $I < 2\sigma(I)$, classified as unobserved; standard reflections 12,0,0, 004, 622: intensity variation over period of data collection < 2%; no absorption correction made. Heavy-atom technique: Ru atom from Patterson map, the remaining non-hydrogen atoms from a subsequent difference Fourier map. Full-matrix least-squares refinement on $F$ (*SHELX*; Sheldrick, 1976), atomic scattering factors and $f'$ and $f''$ from *International Tables for X-ray Crystallography* (1974); anisotropic thermal parameters for non-hydrogen atoms included in final cycles, H positions estimated geometrically using C—H = 1·08 Å.

Because of the ambiguity in the space group, the structure was refined in both $Pnma$ and $Pn2_1a$. Final $R = 0{\cdot}059$ and 0·051 for the centrosymmetric and non-centrosymmetric space groups respectively for 1613 observed reflections. The molecular geometry after refinement in $Pn2_1a$ was much poorer than in the case of the $Pnma$ refinement: for example, the bond lengths in the phenyl rings of the $PMe_2Ph$ ligands ranged from 1·355 to 1·408 Å for the centrosymmetric structure as opposed to 1·287 to 1·561 Å and 1·275 to 1·463 Å for the non-centrosymmetric structure. The correct space group was therefore taken to be $Pnma$. In this space group, the chloride, carbonyl and phenyl ligands and the C—N—C core of the isocyanide ligand were required to lie on crystallographic mirror planes at $y = 0{\cdot}25$ and 0·75, with occupancy factors of 0·5.

After convergence with anisotropic thermal parameters, it was noticed that the Ru—C and C—O distances for the carbonyl ligand were rather shorter than normal. A difference Fourier map calculated at this stage clearly revealed disorder of the chloride and carbonyl ligands. New positions for the appropriate atoms were obtained from the difference map. Occupancy factors were refined for Cl(1), C(5), O(5) and Cl(1′), C(5′), O(5′). Refinement in space group $Pnma$ converged at $R = 0{\cdot}047$, $R_w = 0{\cdot}059$ for 1613 observed reflections; $w = 0{\cdot}7082/[\sigma^2(F_o) + 0{\cdot}0051|F_o|^2]$; $\Delta/\sigma < 0{\cdot}1$ for coordinates, $< 0{\cdot}2$ for thermal parameters; $-0{\cdot}31 \le \Delta\rho \le 0{\cdot}38$ e Å$^{-3}$ in final difference map. The final atomic coordinates for the non-hydrogen atoms are listed in Table 1 and selected bond distances and angles in Table 2.*

Table 1. *Final atomic coordinates* (×10$^4$) *and* $U_{eq}$ *values* (×10$^3$) *for the non-hydrogen atoms*

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{23}\cos\alpha + 2U_{23}\cos\beta + 2U_{12}\cos\gamma).$$

| | $x$ | $y$ | $z$ | $U_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| Ru | 5726 (1) | 2500 | 7431 (1) | 38 |
| P(1) | 5704 (1) | 4222 (1) | 7280 (2) | 48 |
| C(11) | 4983 (3) | 4764 (5) | 7705 (8) | 68 |
| C(12) | 5856 (3) | 4720 (5) | 5629 (7) | 63 |
| C(101) | 6248 (3) | 4869 (5) | 8310 (7) | 53 |
| C(102) | 6095 (4) | 5623 (6) | 9191 (7) | 78 |
| C(103) | 6527 (5) | 6065 (6) | 9922 (9) | 101 |
| C(104) | 7116 (5) | 5815 (7) | 9809 (10) | 104 |
| C(105) | 7289 (4) | 5068 (7) | 8964 (9) | 95 |
| C(106) | 6849 (3) | 4611 (6) | 8218 (8) | 69 |
| C(301) | 5077 (4) | 2500 | 5846 (9) | 48 |
| C(302) | 5215 (4) | 2500 | 4491 (9) | 51 |
| C(303) | 4794 (6) | 2500 | 3450 (11) | 72 |
| C(304) | 4190 (6) | 2500 | 3783 (14) | 77 |
| C(305) | 4016 (5) | 2500 | 5112 (13) | 74 |
| C(306) | 4446 (5) | 2500 | 6116 (12) | 64 |
| C(4) | 6289 (4) | 2500 | 9014 (10) | 48 |
| N(4) | 6546 (4) | 2500 | 10007 (8) | 55 |
| C(40) | 6767 (4) | 2500 | 11384 (10) | 62 |
| C(41) | 6505 (4) | 3396 (6) | 12049 (7) | 79 |
| C(42) | 7445 (7) | 2500 | 11364 (16) | 126 |
| Cl(1) | 6601 (4) | 2500 | 5881 (7) | 52 |
| C(5) | 5149 (11) | 2500 | 8693 (35) | 57 |
| O(5) | 4771 (12) | 2500 | 9476 (30) | 63 |
| Cl(1′) | 4984 (7) | 2500 | 9278 (25) | 49 |
| C(5′) | 6351 (23) | 2500 | 6308 (41) | 28 |
| O(5′) | 6731 (32) | 2500 | 5362 (63) | 74 |

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

| | | | |
|---|---|---|---|
| Ru—P(1) | 2·366 (2) | P(1)—C(12) | 1·812 (7) |
| Ru—C(301) | 2·141 (9) | P(1)—C(101) | 1·818 (7) |
| Ru—C(4) | 2·013 (9) | C(4)—N(4) | 1·143 (12) |
| Ru—C(5) | 1·798 (30) | N(4)—C(40) | 1·458 (13) |
| Ru—C(5′) | 1·784 (47) | C(40)—C(41) | 1·513 (10) |
| Ru—Cl(1) | 2·483 (8) | C(40)—C(42) | 1·508 (17) |
| Ru—Cl(1′) | 2·473 (22) | C(5)—O(5) | 1·148 (41) |
| P(1)—C(11) | 1·817 (8) | C(5′)—O(5′) | 1·266 (81) |

Phenyl ring: 1·379 (18)—1·428 (14), average 1·393 (16)

| | | | |
|---|---|---|---|
| P(1)—Ru—C(301) | 86·5 (0·1) | C(4)—Ru—Cl(1′) | 80·3 (0·5) |
| P(1)—Ru—C(4) | 93·6 (0·1) | C(5)—Ru—C(5′) | 174·4 (1·7) |
| P(1)—Ru—C(5) | 91·7 (0·1) | C(5)—Ru—Cl(1) | 174·1 (1·0) |
| P(1)—Ru—C(5′) | 88·7 (0·1) | C(5)—Ru—Cl(1′) | 3·7 (1·1) |
| P(1)—Ru—Cl(1) | 88·7 (0·1) | C(5′)—Ru—Cl(1) | 0·4 (1·0) |
| P(1)—Ru—Cl(1′) | 91·9 (0·1) | C(5′)—Ru—Cl(1′) | 170·7 (1·5) |
| C(301)—Ru—C(4) | 175·9 (0·4) | Cl(1)—Ru—Cl(1′) | 170·4 (0·5) |
| C(301)—Ru—C(5) | 91·9 (1·0) | Ru—P(1)—C | 115·2 (0·2) |
| C(301)—Ru—C(5′) | 93·7 (1·5) | Ru—C(4)—N(4) | 171·6 (0·8) |
| C(301)—Ru—Cl(1) | 94·0 (0·3) | C(4)—N(4)—C(40) | 169·7 (0·9) |
| C(301)—Ru—Cl(1′) | 95·6 (0·5) | N(4)—C(40)—C(41) | 106·4 (0·5) |
| C(4)—Ru—C(5) | 84·0 (1·0) | N(4)—C(40)—C(42) | 109·0 (0·9) |
| C(4)—Ru—C(5′) | 90·4 (1·5) | Ru—C(5)—O(5) | 178·4 (2·9) |
| C(4)—Ru—Cl(1) | 90·0 (0·3) | Ru—C(5′)—O(5′) | 170·7 (4·7) |

Phenyl ring: 113·6 (0·9)—125·1 (0·9), average 120·0 (1·0)

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* Lists of structure factors, anisotropic thermal parameters, least-squares planes and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38614 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Discussion.** The complex is monomeric: its molecular geometry is shown in Fig. 1, with the numbering scheme used in the structure analysis. A stereoscopic diagram of the packing is shown in Fig. 2. The ligand arrangement around the ruthenium is not far removed from regular octahedral, and the three metal–carbon bonds and the metal–chlorine bond lie on the mirror plane.

The phenyl ligand lies exactly on the mirror plane. This orientation is similar to that adopted by the phenyl ligand in $[\mathrm{Ru(CO)(COPh)Ph(CNCMe_3)(PMe_2Ph)_2}]$ (Chawdhury *et al.*, 1983), and is probably favoured for electronic reasons, since it maximizes the overlap with one particular filled *d* orbital on the metal. The *d* orbital involved, although inevitably shared with the ligand *trans* to phenyl, is *not* shared with the one remaining strongly $\pi$-accepting ligand {CO in this instance; $\mathrm{Me_3CNC}$ in the case of $[\mathrm{Ru(CO)(COPh)Ph(CNCMe_3)(PMe_2Ph)_2}]$}. If the plane of the phenyl ring were parallel with the Ru—P bonds, the *d* orbital concerned would be shared with this ligand as well (it should be noted that there appears to be no *steric* reason why the phenyl ring should not lie parallel with the Ru—P bonds: placing the ring in this position does not result in any short contacts between the ring and the $\mathrm{PMe_2Ph}$ ligands).* An exactly similar explanation has been proposed (Brown, Barnard, Daniels, Mawby & Ibers, 1978) for the orientation of the ethene ligand in $[\mathrm{Ru(CO)(C_2H_4)Cl_2(PMe_2Ph)_2}]$, where the C—C bond lies parallel to the Ru—P bonds, allowing the empty $\pi$-antibonding orbitals on ethene and carbonyl ligands to interact with different *d* orbitals on the metal.

The Ru—C bond to the phenyl ligand in $[\mathrm{Ru(CO)PhCl(CNCMe_3)(PMe_2Ph)_2}]$ [2·141 (9) Å] is slightly shorter than the corresponding bond in $[\mathrm{Ru(CO)(COPh)Ph(CNCMe_3)(PMe_2Ph)_2}]$ [2·187 (12) Å]: this *could* be taken to indicate that the ligand *trans* to phenyl in the former complex ($\mathrm{Me_3CNC}$) is a poorer $\pi$-acceptor than CO, which occupies a similar position in the latter complex. The lengths of the Ru—C bonds to the isocyanide ligands in the two complexes differ very little [2·013 (9) and 2·004 (15) Å, respectively], despite the difference in the ligand *trans* to isocyanide in the two cases. The Ru—C—N—C system is slightly non-linear, with Ru—C(4)—N(4) and C(4)—N(4)—C(40) angles of 171·6 (8) and 169·7 (9)° respectively, making an interesting comparison with $[\mathrm{Ru(CNCMe_3)_4(PPh_3)}]$, where two of the isocyanide ligands show similar near-linear coordination and the other two are markedly bent at nitrogen [mean C—N—C angle 130 (2)°] (Bassett, Berry, Barker, Green, Howard & Stone, 1979). The Ru—P bond length of 2·366 (2) Å is within the range of values observed for other ruthenium(II) complexes containing a pair of mutually *trans* $\mathrm{PMe_2Ph}$ ligands (Ashworth, Nolte, Singleton & Laing, 1977).

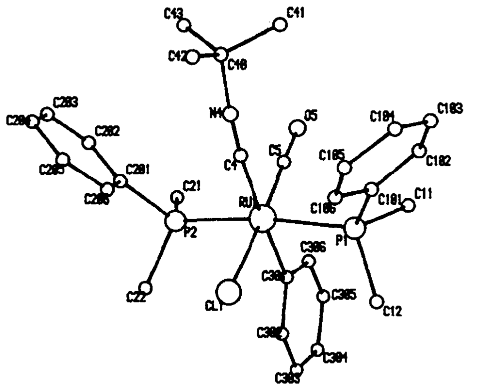

Fig. 1. The molecular structure of $[\mathrm{Ru(CO)PhCl(CNCMe_3)(PMe_2Ph)_2}]$ showing the atomic numbering scheme.

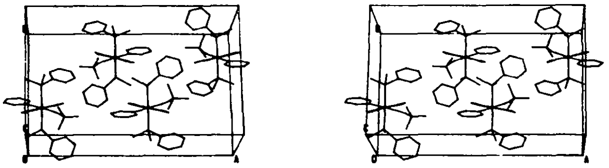

Fig. 2. Stereoview of the packing in the unit cell of $[\mathrm{Ru(CO)PhCl(CNCMe_3)(PMe_2Ph)_2}]$ (*a* horizontal, *b* vertical, *c* into the page).

The mutually *trans* chloride and carbonyl ligands are disordered, with occupancy factors of 0·36 (2) [Cl(1), C(5), O(5)] and 0·14 (2) [Cl(1′), C(5′), O(5′)]. Similar disorder has been observed for the same pair of ligands in the structure of $[\mathrm{Ru(CO)(C_2H_4)Cl_2(PMe_2Ph)_2}]$ (Brown *et al.*, 1978). The Ru—Cl bond lengths [2·483 (8) and 2·473 (22) Å] are at the upper end of the range for Ru—Cl *trans* to CO, while the Ru—CO bonds [1·80 (3) and 1·78 (5)] are slightly shorter than those in other complexes with Ru—CO *trans* to chloride (Brown *et al.*, 1978; Holland, Howard & Mawby, 1983).

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* The observation of separate resonances for the two *ortho* C atoms in the phenyl ligand in the ambient-temperature NMR spectrum of $[\mathrm{Ru(CO)PhCl(CNCMe_3)(PMe_2Ph)_2}]$ in $\mathrm{CDCl_3}$ solution confirms that there is a significant energy barrier to rotation about the metal–phenyl bond.