

Structure of Benzoyl(*tert*-butyl isocyanide)(carbonyl)bis(dimethylphenylphosphine)(phenyl)ruthenium(II), $C_{35}H_{41}NO_2P_2Ru$

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Abstract. $M_r = 670.81$, monoclinic, $P2_1/c$, $a = 12.692(2)$, $b = 27.466(5)$, $c = 11.227(2)$ Å, $\beta = 119.31(3)^\circ$, $V = 3412.7$ Å³, $Z = 4$, $D_x = 1.31$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 4.94$ mm⁻¹, $F(000) = 1391.5$, $T = 290 \pm 1$ K, $R = 0.075$ for 2763 observed reflections. The complex is monomeric, with octahedral coordination geometry. Ru–P distances are 2.375(3) and 2.362(4) Å; –COPh is *trans* to –CNC(Me)₃ with Ru–COPh and Ru–CNC(Me)₃ distances of 2.142(15) and 2.004(15) Å respectively.

Introduction. In the course of a study of the reaction of aryl complexes of Ru^{II} it was found that complexes [Ru(CO)₂R₂(PMe₂Ph)₂] ($R = C_6H_5$, *p*-MeC₆H₄, *p*-MeOC₆H₄, etc.) reacted with equimolar quantities of the isocyanide Me₃CNC. From the analytical data for the products it was difficult to be certain whether the reaction involved substitution of a carbonyl ligand {giving [Ru(CO)R₂(CNCMe₃)(PMe₂Ph)₂] } or combination of aryl and carbonyl ligands, with the isocyanide occupying the coordination site made available in the process {giving [Ru(CO)(COR)R(CNCMe₃)(PMe₂Ph)₂]}. There was no band in the IR spectra of the complexes which could be assigned with certainty to the C=O stretching mode of an acyl group, but a weak resonance was observed at δ 273.1 p.p.m. in the ¹³C NMR spectrum of a CDCl₃ solution of the complex obtained by reaction of [Ru(CO)₂Ph₂(PMe₂Ph)₂] and Me₃CNC. It seemed possible that the resonance was due to the acyl C atom in a benzoyl group. In order to obtain unambiguous proof of the presence of a benzoyl group, an X-ray structure determination was carried out.

Experimental. Yellow prisms elongated along *a*, from chloroform. Crystal: 0.74 × 0.25 × 0.16 mm. Hilger & Watts Y290 computer-controlled four-circle diffractometer. Unit cell: 18 reflections, least-squares refinement. No absorption correction. Intensity measurements by ω scans, count time per step 1 s, range of each scan 0.9°; $\theta_{\text{max}} = 51^\circ$, $h = -12$ to 11, $k = 0$ to 27,

$l = 0$ to 11; 7291 reflections recorded including Friedel pairs, 3604 unique, 841 with $I < 3\sigma(I)$ classified as unobserved, $R_{\text{int}} = 0.0254$. Intensity variation of three standard reflections <5%. Structure solved by conventional heavy-atom techniques; Ru atom from a Patterson map, all other non-hydrogen atoms from a subsequent difference Fourier map. Structure refined by full-matrix least squares using SHELX76 (Sheldrick, 1976). Final refinement cycle included anisotropic thermal parameters for the non-hydrogen atoms; H atoms bonded to C atoms estimated geometrically (C–H 1.08 Å, C–C–H 120.0°). Final $R = R_w = 0.075$ for 2763 observed reflections, unit weights; atomic scattering factors and values of f' and f'' from *International Tables for X-ray Crystallography* (1974). Ratio of maximum least-squares shift to error: large for H thermal parameters (3.1), generally <0.1 for positional parameters and <0.2 for thermal parameters. Maximum and minimum height in final difference Fourier map: 0.95 and –0.86 e Å⁻³ around the Ru atom, generally <0.40 e Å⁻³ elsewhere. No secondary-extinction correction applied.

Discussion. The final atomic coordinates for the non-hydrogen atoms are listed in Table 1 and selected bond lengths and angles in Table 2.†

The crystal contains discrete monomeric units. The Ru atom is six-coordinate with a distorted octahedral geometry and donors comprising *trans* dimethylphenylphosphine, benzoyl, carbonyl, phenyl and *tert*-butyl isocyanide ligands. The overall molecular geometry and atomic numbering scheme are shown in Fig. 1 and a stereoview of the packing is shown in Fig. 2.

The structure confirms the presence of a benzoyl ligand, and shows that the incoming isocyanide ligand has occupied the position *trans* to the acyl ligand. This reaction stereochemistry is similar to that previously observed for the reactions of methyl complexes of Ru^{II}, and is most easily rationalized on the basis of a

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† Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths, bond angles, torsion angles, and least-squares-planes data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38508 (58 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) (e.s.d.'s in parentheses) and equivalent isotropic thermal parameters

$$U_{eq} = \frac{1}{3} (U_{11} + U_{22} + 2U_{23}\cos\alpha + 2U_{13}\cos\beta + 2U_{12}\cos\gamma).$$

| | x | y | z | U_{eq} (Å ²) |
|--------|-----------|----------|------------|----------------------------|
| Ru | 3871 (1) | 1166 (1) | 1246 (1) | 0.052 |
| P(1) | 5072 (2) | 1851 (1) | 1395 (3) | 0.055 |
| C(11) | 5606 (11) | 2257 (4) | 2861 (11) | 0.068 |
| C(12) | 4283 (10) | 2287 (4) | 10 (11) | 0.067 |
| C(101) | 6393 (9) | 1730 (4) | 1226 (12) | 0.064 |
| C(102) | 6293 (13) | 1432 (5) | 184 (14) | 0.076 |
| C(103) | 7251 (14) | 1350 (5) | -41 (17) | 0.090 |
| C(104) | 8307 (16) | 1568 (6) | 710 (20) | 0.108 |
| C(105) | 8493 (15) | 1845 (7) | 1821 (20) | 0.123 |
| C(106) | 7509 (14) | 1941 (6) | 2017 (17) | 0.107 |
| P(2) | 2445 (3) | 581 (1) | 1089 (3) | 0.062 |
| C(21) | 3052 (12) | 36 (5) | 2143 (15) | 0.088 |
| C(22) | 1307 (10) | 771 (5) | 1527 (14) | 0.080 |
| C(201) | 1557 (11) | 321 (4) | -584 (13) | 0.069 |
| C(202) | 2060 (14) | -30 (5) | -1068 (16) | 0.092 |
| C(203) | 1377 (18) | -223 (6) | -2348 (18) | 0.108 |
| C(204) | 255 (18) | -87 (7) | -3202 (17) | 0.106 |
| C(205) | -246 (15) | 262 (6) | -2795 (17) | 0.099 |
| C(206) | 398 (13) | 467 (5) | -1470 (15) | 0.086 |
| C(3) | 4590 (11) | 1119 (4) | 3412 (14) | 0.067 |
| O(3) | 3990 (8) | 1011 (4) | 3933 (9) | 0.087 |
| C(301) | 5900 (11) | 1219 (4) | 4415 (12) | 0.071 |
| C(302) | 6195 (13) | 1410 (5) | 5690 (12) | 0.085 |
| C(303) | 7404 (17) | 1543 (6) | 6574 (14) | 0.112 |
| C(304) | 8320 (14) | 1469 (6) | 6277 (18) | 0.103 |
| C(305) | 8001 (14) | 1268 (6) | 5019 (15) | 0.103 |
| C(306) | 6855 (11) | 1138 (5) | 4132 (13) | 0.080 |
| C(401) | 2516 (9) | 1697 (4) | 1068 (11) | 0.058 |
| C(402) | 1583 (10) | 1818 (4) | -218 (12) | 0.065 |
| C(403) | 673 (11) | 2140 (5) | -344 (14) | 0.077 |
| C(404) | 670 (12) | 2356 (5) | 754 (17) | 0.082 |
| C(405) | 1604 (11) | 2240 (4) | 2042 (14) | 0.074 |
| C(406) | 2530 (10) | 1924 (4) | 2159 (12) | 0.064 |
| C(5) | 3215 (9) | 1179 (4) | -780 (14) | 0.060 |
| N(5) | 2939 (9) | 1168 (3) | -1965 (11) | 0.068 |
| C(50) | 2674 (11) | 1156 (4) | -3381 (11) | 0.067 |
| C(51) | 3249 (12) | 1607 (5) | -3645 (13) | 0.087 |
| C(52) | 3200 (16) | 685 (5) | -3570 (15) | 0.107 |
| C(53) | 1324 (12) | 1164 (5) | -4280 (13) | 0.095 |
| C(6) | 4930 (10) | 658 (5) | 1341 (12) | 0.074 |
| O(6) | 5514 (9) | 339 (3) | 1335 (11) | 0.097 |

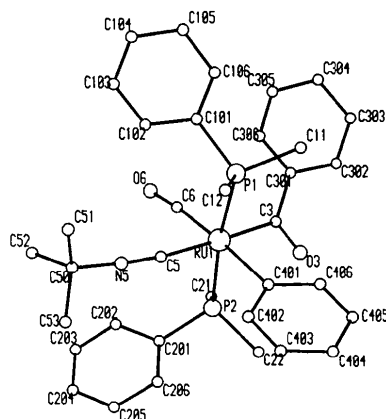


Fig. 1. View of the molecular structure of [Ru(CO)-(COPh)Ph(CNCMe₃)(PMe₂Ph)₂] showing the atomic numbering scheme.

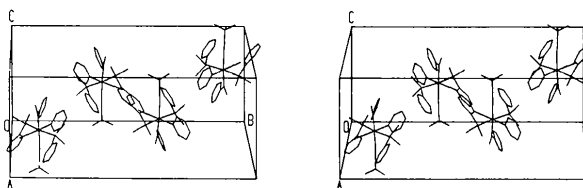


Fig. 2. Stereoview of the packing in the unit cell of [Ru(CO)-(COPh)Ph(CNCMe₃)(PMe₂Ph)₂].

combination of phenyl and carbonyl ligands which is accompanied by the opening out of the angle between the remaining phenyl and carbonyl ligands, and followed by attack opposite to the strongly *trans*-directing acyl ligand (Barnard, Daniels & Mawby, 1979).

The Ru-P bond lengths [2.362 (4) and 2.375 (3) Å] fall within the range observed for other Ru^{II} complexes containing a pair of mutually *trans* PMe₂Ph ligands (Ashworth, Nolte, Singleton & Laing, 1977). The complex contains four different Ru-C bonds, two to *sp*-hybridized C atoms and two to *sp*²-hybridized atoms. The shortest is to the carbonyl ligand, but it is interesting to note that at 1.91 (2) Å it is still longer than the values normally observed for Ru^{II} complexes (1.82 to 1.87 Å; Komiyama, Ito, Cowie, Yamamoto & Ibers, 1976). This presumably reflects the marked *trans*-labilizing effect of the phenyl ligand (Barnard, Daniels & Mawby, 1976). Turning to the isocyanide ligand, the Ru-C-N-C system is essentially linear [Ru-C-N = 173.1 (1.0); C-N-C = 176.9 (1.2)°], and the bond lengths are Ru-C 2.00 (2), C-N 1.20 (2), N-C(Me)₃ 1.46 (2) Å. The *tert*-butyl group shows (within the limitations of the data) the expected tetrahedral geometry.

It is interesting to note that the phenyl ligand lies approximately in the plane defined by the Ru and the three other metal-bonded C atoms. Hoffmann has discussed the orientation of the ethene ligand in

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

| | | | |
|-------------|------------|-------------|------------|
| Ru-P(1) | 2.375 (3) | P(2)-C(22) | 1.815 (16) |
| Ru-P(2) | 2.362 (4) | P(2)-C(201) | 1.799 (13) |
| Ru-C(3) | 2.142 (15) | C(3)-O(3) | 1.203 (21) |
| Ru-C(401) | 2.187 (12) | C(3)-C(301) | 1.508 (15) |
| Ru-C(5) | 2.004 (15) | C(5)-N(5) | 1.199 (19) |
| Ru-C(6) | 1.905 (14) | N(5)-C(50) | 1.455 (18) |
| Ru-O(3) | 2.977 (15) | C(50)-C(51) | 1.539 (20) |
| P(1)-C(11) | 1.822 (12) | C(50)-C(52) | 1.519 (21) |
| P(1)-C(12) | 1.826 (11) | C(50)-C(53) | 1.504 (17) |
| P(1)-C(101) | 1.809 (14) | C(6)-O(6) | 1.149 (18) |
| P(2)-C(21) | 1.828 (14) | | |

C(301)-C(306) (benzoyl ring): 1.348 (18)-1.414 (23), average 1.385 (23)
C(401)-C(406) (phenyl ring): 1.371 (26)-1.415 (19), average 1.386 (19)

| | | | |
|----------------|-------------|------------------|-------------|
| P(1)-Ru-P(2) | 170.5 (0.1) | C(401)-Ru-C(6) | 174.5 (0.5) |
| P(1)-Ru-C(3) | 93.7 (0.3) | C(5)-Ru-C(6) | 88.0 (0.5) |
| P(1)-Ru-C(401) | 85.8 (0.3) | Ru-P(1)-C | 116.3 (0.4) |
| P(1)-Ru-C(5) | 87.8 (0.3) | Ru-P(2)-C | 116.2 (0.5) |
| P(1)-Ru-C(6) | 99.5 (0.4) | Ru-C(3)-O(3) | 123.2 (0.8) |
| P(2)-Ru-C(3) | 85.9 (0.4) | Ru-C(3)-C(301) | 122.6 (1.2) |
| P(2)-Ru-C(401) | 84.7 (0.3) | O(3)-C(3)-C(301) | 114.2 (1.2) |
| P(2)-Ru-C(5) | 92.9 (0.3) | Ru-C(5)-N(5) | 173.1 (1.0) |
| P(2)-Ru-C(6) | 90.0 (0.4) | C(5)-N(5)-C(50) | 176.9 (1.2) |
| C(3)-Ru-C(401) | 91.3 (0.5) | N(5)-C(50)-C(51) | 108.3 (0.9) |
| C(3)-Ru-C(5) | 177.4 (0.4) | N(5)-C(50)-C(52) | 106.9 (1.0) |
| C(3)-Ru-C(6) | 89.7 (0.5) | N(5)-C(50)-C(53) | 108.1 (1.3) |
| C(401)-Ru-C(5) | 90.8 (0.5) | Ru-C(6)-O(6) | 176.1 (0.9) |

C-C-C (benzoyl ring): 116.7 (1.4)-123.5 (1.5), average 120.0 (0.5)
C-C-C (phenyl ring): 116.9 (1.1)-123.4 (1.0), average 120.0 (1.2)

[Cr(CO)₅(C₂H₄)] and has shown that, thanks to the equivalence of the two *d* orbitals with which the π^* molecular orbital can interact, there can be no electronic preference for any particular orientation of the ethene molecule (Albright, Hoffmann, Thibeault & Thorn, 1979). In [Ru(CO)(COPh)Ph(CNCMe₃)(PMe₂Ph)₂], however, the two *d* orbitals with which the π system of the phenyl ligand can interact are *not* equivalent: one must be shared with carbonyl, acyl and isocyanide ligands and the other with carbonyl and PMe₂Ph ligands. The orientation adopted by the phenyl ring allows maximum overlap with the *latter d* orbital, as would be expected since PMe₂Ph is a relatively poor π acceptor.

Delocalization between the carbonyl group and the phenyl ring within the benzoyl ligand must be severely inhibited by the non-planar geometry of this ligand, which may be the result of steric effects. It is noticeable that the Ru—C bond to the benzoyl ligand [2.142 (15) Å] is shorter than that to the phenyl ligand

[2.187 (12) Å]. This may result from the difference in π -acceptor strength between isocyanide (*trans* to benzoyl) and carbonyl (*trans* to phenyl) ligands.

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Trilithium Citrate Pentahydrate, C₆H₅O₇³⁻·3Li⁺·5H₂O

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Abstract. *M_r* = 299.92, monoclinic, *A2/a*, *a* = 12.216 (1), *b* = 19.972 (1), *c* = 10.725 (1) Å, β = 101.52 (8)°, *V* = 2563.9 (4) Å³, *Z* = 8, *D_x* = 1.554 g cm⁻³, Cu *K*α, λ = 1.5418 Å, μ = 13.27 cm⁻¹, *F*(000) = 1248, room temperature. The crystal structure was solved by direct methods and refined by full-matrix least-squares techniques (non-hydrogen atoms anisotropic, H atoms isotropic) to a final *R* = 0.034 for 2244 independent observed reflections. The hydrogen bonding and the charge distribution are discussed.

Introduction. Two types of colorless crystals were obtained by evaporating an aqueous ethanolic solution of anhydrous trilithium citrate (Sigma Chemical Co.). One type, which crystallized first, appeared as plates, but these proved not to be single. The second type did not have a well defined morphology but diffracted well and therefore were used.

Experimental. Nicolet *P2*₁ diffractometer. Space group *A2/a* from systematic absences (*hkl*, *k + l* = 2*n* + 1; *h0l*, *h* = 2*n* + 1; *0k0*, *k* = 2*n* + 1). Unit cell: 14 centered reflections, least-squares fit. Three-dimensional X-ray intensity data collected with θ -2 θ scan technique and graphite-monochromated Cu *K*α radiation. 2522 reflections scanned in the range (sin θ)/ λ = 0.05 to 0.61 Å⁻¹ (2 θ = 138°); 2355 had intensity (*I*) greater than the threshold of 2.0 σ (*I*) [with σ (*I*) derived from counting statistics]; of these, 2244 were unique and used in the structure solution and refinement. σ (*F*) = (*F*/2){[σ^2 (*I*)/*I*²] + δ^2 }^{1/2}, where δ is the instrumental uncertainty (δ = 0.023) determined from the variation in measured intensities in the periodically scanned standard reflections. The 2244 reflections and their associated standard deviations were converted to structure amplitudes by application of Lorentz and polarization factors and placed on an absolute scale with a Wilson plot; no absorption correction.

Structural solution obtained from *MULTAN* (Germain, Main & Woolfson, 1971) by use of 200 *E* values greater than 1.5. The solution with the highest absolute figure of merit (2.94) and lowest residual

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