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# STRUCTURAL STUDIES OF CARBENE COMPLEXES: THE CRYSTAL STRUCTURE OF THE SECONDARY CARBENE COMPLEX $RuI_2[CHN(CH_3)(p\text{-}CH_3C_6H_4)](CO)(CN\text{-}p\text{-}CH_3C_6H_4)(P(C_6H_5)_3)$

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## Summary

Crystal and molecular structures of the title compound have been determined from a three-dimensional X-ray analysis using diffractometer data. The crystals are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions $a = 11.640(1)$, $b = 10.9139(8)$, $c = 16.587(2)$ Å, $\alpha = 87.983(5)$, $\beta = 99.670(6)$, $\gamma = 62.250(5)°$. Full matrix least squares refinement has given a final $R$-factor of 0.043 for 2726 reflections for which $I > 2\sigma(I)$.

The crystal structure consists of discrete molecules of neutral complex together with water molecules which are hydrogen bonded into pairs [O ··· O separation 2.60 Å]. The $(H_2O)_2$ units do not hydrogen bond to any other atoms. The ruthenium coordination is octahedral with *trans* carbene and isocyanide, *cis* iodides, and *cis* phosphine and carbonyl ligands. The Ru-donor distances are 2.776(2) [I *trans* to —$PPh_3$], 2.782(1) [I *trans* to —CO], 2.342(4) [$PPh_3$], 1.855(15) [CO], 2.046(15) [C(carbene)], and 1.998(16) Å [C(isocyanide)]. The bond lengths are discussed in terms of the *trans* effects of the ligands. The C(carbene)—N distance is 1.26(2) Å and the Ru—C(carbene)—N angle is 141.5(5)°.

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## Introduction

Since the first correctly formulated metal—carbene complex was reported [1] in 1964, a wide variety of novel carbene complexes have been synthesized and the reactions of the coordinated ligands investigated. The complexes are most stable when atoms adjacent to the carbene carbon atom are either heteroatoms or else part of a delocalised $\pi$-electron system. Stability results from $\pi$-donation to the electron deficient $p$ orbital of the carbene carbon atom. X-ray structural analyses show the acyclic carbene ligands containing heteroatoms to be stronger $\sigma$-donors and weaker $\pi$-acceptors than CO, and the metal—C bond to be essentially single. The preparations, reactivities, and structures of carbene complexes have been the subject of a number of extensive reviews [2—5].

Secondary carbene complexes [6], i.e. those in which a hydrogen atom is directly attached to the carbene carbon, are not widely known [6—11]. A few [7—9] have been prepared by electrophilic attack on the coordinated imidoyl group, $M-\underset{|}{C}=NR$. The ruthenium complexes show $\nu$C(carbene)—N of about 1550 $cm^{-1}$ and a very low field C(carbene)—H $^1H$ NMR signal which suggests a particularly high bond order for the C—N bond [7].

A crystal structure determination of the neutral secondary carbene complex $RuI_2[CHN(CH_3)(p\text{-}CH_3C_6H_4)](CO)(CN\text{-}p\text{-}CH_3C_6H_4)(PPh_3)$ (recently prepared [12] by reaction of the formimidoyl-containing $Ru(O_2CCH_3)[CHN(CH_3)(p\text{-}CH_3C_6H_4)](CO)(PPh_3)$ [9] with isocyanide, $CH_3I$, and $I_2$) has been completed, and affords a useful comparison with the known structures of the formimidoyl percursor [13] and the isoelectronic secondary carbene complex $RhCl_3(PEt_3)_2\text{-}CHNMe_2$ [11].

## Experimental

The crystals, prepared by Dr. W.R. Roper and Dr. D.F. Christian, were pale lemon-coloured parallelepipeds. Initial X-ray photography showed them to be triclinic (with well developed {0 0 1}, {1 1 0}, and {$\bar{1}$ 1 0} forms). Accurate unit cell constants were determined from a least-squares refinement of the setting angles of twelve high-theta reflections (theta range 14.7—18.0°) using a Hilger and Watts four-circle automatic diffractometer [14].

### *Crystal data*

$C_{35}H_{35}I_2N_2O_2PRu$, $M = 913.56$, Triclinic, $a = 11.640(1)$, $b = 10.9139(8)$, $c = 16.587(2)$ Å, $\alpha = 87.983(5)$, $\beta = 99.670(6)$, $\gamma = 62.250(5)$, $V = 1822.86$ Å$^3$, space group $P\bar{1}$, $Z = 2$, $d_m = 1.73$, $d_c = 1.69$, $F(0\ 0\ 0) = 892$, Mo-$K_\alpha$ radiation of $\lambda = 0.71069$ Å, Zr filter, $\mu(\text{Mo}K_\alpha) = 23.14$ $cm^{-1}$, crystal size = 0.125 × 0.146 × 0.137 mm, mosaic spread 0.16°.

Intensity data to a Bragg limit of 20° ($\sin\theta/\lambda = 0.48$) were collected using a symmetric $2\theta$—$\omega$ scan of 1.20° at a scan rate of 0.02° $s^{-1}$. Each background was counted for 10 s. Reflections examined were $\pm h \pm kl$ and these yielded 2726 "observed" independent reflections with $I > 2\sigma(I)$ ($\sigma(I) = [T + t^2B + (pI)^2]^{1/2}$, $T$ = integrated peak count, $B$ = average background count, $t$ = ratio of scan to background times, $p$ was assigned an initial value of 0.04 [15], but this was later increased to 0.06). The data were corrected for Lorentz and polarisation factors and for absorption (maximum and minimum transmission coefficients were 0.7956 and 0.6692 respectively) [16].

## Structure determination and refinement

Positions for the ruthenium and two iodine atoms were deduced from the Patterson synthesis and were used to phase a 'heavy-atoms' electron density map. All remaining non-hydrogen atoms were readily located with the exception of a solvent water molecule which was observed in a subsequent 'difference' synthesis. Full matrix least-squares refinement was then commenced [17]. Atoms were assigned initial isotropic temperature factors of 3.0 Å$^2$ for the heavy atoms, and 4.0 Å$^2$ for the remainder. Atomic scattering factors used were from standard listings [18] with those for I and Ru corrected for real dispersion effects [19]. The function minimised was $\Sigma\, w(|F_o| - |F_c|)^2$, with weights $\omega = 4|F_o|^2/(\sigma^2(F_o)^2)$. After two cycles the residual $R$ was 0.13 and the weighted residual $R'(= \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2\}^{1/2})$ was 0.16. The temperature factors for the three heaviest atoms were then relaxed to allow for possible thermal or vibrational anisotropy and a further least squares cycle reduced $R$ and $R'$ to 0.055 and 0.073

TABLE 1

POSITIONAL PARAMETERS WITH STANDARD DEVIATIONS FOR $RuI_2[CHN(CH_3)(p\text{-}CH_3C_6H_4)](CO)(CN\text{-}p\text{-}CH_3C_6H_4)(PPh_3)$

| Atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Ru | 0.53497(9) | 0.04018(9) | 0.20646(5) |
| I(1) | 0.34602(9) | 0.30337(9) | 0.12904(6) |
| I(2) | 0.61472(9) | 0.15976(8) | 0.33461(5) |
| P | 0.6912(3) | —0.1848(3) | 0.2711(2) |
| O(1) | 0.4258(11) | —0.0464(11) | 0.0593(7) |
| O(2) | 0.4179(13) | 0.5990(14) | 0.4411(9) |
| N(1) | 0.7297(12) | 0.0865(12) | 0.1138(8) |
| N(2) | 0.3044(11) | 0.0208(11) | 0.2700(7) |
| C(1) | 0.6613(13) | 0.0668(13) | 0.1493(8) |
| C(2) | 0.8014(13) | 0.1333(14) | 0.0716(9) |
| C(3) | 0.7370(14) | 0.2278(15) | 0.0013(9) |
| C(4) | 0.8081(17) | 0.2776(16) | —0.0348(10) |
| C(5) | 0.9393(18) | 0.2334(17) | —0.0038(11) |
| C(6) | 1.0012(20) | 0.1358(21) | 0.0650(13) |
| C(7) | 0.9337(17) | 0.0875(17) | 0.1046(10) |
| C(8) | 1.0213(19) | 0.2813(20) | —0.0464(12) |
| C(9) | 0.3852(12) | 0.0662(12) | 0.2649(7) |
| C(10) | 0.3191(16) | —0.1102(16) | 0.2326(10) |
| C(11) | 0.1976(13) | 0.0798(13) | 0.3168(8) |
| C(12) | 0.2167(14) | 0.0242(15) | 0.3950(10) |
| C(13) | 0.1181(15) | 0.0782(15) | 0.4377(9) |
| C(14) | —0.0008(14) | 0.1921(14) | 0.4050(9) |
| C(15) | —0.0175(15) | 0.2509(16) | 0.3264(10) |
| C(16) | 0.0844(15) | 0.1925(15) | 0.2827(8) |
| C(17) | —0.1121(15) | 0.2567(15) | 0.4519(9) |
| C(18) | 0.4704(12) | —0.0215(13) | 0.1159(8) |
| C(19) | 0.7025(11) | —0.2283(11) | 0.3804(7) |
| C(20) | 0.6023(12) | —0.1497(12) | 0.4200(8) |
| C(21) | 0.6051(13) | —0.1907(14) | 0.5005(8) |
| C(22) | 0.7132(14) | —0.3089(14) | 0.5435(8) |
| C(23) | 0.8162(14) | —0.3867(14) | 0.5071(9) |
| C(24) | 0.8111(14) | —0.3438(14) | 0.4258(9) |
| C(25) | 0.8675(11) | —0.2439(12) | 0.2698(7) |
| C(26) | 0.9194(13) | —0.1574(13) | 0.2903(8) |
| C(27) | 1.0522(14) | —0.2007(15) | 0.2968(9) |
| C(28) | 1.1334(15) | —0.3343(17) | 0.2816(9) |
| C(29) | 1.0828(15) | —0.4209(14) | 0.2603(8) |
| C(30) | 0.9498(13) | —0.3774(13) | 0.2547(8) |
| C(31) | 0.6617(10) | —0.3193(10) | 0.2241(7) |
| C(32) | 0.6748(12) | —0.3392(13) | 0.1446(8) |
| C(33) | 0.6467(14) | —0.4354(15) | 0.1053(9) |
| C(34) | 0.6025(14) | —0.5111(15) | 0.1460(10) |
| C(35) | 0.5872(14) | —0.4914(15) | 0.2262(10) |
| C(36) | 0.6175(11) | —0.3971(12) | 0.2650(7) |

respectively. A difference electron density synthesis was then computed to attempt to locate the hydrogen atoms before further anisotropic refinement. The hydrogen atoms of the benzene rings were found readily, but those of the methyl groups were not clearly resolved. Accordingly, it was decided to include in future cycles only benzene ring hydrogen atoms (in calculated positions, C—H distance 1.0 Å) and the hydrogen attached to C(9)(carbene). At this time the validity of the weighting scheme and the particular value given to $p$ (0.04) in the calculation of $\sigma(I)$ were checked by a weighting scheme analysis. The more intense reflections were found to be systematically overweighted in the least squares refinement, and so $\sigma(I)$ was re-evaluated using a value for $p$ of 0.06.

Refinement was then continued, each cycle being computed in four blocks, with Ru, 2$I$, $P$ varied in each block. Hydrogen atoms (not refined) were given isotropic temperature factors 1.0 Å$^2$ greater than those of the carbon atoms to which they were bonded. All non-hydrogen atoms were assigned anisotropic thermal parameters. In this way the residuals, $R$ and $R'$, were lowered to 0.043 and 0.060 respectively. An error analysis showed that the function $<\Sigma w(|F_o| - |F_c|)^2>$ was now very satisfactorily constant over all ranges of both $F_o$ and $\sin\theta/\lambda$. Finally, a structure factor calculation from which all hydrogen atoms were removed was computed, followed by a difference synthesis. Positions for all the previously located hydrogen atoms were re-determined from the peak maxima, but although the resolution was better than in the previous difference map, it was still not possible to unambiguously locate all hydrogen atoms of the methyl groups or water molecule.

TABLE 2

HYDROGEN ATOM POSITIONS AND ISOTROPIC TEMPERATURE FACTORS FOR $RuI_2[CHN(CH_3)(p\text{-}CH_3C_6H_4)](CO)(CN\text{-}p\text{-}CH_3C_6H_4)(PPh_3)$

| Atom | $x/a$ | $y/b$ | $z/c$ | $B$ |
|---|---|---|---|---|
| H(3) | 0.656 | 0.242 | −0.024 | 5.7 |
| H(4) | 0.766 | 0.339 | −0.079 | 6.3 |
| H(6) | 1.083 | 0.106 | 0.076 | 9.4 |
| H(7) | 0.951 | 0.036 | 0.160 | 8.3 |
| H(9) | 0.330 | 0.153 | 0.315 | 4.9 |
| H(12) | 0.302 | −0.066 | 0.408 | 6.4 |
| H(13) | 0.125 | 0.060 | 0.495 | 6.3 |
| H(15) | −0.103 | 0.368 | 0.310 | 7.2 |
| H(16) | 0.068 | 0.234 | 0.224 | 6.0 |
| H(20) | 0.575 | −0.185 | 0.390 | 4.9 |
| H(21) | 0.536 | −0.136 | 0.532 | 5.9 |
| H(22) | 0.708 | −0.323 | 0.590 | 5.7 |
| H(23) | 0.872 | −0.465 | 0.463 | 6.6 |
| H(24) | 0.875 | −0.405 | 0.395 | 6.2 |
| H(26) | 0.855 | −0.066 | 0.302 | 5.8 |
| H(27) | 1.062 | −0.132 | 0.312 | 7.0 |
| H(28) | 1.222 | −0.360 | 0.282 | 7.7 |
| H(29) | 1.110 | −0.495 | 0.240 | 6.8 |
| H(30) | 0.925 | −0.446 | 0.247 | 6.0 |
| H(32) | 0.704 | −0.285 | 0.112 | 6.0 |
| H(33) | 0.662 | −0.448 | 0.053 | 7.2 |
| H(34) | 0.586 | −0.581 | 0.116 | 7.5 |
| H(35) | 0.572 | −0.545 | 0.266 | 7.4 |
| H(36) | 0.615 | −0.390 | 0.328 | 5.2 |

The final atomic positions and, where appropriate, estimated standard deviations are listed in Tables 1 and 2. The atomic numbering scheme is shown in Fig. 1. Anisotropic thermal parameters are given in Table 3, and are depicted in the form of 50% probability ellipsoids in the perspective ORTEP diagram, Fig. 1 [20]. Bond lengths and angles are recorded in Tables 4 and 5 respectively and the more important values are shown in Fig. 2. The standard deviations listed are derived from the least-squares inverse matrix. By comparison, the spread of

*(continued on p. 58)*

TABLE 3

ANISOTROPIC TEMPERATURE FACTORS [a] WITH STANDARD DEVIATIONS ($\times 10^4$) FOR $RuI_2[CHN(CH_3)(p\text{-}CH_3C_6H_4)](CO)(CN\text{-}p\text{-}CH_3C_6H_4)(PPh_3)$

| Atom | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{12}$ | $b_{13}$ | $b_{23}$ |
|---|---|---|---|---|---|---|
| Ru | 81(1) | 89(1) | 29(0) | 47(1) | 15(1) | 4(1) |
| I(1) | 26(1) | 122(1) | 58(1) | —35(1) | 16(1) | 16(1) |
| I(2) | 52(1) | 130(1) | 40(0) | —93(1) | 26(1) | —19(1) |
| P | 85(4) | 91(4) | 30(2) | —49(4) | 16(2) | —6(2) |
| O(1) | 175(15) | 273(16) | 33(6) | —157(13) | —5(8) | 4(8) |
| O(2) | 230(22) | 358(24) | 73(8) | 191(19) | —16(11) | 14(11) |
| N(1) | 81(17) | 171(17) | 44(7) | —65(15) | 17(9) | —3(8) |
| N(2) | 83(15) | 138(15) | 54(6) | —58(13) | 24(7) | —1(7) |
| C(1) | 75(17) | 85(17) | 35(6) | —38(14) | 14(9) | —5(8) |
| C(2) | 93(18) | 142(19) | 37(7) | —65(16) | 22(10) | —6(10) |
| C(3) | 118(20) | 113(21) | 45(8) | —57(18) | 8(11) | 4(11) |
| C(4) | 160(23) | 163(22) | 40(8) | —110(19) | 0(12) | 27(11) |
| C(5) | 157(27) | 249(26) | 44(10) | —145(21) | 17(13) | 12(13) |
| C(6) | 89(31) | 392(32) | 75(12) | —150(27) | 6(16) | 51(17) |
| C(7) | 165(24) | 272(25) | 53(9) | —131(21) | —2(12) | 45(12) |
| C(8) | 252(31) | 373(32) | 71(12) | —251(26) | 39(15) | 15(15) |
| C(9) | 86(16) | 95(16) | 40(6) | —54(13) | 2(8) | 7(8) |
| C(10) | 165(23) | 146(25) | 93(9) | —90(20) | 46(12) | —48(12) |
| C(11) | 58(18) | 104(18) | 49(7) | —32(16) | 14(9) | 8(9) |
| C(12) | 75(21) | 152(21) | 55(8) | —34(17) | 16(11) | 10(11) |
| C(13) | 155(21) | 154(22) | 51(7) | —83(19) | 40(11) | 0(10) |
| C(14) | 117(20) | 134(20) | 60(8) | —84(18) | 51(10) | —24(10) |
| C(15) | 89(23) | 173(23) | 63(9) | —29(19) | 26(12) | 3(12) |
| C(16) | 84(20) | 162(21) | 49(7) | —36(18) | 31(11) | —2(10) |
| C(17) | 168(22) | 207(23) | 74(8) | —109(19) | 67(11) | —50(11) |
| C(18) | 138(17) | 131(18) | 38(7) | —92(15) | 14(9) | —9(9) |
| C(19) | 65(15) | 79(15) | 34(5) | —26(14) | 9(8) | 5(8) |
| C(20) | 110(16) | 109(17) | 29(6) | —50(14) | 15(8) | —9(8) |
| C(21) | 147(19) | 129(20) | 27(8) | —51(17) | 11(9) | 11(10) |
| C(22) | 151(18) | 155(20) | 25(7) | —85(17) | 12(10) | 7(10) |
| C(23) | 102(21) | 157(21) | 33(8) | —7(18) | 1(10) | 11(10) |
| C(24) | 139(20) | 169(21) | 28(8) | —48(18) | 17(10) | —15(10) |
| C(25) | 99(15) | 131(16) | 27(6) | —64(14) | 14(7) | 3(8) |
| C(26) | 68(17) | 174(19) | 44(7) | —57(16) | 13(8) | —3(9) |
| C(27) | 135(19) | 192(22) | 61(8) | —93(18) | 18(10) | —11(10) |
| C(28) | 88(22) | 250(25) | 52(8) | —59(21) | 5(11) | 17(11) |
| C(29) | 125(22) | 176(21) | 54(8) | —35(18) | 35(10) | —3(10) |
| C(30) | 110(19) | 153(18) | 46(7) | —51(15) | 32(9) | 2(8) |
| C(31) | 85(13) | 80(14) | 31(6) | —33(12) | 26(7) | —9(7) |
| C(32) | 148(18) | 123(19) | 48(7) | —68(15) | 22(9) | —23(9) |
| C(33) | 215(21) | 152(22) | 59(8) | —106(18) | 32(10) | —41(11) |
| C(34) | 176(22) | 141(23) | 78(9) | —95(19) | 4(11) | —21(12) |
| C(35) | 202(21) | 137(23) | 70(9) | —127(18) | 30(11) | —8(11) |
| C(36) | 111(16) | 104(16) | 43(6) | —66(14) | 1(8) | —4(8) |

[a] The scattering factor is of the form $f = f_0 \exp -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$.

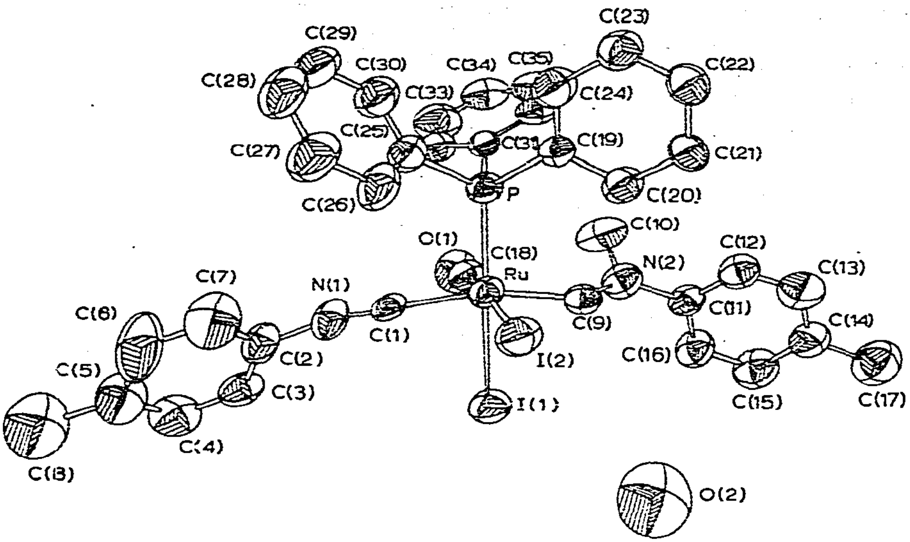

Fig. 1. Perspective ORTEP diagram showing the atomic numbering scheme and 50% probability anisotropic thermal ellipsoids.

TABLE 4

BOND LENGTHS (Å) AND STANDARD DEVIATION FOR $RuI_2[CHN(CH_3)(p\text{-}CH_3C_6H_4)](CO)(CN\text{-}p\text{-}CH_3C_6H_4)(PPh_3)$

| | | | |
|---|---|---|---|
| Ru—I(1) | 2.766(2) | C(11)—C(16) | 1.327(24) |
| Ru—I(2) | 2.782(1) | C(12)—C(13) | 1.356(26) |
| Ru—P | 2.342(4) | C(13)—C(14) | 1.361(25) |
| Ru—C(1) | 1.998(16) | C(14)—C(15) | 1.374(26) |
| Ru—C(9) | 2.046(15) | C(14)—C(17) | 1.519(25) |
| Ru—C(18) | 1.855(15) | C(15)—C(16) | 1.399(26) |
| P—C(19) | 1.825(14) | C(19)—C(20) | 1.376(20) |
| P—C(25) | 1.847(14) | C(19)—C(24) | 1.372(22) |
| P—C(31) | 1.828(13) | C(20)—C(21) | 1.383(22) |
| O(1)—C(18) | 1.100(20) | C(21)—C(22) | 1.371(23) |
| N(1)—C(1) | 1.155(22) | C(22)—C(23) | 1.362(24) |
| N(1)—C(2) | 1.420(22) | C(23)—C(24) | 1.394(24) |
| N(2)—C(9) | 1.263(20) | C(25)—C(26) | 1.363(21) |
| N(2)—C(10) | 1.526(24) | C(25)—C(30) | 1.382(21) |
| N(2)—C(11) | 1.475(21) | C(26)—C(27) | 1.373(24) |
| C(2)—C(3) | 1.374(24) | C(27)—C(28) | 1.380(26) |
| C(2)—C(7) | 1.379(26) | C(28)—C(29) | 1.355(26) |
| C(3)—C(4) | 1.379(27) | C(29)—C(30) | 1.376(23) |
| C(4)—C(5) | 1.365(29) | C(31)—C(32) | 1.366(20) |
| C(5)—C(6) | 1.371(33) | C(31)—C(36) | 1.389(19) |
| C(5)—C(8) | 1.533(32) | C(32)—C(33) | 1.389(23) |
| C(6)—C(7) | 1.364(32) | C(33)—C(34) | 1.370(25) |
| C(11)—C(12) | 1.350(24) | C(34)—C(35) | 1.383(26) |
| | | C(35)—C(36) | 1.381(23) |
| H(3)—C(3) | 0.906 | H(23)—C(23) | 1.168 |
| H(4)—C(4) | 0.872 | H(24)—C(24) | 0.974 |
| H(6)—C(6) | 0.831 | H(26)—C(26) | 0.984 |
| H(7)—C(7) | 1.004 | H(27)—C(27) | 0.855 |
| H(9)—C(9) | 1.286 | H(28)—C(28) | 0.936 |
| H(12)—C(12) | 1.002 | H(29)—C(29) | 0.827 |
| H(13)—C(13) | 0.946 | H(30)—C(30) | 0.932 |
| H(15)—C(15) | 1.182 | H(32)—C(32) | 1.000 |
| H(16)—C(16) | 1.009 | H(33)—C(33) | 0.911 |
| H(20)—C(20) | 0.756 | H(34)—C(34) | 0.997 |
| H(21)—C(21) | 0.994 | H(35)—C(35) | 0.957 |
| H(22)—C(22) | 0.801 | H(36)—C(36) | 1.055 |

TABLE 5

BOND ANGLES (°) AND STANDARD DEVIATIONS FOR $RuI_2[CHN(CH_3)(p\text{-}CH_3C_6H_4)](CO)\text{-}(CN\text{-}p\text{-}CH_3C_6H_4)(PPh_3)$

| | | | |
|---|---|---|---|
| I(1)—Ru—I(2) | 89.83(4) | C(14)—C(15)—H(15) | 114.1 |
| I(1)—Ru—P | 178.54(11) | C(16)—C(15)—H(15) | 122.6 |
| I(1)—Ru—C(1) | 86.4(5) | C(11)—C(16)—C(15) | 120.2(11) |
| I(1)—Ru—C(9) | 81.4(4) | C(11)—C(16)—H(16) | 121.1 |
| I(1)—Ru—C(18) | 84.4(0.4) | C(15)—C(16)—H(16) | 118.6 |
| I(2)—Ru—P | 91.3(10) | Ru—C(18)—O(1) | 173.9(7) |
| I(2)—Ru—C(1) | 86.4(5) | P—C(19)—C(20) | 121.8(6) |
| I(2)—Ru—C(9) | 85.9(4) | P—C(19)—C(24) | 120.7(7) |
| I(2)—Ru—C(18) | 174.3(5) | C(20)—C(19)—C(24) | 117.4(10) |
| P—Ru—C(1) | 84.6(5) | C(19)—C(20)—C(21) | 121.7(9) |
| P—Ru—C(9) | 97.8(4) | C(19)—C(20)—H(20) | 73.8 |
| P—Ru—C(18) | 94.4(5) | C(21)—C(20)—H(20) | 111.2 |
| C(1)—Ru—C(9) | 165.5(10) | C(20)—C(21)—C(22) | 119.4(9) |
| C(1)—Ru—C(18) | 92.8(9) | C(20)—C(21)—H(21) | 124.4 |
| C(9)—Ru—C(18) | 93.7(9) | C(22)—C(21)—H(21) | 116.0 |
| Ru—P—C(19) | 118.6(4) | C(21)—C(22)—C(23) | 120.4(10) |
| Ru—P—C(25) | 117.8(4) | C(21)—C(23)—H(22) | 112.6 |
| Ru—P—C(31) | 112.0(4) | C(23)—C(22)—H(22) | 126.9 |
| C(19)—P—C(25) | 100.6(9) | C(22)—C(23)—C(24) | 119.2(10) |
| C(19)—P—C(31) | 102.7(9) | C(22)—C(23)—H(23) | 156.4 |
| C(25)—P—C(31) | 102.9(9) | C(24)—C(23)—H(23) | 57.5 |
| C(1)—N(1)—C(2) | 170.9(10) | C(19)—C(24)—C(23) | 121.7(9) |
| C(9)—N(2)—C(10) | 120.8(10) | C(19)—C(24)—H(24) | 116.0 |
| C(9)—N(2)—C(11) | 124.3(9) | C(23)—C(24)—H(24) | 121.0 |
| C(10)—N(2)—C(11) | 114.7(10) | P—C(25)—C(26) | 119.0(7) |
| Ru—C(1)—N(1) | 177.1(7) | P—C(25)—C(30) | 121.3(7) |
| N(1)—C(2)—C(3) | 119.8(10) | C(26)—C(25)—C(30) | 119.5(14) |
| N(1)—C(2)—C(7) | 118.9(11) | C(25)—C(26)—C(27) | 121.2(10) |
| C(3)—C(2)—C(7) | 121.3(11) | C(25)—C(26)—H(26) | 114.4 |
| C(2)—C(3)—C(4) | 118.0(11) | C(27)—C(26)—H(26) | 124.4 |
| C(2)—C(3)—H(3) | 117.8 | C(26)—C(27)—C(28) | 118.8(10) |
| C(4)—C(3)—H(3) | 123.2 | C(26)—C(27)—H(27) | 104.7 |
| C(3)—C(4)—C(5) | 122.0(12) | C(28)—C(27)—H(27) | 136.4 |
| C(3)—C(4)—H(4) | 117.5 | C(27)—C(28)—C(29) | 120.6(10) |
| C(5)—C(4)—H(4) | 120.6 | C(27)—C(28)—H(28) | 117.6 |
| C(4)—C(5)—C(6) | 118.3(14) | C(29)—C(28)—H(28) | 121.6 |
| C(4)—C(5)—C(8) | 122.4(12) | C(28)—C(29)—C(30) | 120.4(11) |
| C(6)—C(5)—C(8) | 119.2(14) | C(28)—C(29)—H(29) | 134.7 |
| C(5)—C(6)—C(7) | 121.7(13) | C(30)—C(29)—H(29) | 103.8 |
| C(5)—C(6)—H(6) | 112.2 | C(25)—C(30)—C(29) | 119.6(9) |
| C(7)—C(6)—H(6) | 125.9 | C(25)—C(30)—H(30) | 124.7 |
| C(2)—C(7)—C(6) | 118.6(13) | C(29)—C(30)—H(30) | 115.4 |
| C(2)—C(7)—H(7) | 105.0 | P—C(31)—C(32) | 119.9(7) |
| C(6)—C(7)—H(7) | 135.4 | P—C(31)—C(36) | 121.9(6) |
| Ru—C(9)—N(2) | 141.5(5) | C(32)—C(31)—C(36) | 118.1(13) |
| Ru—C(9)—H(9) | 130.9 | C(31)—C(32)—C(33) | 121.6(15) |
| N(2)—C(9)—H(9) | 87.6 | C(31)—C(32)—H(32) | 121.5 |
| N(2)—C(11)—C(12) | 120.6(6) | C(33)—C(32)—H(32) | 116.9 |
| N(2)—C(11)—C(16) | 119.3(9) | C(32)—C(33)—C(34) | 119.9(10) |
| C(12)—C(11)—C(16) | 120.1(11) | C(32)—C(33)—H(33) | 117.6 |
| C(11)—C(12)—C(13) | 120.4(11) | C(34)—C(33)—H(33) | 122.5 |
| C(11)—C(12)—H(12) | 109.4 | C(33)—C(34)—C(35) | 119.4(11) |
| C(13)—C(12)—H(12) | 129.1 | C(33)—C(34)—H(34) | 116.7 |
| C(12)—C(13)—C(14) | 121.8(11) | C(35)—C(34)—H(34) | 123.8 |
| C(12)—C(13)—H(13) | 127.5 | C(34)—C(35)—C(36) | 120.1(10) |
| C(14)—C(13)—H(13) | 109.3 | C(34)—C(35)—H(35) | 130.3 |
| C(13)—C(14)—C(15) | 117.3(11) | C(36)—C(35)—H(35) | 108.7 |
| C(13)—C(14)—C(17) | 123.0(10) | C(31)—C(36)—C(35) | 120.9(13) |
| C(15)—C(14)—C(17) | 119.7(11) | C(31)—C(36)—H(36) | 119.2 |
| C(14)—C(15)—C(16) | 120.2(11) | C(35)—C(36)—H(36) | 119.7 |

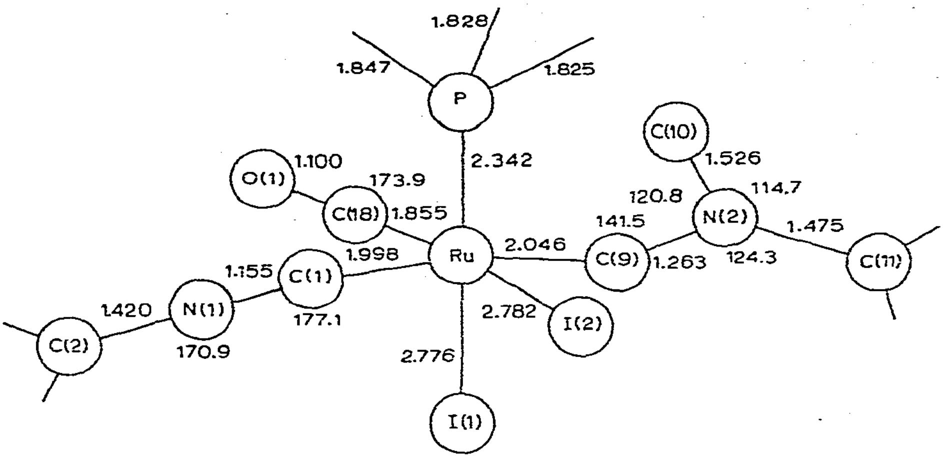

Fig. 2. Important bond distances and angles.

the carbon—carbon bond lengths in the triphenylphosphine ligand (mean distance 1.376 Å) gives a standard deviation of 0.0024 Å, which is approximately ten times smaller than the least-squares derived values. It is therefore likely that the quoted values are overestimated. Details of least-squares planes and short intermolecular approaches are given in Tables 6 and 7 respectively. Tables of observed and calculated structure factors are available from the author.

## Description of the structure

The unit cell contains two monomers of neutral complex together with two water molecules of crystallisation (Fig. 3). The overall geometry of the com-

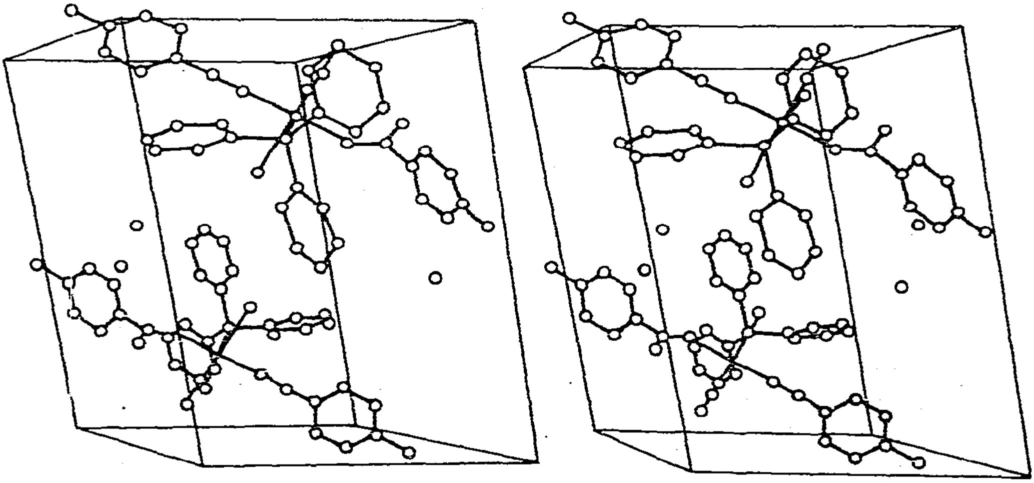

Fig. 3. Stereoscopic diagrams showing the molecular packing.

TABLE 6

PLANES OF "BEST FIT" THROUGH BENZENE RINGS

*(1) Benzene ring C(2)—C(7)*

$0.013X + 0.825Y + 0.564Z - 1.970 = 0$

| | | | | | |
|---|---|---|---|---|---|
| C(2) | 0.002 | C(4) | 0.007 | C(6) | −0.019 |
| C(3) | −0.012 | C(5) | 0.009 | C(7) | 0.013 |
| C(8) | −0.057 | N(1) | 0.074 | C(1) | 0.291 |

*(2) Benzene ring C(11)—C(16)*

$0.671X + 0.647Y + 0.362Z - 4.033 = 0$

| | | | | | |
|---|---|---|---|---|---|
| C(11) | −0.016 | C(13) | −0.004 | C(15) | 0.007 |
| C(12) | 0.016 | C(14) | −0.008 | C(16) | 0.005 |
| N(2) | −0.003 | C(10) | −1.355 | C(9) | 1.039 |

*(3) Benzene ring C(19)—C(24)*

$0.746X + 0.589Y + 0.312Z - 5.569 = 0$

| | | | | | |
|---|---|---|---|---|---|
| C(19) | −0.024 | C(21) | −0.004 | C(23) | −0.002 |
| C(20) | 0.019 | C(22) | −0.004 | C(24) | 0.016 |
| P | −0.173 | | | | |

*(4) Benzene ring C(25)—C(30)*

$-0.140X - 0.214Y + 0.967Z - 3.472 = 0$

| | | | | | |
|---|---|---|---|---|---|
| C(25) | 0.002 | C(27) | 0.001 | C(29) | −0.006 |
| C(26) | −0.004 | C(28) | 0.003 | C(30) | 0.003 |
| P | 0.145 | | | | |

*(5) Benzene ring C(31)—C(36)*

$-0.654X + 0.678Y - 0.335Z + 6.552 = 0$

| | | | | | |
|---|---|---|---|---|---|
| C(31) | −0.002 | C(33) | −0.005 | C(35) | 0.006 |
| C(32) | 0.006 | C(34) | −0.001 | C(36) | −0.005 |
| P | 0.106 | | | | |

*(6) Plane defined by Ru, C(9), N(2)*

$0.271X - 0.606Y + 0.748Z - 3.588 = 0$

| | | | | | |
|---|---|---|---|---|---|
| Ru | 0.000 | N(2) | 0.000 | C(10) | 0.256 |
| C(9) | 0.000 | H(9) | −0.063 | C(11) | −0.129 |

[a] The equations of the planes of best fit are referred to orthogonal axes and are given in direction cosine form, $AX + BY + CZ - D = 0$, where $A$, $B$ and $C$ are the direction cosines. The relationships between the orthogonal and crystallographic axes are $X = x + y\cos\gamma + z\cos\beta$, $Y = y\sin\gamma + z\sin\beta\cos\alpha^*$, $Z = z\sin\beta\sin\alpha^*$. The displacements of the atoms are given in Å.

plex is shown in the perspective diagram of Fig. 1. The ruthenium atom lies within an octahedral array of ligands. The carbene and isocyanide ligands are *trans* to one another, I(1) is *trans* to triphenylphosphine, and I(2) is *trans* to the carbonyl group. This geometry had been postulated on the basis of spectroscopic studies and chemical reactivity [21]. The coordination octahedron is slightly distorted. The angles I(1)—Ru—C(9) 81.4°, P—Ru—C(9) 97.8°, and C(1)—Ru—C(9) 165.5° show atom C(9) to be the most displaced from its ideal octahedral position, apparently as a result of the carbene *p*-tolyl system twisting away from the neighbouring triphenylphosphine group.

TABLE 7

INTERMOLECULAR APPROACHES (<3.5 Å) FOR $RuI_2[CHN(CH_3)(p\text{-}CH_3C_6H_4)](CO)(CN\text{-}p\text{-}CH_3C_6H_4)(PPh_3)$

| Atom(1)—Atom(2) | Distance (Å) | Position of Atom(2) | | |
|---|---|---|---|---|
| O(1)—O(1) | 3.24 | $-x$ | $-y$ | $-z$ |
| O(1)—N(1) | 3.29 | $-x$ | $-y$ | $-z$ |
| O(1)—C(1) | 3.48 | $-x$ | $-y$ | $-z$ |
| O(1)—C(3) | 3.39 | $-x$ | $-y$ | $-z$ |
| O(2)—O(2) | 2.60 | $1-x$ | $1-y$ | $1-z$ |

### The iodide donors

The Ru—I bond distances (Ru—I(1) 2.766(2), Ru—I(2) 2.782(1) Å) differ by 10 $\sigma$, the longer bond being *trans* to —CO, the shorter *trans* to $-PPh_3$. This is consistent with the slightly stronger *trans* influence of —CO over $-PPh_3$. Further comparisons of the Ru—I bond lengths suffer from a paucity of relevant structural data. However a small number of rhodium complexes have been investigated and Rh—I distances observed are 2.643 Å in $RhI_2(Me)(PPh_3)_2 \cdot C_6H_6$ [22], 2.653(3) Å in $\pi$-$CpRh(CO)(C_2F_5)I$ [23], and 2.662, 2.680(4) Å for *trans* Rh—I bonds in $RhI_3(CO)CPh(NMe)CPhNMe$ [24]. All are considerably shorter than Ru—I considering that the difference between the octahedral covalent radii for Ru(II) and Rh(III) is only 0.01 [25]. Perhaps a more specific comparison can be made by adding the difference (0.34 Å) between the covalent radii for I and Cl to the Ru—Cl distances found in octahedral complexes containing mutually *trans* Ru—Cl bonds. For example, the appropriate Ru—Cl bond distances are 2.393, 2.386(3) Å in $RuCl_3(p\text{-}N_2C_6H_4Me)(PPh_3)_2$ [26], 2.392, 2.384(2) Å in $Ru(NPEt_2Ph)Cl_3(PEt_2Ph)_2$ [27], and 2.405, 2.391(2) Å in $RuCl_3(NO)(PMePh_2)_2$ [28]. Adding 0.34 Å gives expected Ru—I bond lengths of approximately 2.73 Å. That the observed distances are both longer than this figure, and longer than 2.61 Å calculated from the sums of covalent radii [25] reflects the stronger *trans* influence of —CO and $-PPh_3$ compared with the halogens.

### The triphenylphosphine ligand

The Ru—P distance of 2.342(4) Å can be compared with a variety of other Ru—P bonds in octahedral complexes of Ru where two phosphine ligands are mutually *trans*. Some typical values are 2.429, 2.438(4) Å in $RuCl_3(p\text{-}N_2C_6H_4Me)(PPh_3)_2$ [26], 2.439, 2.415(2) Å in $[RuCl(CO)_2(HN_2C_6H_5)(PPh_3)_2] \cdot ClO_4 \cdot CH_2Cl_2$ [29], 2.441, 2.429(2) Å in $RuCl_3(NO)(PMePh_2)_2$ [28], 2.425, 2.430(7) Å in $RuCl_2(CO)(CSe)(PPh_3)_2$ [30], 2.425, 2.426(2) Å in $Ru(NPEt_2Ph)Cl_3(PEt_2Ph)_2$ [27], and 2.373, 2.386(3) Å in the formimidoyl complex $Ru(O_2CCH_3)[CHN(CH_3)(p\text{-}CH_3C_6H_4)](CO)(PPh_3)$ [13]. The present value is considerably shorter than these, consistent with the known weak *trans* effect of the iodide ligand. It would normally be expected to be about 2.43 Å [25].

The geometry within the triphenylphosphine ligand is normal as shown by the P—C(phenyl) distances [1.825, 1.847, 1.828(14) Å], Ru—P—C angles [118.6, 117.8, 112.0(4) Å] and C—P—C angles [100.6, 102.7, 102.9(9)°]. The widening of the Ru—P—C angles and concomitant closure of the C—P—C angles from the ideal tetrahedral values, has been previously observed *. The best planes of the benzene rings are defined in Table 6. It is noted that the P atom is not coplanar with the benzene rings, but is displaced from the planes by 0.17, 0.15 and 0.11 Å.

### The carbonyl group

The carbonyl group is *trans* to I(2) with Ru—C(18) 1.855(15) Å. Observed Ru—CO bond distances range from 1.77 to 2.05 Å, with the longer distances occurring in polynuclear cluster complexes [32,33]. The present distance is the same as that found for —CO *trans* to —Cl (1.85(3) Å) in [$RuCl_2(CO)(CSe)(PPh_3)_2$] [30] but longer than for —CO *trans* to —OAc (1.81(1) Å) in [Ru(OAc)(*p*-$MeC_6H_4NCH)(CO)(PPh_3)_2$] [13]. The shorter Ru—CO bonds are associated with efficient $\pi$ back donation to the carbon atom from the ruthenium centre [34].

The coordination of the carbonyl group is described as linear, although the Ru—C—O angle is 173.9(7)°. It is significant that the oxygen atom of the carbonyl group makes four intermolecular approaches shorter than 3.5 Å (Table 7) and the —CO ligand has best minimised these interactions by bending slightly. Similar distortions have been observed in a large number of other metal—carbonyl complexes.

### The carbene ligand

The Ru—C(carbene) distance of 2.046(5) Å is longer than most other Ru—C distances, and can be compared with Ru—CO (range 1.77—2.05 Å), Ru—isocyanide (1.998 Å), and Ru—formimidoyl (1.96 Å). The longest Ru—CO bonds are found in cluster complexes, e.g. $Ru_3(CO)_{12}$ [35] where several carbonyl groups compete for $\pi$ back-bonding from the metal centre. The long Ru—C(carbene) bond in the present compound supports the contention that carbene ligands are only very weak $\pi$-acceptors. However the bond remains considerably shorter than Ru—C distances in octahedral complexes of 2.128(4) Å in [$(C_5H_8N_2)Ru(NH_3)_4(CO)]^{2+}$ [36] and 2.16(1) Å in $RuH(C_{10}H_7)(Me_2PCH_2CH_2PMe_2)_2$ [37] and it may thus have a small degree of double bond character. The group *trans* to the carbene is isocyanide, with the bond length Ru—C(isocyanide) (1.998(16) Å) also being comparatively long. As the isocyanide ligand can act both as a good $\sigma$ donor and $\pi$ acceptor the metal—C(isocyanide) bond is usually considered to have a bond order greater than 1.0 [38] and the long bond observed here would indicate a strong *trans* effect for the carbene ligand. In structural studies of other carbene complexes the *trans* effect of the ligand has ranged from no effect [2] to that equivalent to or greater than a tertiary phosphine ligand [39,40]. All secondary carbene complexes studied have exhibited strong *trans* effects, as strong as for any neutral ligand [11]. It is not surprising therefore that the *trans* influence of the closely related formimidoyl ligand is greater than that of the carbonyl group [13].

Within the carbene ligand the C(9)—N(2) distance (1.263(20) Å) is very short, and approaches the value of 1.24(1) Å for the C—N bond in Ru(OAc)(*p*-

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* An example which clearly shows this trend is [$Ir(PPh_2Me)_4BF_4 \cdot C_6H_{12}$] [31].

TABLE 8

GEOMETRIES IN FORMIMIDOYL AND SECONDARY CARBENE COMPLEXES (bond lengths in Å, bond angles in degrees, $\nu$ in $cm^{-1}$)

| | Fe [a] | Rh [b] | Ru [c] | Ru [d] |
|---|---|---|---|---|
| M—C | | 1.961(11) | 2.046(15) | 1.96(1) |
| C—N | 1.293(17)<br>1.337(16) | 1.289(14) | 1.263(20) | 1.24(1) |
| C—H | | 1.14 | 1.29 | |
| M—C—N | 130.4(11)<br>124.1(10) | 139.6(9) | 141.5(5) | 135.3(9) |
| M—C—H | | 114 | 130.9 | |
| N—C—H | | 106 | 87.6 | |
| $\nu$(CN) | 1555 | 1589 | 1520 | 1556[9] |
| Ref. | 44 | 11 | This work | 13 |

[a] ($\pi$-Cp)Fe(CO)[$(CHNCH_3)_2BH_2$]. [b] $RhCl_3(PEt_3)_2CHNMe_2$. [c] $RuI_2[CHN(CH_3)(p\text{-}CH_3C_6H_4)](CO)(CN\text{-}p\text{-}CH_3C_6H_4)(PPh_3)$. [d] $Ru(O_2CCH_3)[CHN(CH_3)(p\text{-}CH_3C_6H_4)](CO)(PPh_3)_2$.

$MeC_6H_4NCH)(CO)(PPh_3)_2$ [13] which, although formally a double bond, is believed to have a bond order greater than two. The corresponding bonds in other carbene complexes where the C($sp^2$) atom is also stabilised by only one adjacent nucleophilic heteroatom are 1.266(15) Å in *trans*-$Pt[CH_3\{CH_3CN(CH_3)_2\}\{P(CH_3)_2C_6H_5\}_2]PF_6$ [41], 1.289(14) Å in $RhCl_3(PEt_3)_2CHNMe_2$ [11], 1.31(1) Å in $(CO)_5Cr[CH_3CN(C_2H_5)_2]$ [42], 1.33(3) Å in $(CO)_5Cr(CH_3CNHCH_3)$ [43], and 1.293(17), 1.337(16) Å in ($\pi$-Cp)Fe(CO)[$(CHNCH_3)_2BH_2$] [44]. When the C($sp^2$) atom is stabilised by two adjacent heteroatoms the distances are longer, 1.30—1.38 Å [2,4,5,41]. The Ru—C(9)—N(2) angle [141.5(5)°] is the largest yet observed for a secondary carbene complex, and exceeds values of 124.1(10), 130.4(11)° in ($\pi$-Cp)Fe(CO)[$(CHNCH_3)_2BH_2$] [44], and 139.6(9)° in $RhCl_3(PEt_3)_2CHNMe_2$ [11]. The angle is also greater than in the formimidoyl complex [135.3(9)°], which would again imply considerable multiple bond character in the C(carbene)—N bond. Pertinent to this argument we can note that the angles C(9)—N(2)—C(10), C(9)—N(2)—C(11), and C(10)—N(2)—C(11) are 120.8, 124.3, and 114.7(10)° respectively, which implies that the hybridisation of the N atom is $sp^2$. The corresponding angles in [$RhCl_3(PEt_3)_2CHNMe_2$] [11] are 127, 121, 112°. The corresponding C—N—C angle in the formimidoyl complex is 119.1(10)° [13]. Table 8 lists relevant data for the geometries of secondary carbene complexes, and for the closely related formimidoyl complex, all of which are characterised by relatively long Metal—C bonds, a high bond order in the C—N bonds, metal—C—N angles widely deviant from 120°, and $sp^2$ hybridisation of the N atom. The high bond order of the C—N bonds is supported by the high frequency CN stretch in the IR spectrum ($\nu$(CN) 1520 $cm^{-1}$ in the Ru complex, 1589 $cm^{-1}$ in the Rh complex, and 1556 $cm^{-1}$ in the formimidoyl complex). Other neutral, cationic, and dicationic ruthenium secondary carbene complexes also show $\nu$(CN) at about 1550 $cm^{-1}$ [7].

## The isocyanide ligand

There have been few crystal structure determinations of compounds containing the coordinated isocyanide ligand. The present compound contains the *p*-tolyl derivative. It can be seen (Fig. 2) that the isocyanide bonds to the ruthenium in an essentially linear manner. The bond angles at C(1) and N(1) [177.1(7) and 170.9(10)°] are similar to those observed in other isocyanide complexes, e.g. 176.6(2.8) and 168.0(3.1)° in $(CO)(NO)(p\text{-}CH_3C_6H_4NC)(PPh_3)_2Os^+$ [38], 174—177(4)° and 173—175(4)° in *trans*-$(C_4H_9NC)_2PdI_2$ [45], 174—179(2)° and 169—178(2)° in $[(C_4H_9NC)_6MoI]^+$ [46], and 178.7—179.1(5)° and 175.3—177.5(6)° in $Ni(C_6H_5N{=}NC_6H_5)((CH_3)_3CNC)_2$ [47]. The deviation from linearity is almost always greater at the N atom than at C. The maximum deviation so far observed is 165.5(30)° at N in *cis*-$(C_6H_5NC)_2(PEt_3)PtCl_2$ [48]. Even this is still considered to be linear coordination in the electronic sense, as the forces due to crystal packing requirements could easily dominate in determining the particular geometry adopted by such elongated ligands as aromatic isocyanides. Other bond distances and angles are normal.

## The water dimers

The water molecules are hydrogen-bonded together [O—O separation 2.60(2) Å] to form a $(H_2O)_2$ dimeric unit, with no contact distances between the oxygen atoms and any other non-hydrogen atoms being shorter than 3.5 Å. The pairs of water molecules occupy what would otherwise be a large interstice in the crystal lattice, and are surrounded by hydrophobic phenyl groups from the triphenylphosphine and carbene ligands. It is quite uncommon for water molecules to be included in crystals of this type, without their being involved in hydrogen bonding to other parts of the complex molecule. In the many reviews of hydrogen bonding that have appeared in recent years [49—56] this kind of inclusion has only been briefly alluded to. For example, Hamilton and Ibers [49] pose the question "Does the water molecule ever appear in a crystal without being hydrogen bonded or without being a ligand of a metal ion? That is, does it sometimes simply fill a hole without forming any specific directional bonds?" In reply to this, we have here an $(H_2O)_2$ unit in the crystal lattice assuming a purely space-filling function.

Attempts have been made to classify crystalline hydrates [49,54,56]. The most relevant classification group for the present compound would be Class 2, type L of Chidambaram, Sequiera, and Sikka [54]. The only previous entry in this category, potassium oxalate monohydrate, has been reclassified by Hamilton and Ibers on the grounds that the $H_2O$ hydrogen bonds to the organic anion [49]. The author is unaware of any other hydrate in which an isolated $(H_2O)_2$ dimer forms with no further hydrogen bonding. It is noteworthy that the hydrogen bond formed between the two water molecules is particularly strong *. Shorter hydrogen bonds (O—O separations 2.4—2.6 Å) have certainly been commonly observed, but these are generally intramolecular interactions in acid salts of carboxylic acids, and not those involving ordinary water molecules [53]. For comparison, we can note the O—O distance in ice [ice Ih, 2.76; other high pressure modifications ice II—IX, 2.76—2.95 Å] [52,57]. The shortness of

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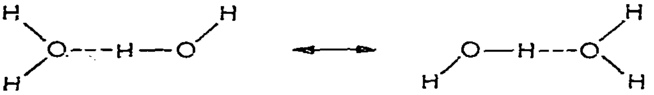
* In a survey of recent neutron diffraction studies, Ferraris and Franchini-Angela note [56] "The O—O distance was never found to be shorter than 2.6 Å, the more usual values are between 2.7 and 2.9 Å, the region of weak hydrogen bonds".

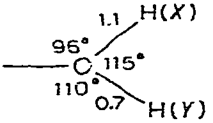
the present bond is quite surprising, as it has been suggested that the formation of one hydrogen bond increases the energy of formation of a second to the same centre, i.e. hydrogen bonds of polymers are stronger (and therefore shorter) than those of the dimer [58].

Being surrounded by hydrophobic groups, the $(H_2O)_2$ unit resembles the classical water dimer, which has been studied by spectroscopic methods in a frozen inert gas matrix [55]. There has been considerable controversy over the structure of this dimer, with the most recent investigations favouring a linear (as opposed to cyclic or bifurcated) structure with a moderately weak hydrogen bond (O—O 2.71 Å) [59]. Other theoretical calculations have postulated O—O separations in the wide range of 2.53—3.00 Å. The shortest distance, 2.53 Å, is derived from a method acknowledged as giving "invariably too-short" bond distances. Most calculations predict a distance greater than that of ice [60].

It should be noted that the $(H_2O)_2$ pairing is centred about a crystallographic centre of symmetry. Only the cyclic structure for the dimer is capable of possessing a centre of symmetry, if the structure is linear or bifurcated then the hydrogen atoms must be disordered. The largest peak in the final difference map occurs at this centre of symmetry, and since both the cyclic and bifurcated structures would have two regions of electron density, each displaced from the centre, the true structure must be linear. The disorder of the hydrogen atoms is assumed to be of a type resembling.



The next two largest peaks near O(2) are at (0.467 0.550 0.392) and (0.417 0.662 0.449). If these are labelled H(*X*) and H(*Y*) their geometry relative to the hydrogen bond is



and one could speculate that the outer hydrogen atoms interchange between two specific sites. Unfortunately, the resolution is not sufficiently high to enable these hydrogen atoms to be unambiguously located.

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