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Structure of Carbonyldichloro(*p*-chlorophenyl isocyanide)bis(triphenylphosphine)ruthenium(II) Ethanol Solvate

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Abstract. C₄₄H₃₄Cl₃NOP₂Ru·C₂H₆O, *M_r* = 908·15, monoclinic, *P*2₁/*c*, *a* = 12·257 (1), *b* = 18·547 (2), *c* = 18·744 (4) Å, β = 93·33 (1)°, *V* = 4254 (2) Å³, *T* = 295 ± 1 K, *Z* = 4, *D_c* = 1·41 Mg m⁻³, μ(Mo *K*α) = 0·661 mm⁻¹, *R* = 0·066 for 2183 observed reflections. The complex is monomeric, with octahedral coordination geometry. Ru–P distances are 2·420 (6) and 2·422 (6) Å; Ru–Cl *trans* to –CNR [2·460 (6) Å] is significantly longer than that *trans* to –CO [2·428 (6) Å]; Ru–CNR is 1·94 (2) Å. The isocyanide is non-linear [C–N–Ph 165 (2)°].

Introduction. An X-ray structure determination has been carried out on crystals grown from the product of a reaction in which it was hoped to prepare a chloro amino carbene complex of formula RuCl(CO){C(Cl)NMe₂}(CN-*p*-ClC₆H₄)(PPh₃)₂ (Wright & Roper, 1981). However, the analysis shows that the particular crystal selected for investigation is the dichloro isocyanide compound RuCl₂(CO)(CN-*p*-ClC₆H₄)(PPh₃)₂·ethanol.

Intensities from a crystal fragment, approximately 0·32 × 0·20 × 0·14 mm, were recorded with a Nonius CAD-4 diffractometer using Zr-filtered Mo *K*α radiation. Data were collected to the practical upper limit for the crystal (sin θ/λ 0·55 Å⁻¹) with a 2θ/ω scan, yielding 2183 unique observed reflections [*I* > 3σ(*I*), σ(*I*) = 20·116/NPI √*C* + *R*²*B*, where the number 20·116 is the maximum possible scan rate, NPI is the ratio of the maximum scan rate to the scan rate for the actual measurement, *C* = total count, *R* = ratio of scan time to background counting time (=2), *B* = total background counts] which were used in the full-matrix least-squares refinement.

The structure was solved using *MULTAN* (Main, Germain & Woolfson, 1970) to locate the five heaviest

atoms, followed by a 'difference' electron-density map to locate the remaining non-H atoms. An ethanol solvent molecule was also found to be present in the unit cell. In the initial least-squares refinement cycles the C and O atoms of the carbonyl ligand tended to merge towards each other to give an unrealistically short C–O distance, and the ethanol solvent molecule behaved similarly. These atoms were therefore repositioned by an analysis of the peak profiles of their partially overlapping peaks in a difference map. The resulting geometries were chemically reasonable, and these atoms have not been refined further. The possibility of lowering the σ cut-off limit was considered, but as there were only 60 reflections for which 2σ(*I*) < *I* < 3σ(*I*) it was felt that inclusion of these few extra reflections would do little to improve the resolution.

The final refinement cycles included anisotropic thermal parameters for all remaining non-H atoms except the C atoms of the phenyl rings which were constrained to be isotropic. H atoms were included in calculated positions (C–H 1·02 Å) but were not refined. Their isotropic *B* values were set 20% higher than that of the C atom to which each was bonded. Final residuals were *R* [= ∑ ||*F_o*| – |*F_c*|| / ∑ *F_o*] 0·066 and *R_w* [= (∑ *w* ||*F_o*| – |*F_c*||² / ∑ *w* |*F_o*|²)^{1/2}] 0·074 [*w* = 4|*F_o*|² / σ²(*F_o*)²]. No corrections were made for extinction or absorption effects [μ(Mo *K*α) = 0·661 mm⁻¹].

Atomic positional parameters are listed in Table 1.* Interatomic distances and angles are given in Table 2.

* Lists of structure factors, anisotropic thermal parameters, assigned H-atom positions and bond lengths and angles for phenyl rings have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36810 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic positional parameters ($\times 10^4$) and isotropic temperature factors for RuCl₂(CO)(CN-*p*-ClC₆H₄)(PPh₃)₂·C₂H₅OH

	x	y	z	B_{eq}/B_{iso} (\AA^2)
Ru	890 (1)	5143 (1)	2246 (1)	2.44*
Cl(1)	633 (5)	4633 (3)	1055 (3)	4.94*
Cl(2)	1628 (4)	4051 (3)	2842 (3)	3.65*
Cl(3)	-1844 (7)	8361 (4)	-805 (4)	8.88*
P(1)	-974 (4)	4780 (3)	2413 (3)	2.61*
P(2)	2714 (5)	5454 (3)	1919 (3)	2.80*
O(1)	1100	5900	3649	5.0
N(1)	17 (14)	6497 (10)	1455 (9)	3.21*
C(1)	950	5640	3107	3.0
C(2)	350 (17)	6013 (11)	1770 (11)	2.58*
C(3)	-383 (18)	6948 (13)	944 (12)	3.77*
C(4)	-468 (18)	6691 (12)	250 (12)	4.64*
C(5)	-933 (18)	7143 (13)	-305 (11)	4.63*
C(6)	-1257 (19)	7835 (13)	-123 (13)	4.84*
C(7)	-1226 (19)	8065 (13)	558 (14)	4.48*
C(8)	-737 (20)	7622 (14)	1111 (13)	4.86*
C(11)	-1402 (15)	3894 (9)	2104 (9)	2.5 (4)
C(12)	-2497 (15)	3721 (10)	2042 (9)	2.8 (4)
C(13)	-2916 (17)	3029 (12)	1836 (11)	3.7 (5)
C(14)	-2145 (17)	2538 (12)	1663 (11)	3.6 (5)
C(15)	-1075 (18)	2688 (11)	1738 (12)	3.5 (5)
C(16)	-691 (16)	3349 (11)	1955 (10)	3.3 (5)
C(21)	-1425 (14)	4739 (10)	3335 (8)	2.5 (4)
C(22)	-713 (15)	4511 (10)	3866 (10)	3.2 (4)
C(23)	-1026 (18)	4421 (11)	4547 (11)	4.8 (5)
C(24)	-2083 (18)	4543 (11)	4704 (11)	4.7 (5)
C(25)	-2832 (18)	4805 (12)	4195 (11)	4.9 (5)
C(26)	-2502 (16)	4884 (11)	3490 (10)	4.4 (5)
C(31)	-1880 (14)	5404 (9)	1908 (9)	2.7 (4)
C(32)	-2204 (17)	6035 (11)	2206 (11)	4.2 (5)
C(33)	-2814 (18)	6532 (11)	1792 (12)	4.1 (5)
C(34)	-3063 (20)	6365 (13)	1080 (13)	5.2 (6)
C(35)	-2765 (19)	5761 (13)	782 (12)	5.2 (6)
C(36)	-2148 (16)	5243 (11)	1182 (10)	3.9 (5)
C(41)	3519 (15)	4745 (10)	1492 (9)	2.8 (4)
C(42)	4527 (17)	4936 (11)	1226 (10)	4.5 (5)
C(43)	5118 (17)	4396 (12)	855 (11)	5.1 (5)
C(44)	4746 (18)	3721 (12)	786 (11)	3.8 (5)
C(45)	3776 (18)	3542 (11)	1049 (11)	4.3 (5)
C(46)	3138 (16)	4043 (11)	1422 (10)	3.6 (5)
C(51)	3665 (15)	5793 (10)	2659 (10)	3.6 (5)
C(52)	4491 (17)	6291 (11)	2535 (11)	4.2 (5)
C(53)	5104 (16)	6527 (11)	3106 (11)	3.9 (5)
C(54)	5032 (17)	6236 (11)	3799 (11)	4.0 (5)
C(55)	4291 (19)	5707 (12)	3889 (11)	4.3 (5)
C(56)	3598 (16)	5460 (10)	3331 (10)	3.9 (5)
C(61)	2667 (15)	6200 (10)	1289 (10)	3.2 (4)
C(62)	2576 (15)	6064 (10)	543 (10)	3.7 (5)
C(63)	2412 (16)	6613 (12)	62 (11)	4.9 (5)
C(64)	2348 (18)	7301 (12)	295 (13)	5.1 (6)
C(65)	2377 (17)	7451 (12)	986 (12)	4.5 (5)
C(66)	2562 (17)	6887 (11)	1487 (11)	4.0 (5)
O(S)	4050	3135	2860	6.0
C(1S)	4980	3359	3380	5.5
C(2S)	4350	3539	4030	6.0

* B_{eq} is as defined by Hamilton (1959).

The molecular geometry and atomic-numbering scheme are shown in Fig. 1.

Table 2. Bond lengths (\AA) and angles ($^\circ$) for RuCl₂(CO)(CN-*p*-ClC₆H₄)(PPh₃)₂·C₂H₅OH

Ru—Cl(1)	2.428 (6)	N(1)—C(2)	1.14 (3)
Ru—Cl(2)	2.460 (6)	N(1)—C(3)	1.34 (3)
Ru—P(1)	2.420 (6)	C(3)—C(4)	1.38 (3)
Ru—P(2)	2.422 (6)	C(3)—C(8)	1.37 (3)
Ru—C(1)	1.86	C(4)—C(5)	1.43 (3)
Ru—C(2)	1.94 (2)	C(5)—C(6)	1.39 (3)
Cl(3)—C(6)	1.73 (2)	C(6)—C(7)	1.34 (3)
O(1)—C(1)	1.13	C(7)—C(8)	1.43 (3)
Cl(1)—Ru—Cl(2)	97.0 (2)	C(1)—Ru—C(2)	89.0
Cl(1)—Ru—P(1)	86.4 (2)	C(2)—N(1)—C(3)	165 (2)
Cl(1)—Ru—P(2)	86.1 (2)	Ru—C(1)—O(1)	172
Cl(1)—Ru—C(1)	171.6 (2)	Ru—C(2)—N(1)	176 (2)
Cl(1)—Ru—C(2)	83.0 (6)	N(1)—C(3)—C(4)	117 (2)
Cl(2)—Ru—P(1)	92.2 (2)	N(1)—C(3)—C(8)	121 (2)
Cl(2)—Ru—P(2)	89.4 (2)	C(4)—C(3)—C(8)	122 (2)
Cl(2)—Ru—C(1)	91.1	C(3)—C(4)—C(5)	119 (2)
Cl(2)—Ru—C(2)	178.3 (6)	C(4)—C(5)—C(6)	118 (2)
P(1)—Ru—P(2)	172.5 (2)	Cl(3)—C(6)—C(5)	117 (2)
P(1)—Ru—C(1)	90.9	Cl(3)—C(6)—C(7)	121 (2)
P(1)—Ru—C(2)	89.5 (6)	C(5)—C(6)—C(7)	122 (2)
P(2)—Ru—C(1)	96.4	C(6)—C(7)—C(8)	120 (2)
P(2)—Ru—C(2)	88.9 (6)	C(3)—C(8)—C(7)	119 (2)

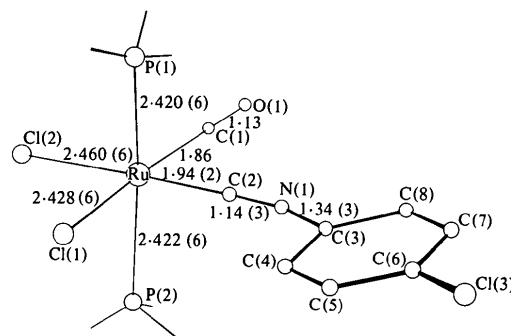


Fig. 1. The coordination geometry for RuCl₂(CO)(CN-*p*-ClC₆H₄)(PPh₃)₂·C₂H₅OH.

Discussion. The complex is monomeric. The coordination geometry is octahedral, with donors comprising *trans* triphenylphosphines, *cis* chlorides, carbonyl and *p*-chlorophenyl isocyanide ligands. The overall molecular geometry is shown in Fig. 1, while Fig. 2 gives a stereoview of the unit-cell contents and packing.

The Ru—P bonds, av. 2.421 (4) \AA , are equivalent, and are at the longer end of the range, 2.33–2.45 \AA , normally observed in Ru complexes containing mutually *trans* triphenylphosphines (summarized by Boniface, Clark, Collins & Roper, 1981). However, the Ru—Cl bonds differ significantly, that *trans* to —CO being 2.428 (6) \AA , whereas that *trans* to the isocyanide is 2.460 (6) \AA . The difference presumably reflects a greater *trans* influencing ability of a phenyl isocyanide over a carbonyl and is of a similar order to that found in RuCl₂(CO)(CSe)(PPh₃)₂ where Ru—Cl

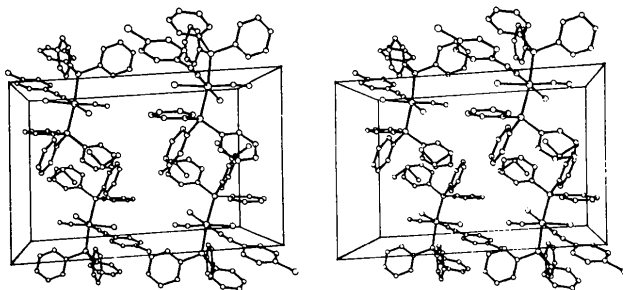


Fig. 2. Stereoview of the packing in the cell of $\text{RuCl}_2(\text{CO})(\text{CN-}p\text{-ClC}_6\text{H}_4)(\text{PPh}_3)_2 \cdot \text{C}_2\text{H}_5\text{OH}$.

trans to CO was 2.428 (6) Å and Ru–Cl *trans* to CSe was 2.477 (7) Å. The longer values are at the upper end of the range found for Ru–Cl bonds in similar complexes (Clark & James, 1977).

The isocyanide coordination is characterized by Ru–C 1.94 (2), C–N 1.14 (3) and N–PhCl 1.34 (3) Å; Ru–C–N 176 (2) and C–N–PhCl 165 (2)°. Unfortunately, the uncertainties in these bond lengths and angles are too high to permit detailed interpretation. However, the geometry can be compared with that in $\text{RuI}_2\{\text{CHN}(\text{CH}_3)(p\text{-CH}_3\text{C}_6\text{H}_4)\}(\text{CO})(\text{CN-}p\text{-CH}_3\text{C}_6\text{H}_4)(\text{PPh}_3)$ (Clark, 1977) with Ru–C 1.998 (16), C–N 1.15 (2), N–PhCH₃ 1.42 (2) Å; Ru–C–N 177.1 (7), C–N–PhCH₃ 170.9 (10)°. It is noted that the secondary carbene situated *trans* to CNR in the latter complex exerts a not insignificant *trans* influence in comparison with the chloride ligand in the present complex. Both isocyanides are very significantly bent from linearity, as has been observed in many other isocyanide complexes, with the larger bend occurring

at N. The angle C–N–Ph in the present complex (165°) gives a slightly greater deviation from linearity than has been found hitherto (Badley, 1969). As has been commented previously (Clark, 1977), there is no suggestion that the isocyanide coordination should be described as anything other than linear in the electronic sense. The influence of packing forces becomes particularly evident in the present complex when intermolecular distances are calculated. It is found that there are ten such contacts shorter than 3.6 Å [shortest 3.35 Å, O(1)⋯C(24)']. However, in a trial calculation in which the isocyanide group as a whole was rotated so that Ru–C–N–Ph–Cl was made collinear a large number of catastrophically close contacts resulted (shortest approximately 0.8 Å). It is clear that forces due to crystal-packing requirements can easily dominate in determining the particular geometry adopted by such elongated ligands as *p*-substituted aromatic isocyanides.

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Bis(tetraphenylarsonium) Di- μ -oxo-bis[dichloro(oxo)molybdate(V)] Dichloromethane Hydrogen Chloride Solvate

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Abstract. $[\text{As}(\text{C}_6\text{H}_5)_4]_2[\text{Mo}_2\text{Cl}_4\text{O}_4] \cdot \text{CH}_2\text{Cl}_2 \cdot \frac{1}{2}\text{HCl}$, $M_r = 1267.5$, triclinic, $P\bar{1}$, $a = 12.280$ (7), $b = 13.632$ (6), $c = 18.532$ (6) Å, $\alpha = 71.85$ (3), $\beta = 74.12$ (4), $\gamma = 62.45$ (4)°; reduced-cell parameters: $a' = 12.280$ (7), $b' = 13.482$ (6), $c' = 18.532$ (6) Å, $\alpha' = 93.77$ (3),

$\beta' = 105.88$ (4), $\gamma' = 116.31$ (4)°, transformation matrix (100)/(110)/(001); $U = 2582.3$ Å³, $Z = 2$, $D_m = 1.64$ (1), $D_x = 1.630$ Mg m⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 2.20$ mm⁻¹, $F(000) = 1258$; final $R = 0.087$ for 4799 observed reflections. The structure of the title compound consists of discrete anions, cations and solvent molecules. In the dinuclear anion, the two

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