Crystal and Molecular Structure of Trichlorobis(diethylphenylphosphine)-(diethylphenylphosphineiminato)ruthenium(IV): A Complex with an Almost Linear Ru–N–P System

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Crystals of the title complex are orthorhombic with unit-cell dimensions $a = 19.870(3)$, $b = 11.933(3)$, $c = 14.194(3)$ Å, space group $P2_12_12_1$, and $Z = 4$. The *X*-ray crystal structure has been determined by the heavy-atom method from diffractometer data, and least-squares refinement has reached *R* 0.025 for 3 586 independent reflections.

A slightly distorted octahedral environment is found for the ruthenium atom, comprising three *mer*-chlorine atoms, two $PPhEt_2$ groups mutually *trans*, and an Et_2PhPN^- ligand. This ligand bonds in an essentially linear fashion with Ru–N–P 174.9° and Ru–N and N–P distances 1.841 and 1.586 Å. The mean Ru–Cl (*trans* to Cl) distance is 2.388 while Ru–Cl (*trans* to N) is 2.397 Å, suggesting that the tertiary phosphineiminato-group exerts little, if any, *trans*-influence. Mean Ru–P is 2.425 Å.

A possible bonding scheme is suggested for the Ru–N–P system.

THE nitride ligand in some metal–nitrido-complexes exhibits nucleophilic behaviour. Thus $[MoN(S_2CNR_2)_3]$ $\{R_2 = 2Me,2Et$, or $[CH_2]_5\}$ reacts with sulphur, giving high yields of thionitrosyl compounds $[Mo(NS)(S_2CNR_2)_3]$.[1] Under the same reaction conditions neither $[ReNCl_2(PMe_2Ph)_3]$ nor $[ReN(S_2CNEt_2)_2]$ gives a thionitrosyl, although the former has been observed to form weak complexes with acceptor molecules such as boron halides or $[Pt_2Cl_4(PEt_3)_2]$,[2] and is stable in the presence of good nucleophiles like phosphines [3] and phenyl-lithium.[4]

A contrasting situation obtains for Ru⋮N and Os⋮N compounds: the nitride ligands in $[MNCl_3(AsPh_3)_2]$ (M = Ru or Os) are electrophilic, reacting with a wide range of tertiary phosphines R_3P to produce species containing a phosphineiminato-ligand $[R_3P{:}N^-]$.[5-7] The

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[1] J. Chatt and J. R. Dilworth, *J.C.S. Chem. Comm.*, 1974, 508.

[2] J. Chatt and B. T. Heaton, *Chem. Comm.*, 1968, 274.

[3] J. Chatt, C. D. Falk, G. J. Leigh, and R. J. Paske, *J. Chem. Soc. (A)*, 1969, 2288.

[4] J. Chatt and G. A. Rowe, *J. Chem. Soc. (A)*, 1966, 1834.

[5] W. P. Griffith and D. Pawson, *J.C.S. Chem. Comm.*, 1973, 418.

[6] W. P. Griffith and D. Pawson, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 253.

[7] D. Pawson and W. P. Griffith, *J.C.S. Dalton*, 1975, 417.

title complex is one such product and we report here the details of its X-ray crystal structure, a preliminary account of which has appeared.[8]

EXPERIMENTAL

Black, well-formed prisms of trichlorobis(diethylphenylphosphine)(diethylphenylphosphineiminato)ruthenium(IV) were obtained [7] from acetone. Preliminary X-ray photographs showed them to be orthorhombic. Accurate unit-cell dimensions were calculated from some high-angle α_1 and α_2 axial reflections measured on a diffractometer.

Crystal Data.—$C_{30}H_{45}Cl_3NP_3Ru$, $M = 719.6$, Orthorhombic, $a = 19.870(3)$, $b = 11.933(3)$, $c = 14.194(3)$ Å, $U = 3\,365.5$ Å^3, $D_m = 1.41$ (by flotation), $Z = 4$, $D_c = 1.42$ g cm^{-3}, $F(000) = 1\,488$. Space group $P2_12_12_1$ (No. 19) from systematic absences. Cu-K_α radiation, $\lambda = 1.541\,8$ Å; μ(Cu-K_α) $= 75.9$ cm^{-1}.

Intensity measurements were carried out on an off-line Siemens four-circle single-crystal diffractometer fitted with a Na(Tl)I scintillation counter. Cu-K_α radiation at a take-off angle of 3.0° and a nickel β filter were used. Data were collected in two concentric spheres (θ 0—37° and 37—70°) over a period of *ca.* 7 days from a crystal $0.31 \times 0.26 \times 0.36$ mm mounted about its c axis. A θ—2θ scan technique with a ' five-value ' measuring procedure [9] was employed. Of the 3 591 independent reflections thus measured, 44 having net counts $<2.58\sigma$ were denoted unobserved. Lorentz and polarisation corrections were applied to the data, and intensities were scaled on the basis of the 14,3,0 reflection which had been monitored as a reference every 50 reflections.

Solution and Refinement of the Structure.—The July 1970 version of the Crystal Structure Calculations System ' X-Ray '63 ' [10] was used for solution and refinement of the structure. Calculations were carried out on the University of London CDC 7600 computer, and structural illustrations were drawn with the aid of the Imperial College CDC 6400.

A three-dimensional Patterson vector map was calculated as soon as the inner sphere of 994 reflections had been measured. It gave a straightforward solution for the position of the ruthenium atom, and a few cycles of isotropic refinement gave R 0.43. Two rounds of difference-Fourier syntheses led to the location of all the non-hydrogen atoms, and isotropic refinement on the complete set of intensity data reduced R to 0.096. Anisotropic refinement with the least-squares program CRYLSQ lowered R to 0.062. At this point an absorption correction according to the method of Busing and Levy [11] was applied to all reflections using a $12 \times 12 \times 12$ grid and with path lengths determined by the vector analysis procedure of Coppens *et al.*[12] Heavy damping was necessary before refinement as previously converged to R 0.046. The 45 hydrogen atoms were now located from a difference-Fourier synthesis (although in the case of two methyl hydrogens calculated positions were used as they were thought to be more realistic). Hydrogen atoms were included in subsequent refinements as a fixed-atom contribution with the isotropic temperature factors of their parent carbon atoms. Introduction of a Hughes-type weighting scheme,[13] the removal of five strong low-angle reflections thought to be affected by extinction, and correction for anomalous dispersion, led to a final R of 0.025.

Weights in the final cycles were such that $w = 1$ for $F < F^*$, $\sqrt{w} = F^*/F$ for $F \geqslant F^*$, with $F^* = 29$. Atomic scattering factors were taken from ref. 14, except those for hydrogen,[15] while the real and the imaginary parts of the anomalous dispersion correction for ruthenium, phosphorus, and chlorine were those listed in ref. 16.

TABLE 1

Fractional co-ordinates, with estimated standard deviations in parentheses

	x	y	z
Ru(1)	0.086 37(1)	0.072 81(2)	0.028 16(2)
Cl(1)	0.011 97(5)	0.074 77(10)	0.161 07(7)
Cl(2)	−0.007 08(4)	0.124 96(9)	−0.068 68(7)
Cl(3)	0.177 53(5)	0.017 82(9)	0.126 82(8)
P(1)	0.185 72(5)	0.080 29(9)	−0.168 85(7)
P(2)	0.114 80(5)	0.264 72(8)	0.068 28(7)
P(3)	0.051 56(5)	−0.121 88(8)	0.026 40(7)
N(1)	0.141 4(2)	0.071 5(3)	−0.076 2(2)
C(11)	0.275 6(2)	0.075 1(4)	−0.141 6(3)
C(12)	0.298 2(3)	−0.021 6(6)	−0.087 1(6)
C(21)	0.164 8(2)	−0.028 9(4)	−0.251 7(3)
C(22)	0.092 8(3)	−0.018 8(5)	−0.289 0(5)
C(31) *	0.173 0(2)	0.210 1(3)	−0.231 0(3)
C(32)	0.221 2(3)	0.250 6(4)	−0.293 6(4)
C(33)	0.210 5(3)	0.353 0(5)	−0.339 5(4)
C(34)	0.153 6(3)	0.411 4(4)	−0.325 1(4)
C(35)	0.105 2(3)	0.372 4(4)	−0.265 3(4)
C(36)	0.113 4(2)	0.270 0(4)	−0.217 6(3)
C(41)	0.119 9(2)	0.285 2(4)	0.196 3(3)
C(42)	0.139 4(3)	0.401 1(4)	0.229 8(4)
C(51)	0.057 1(2)	0.375 0(4)	0.028 2(4)
C(52)	−0.011 4(2)	0.372 0(5)	0.077 0(4)
C(61) *	0.197 5(2)	0.311 2(3)	0.028 5(3)
C(62)	0.255 9(2)	0.265 9(4)	0.070 1(3)
C(63)	0.318 3(2)	0.297 7(4)	0.038 9(4)
C(64)	0.325 8(2)	0.371 2(4)	−0.035 3(4)
C(65)	0.269 9(2)	0.415 1(5)	−0.076 9(4)
C(66)	0.205 8(2)	0.387 2(4)	−0.045 7(3)
C(71)	0.064 7(3)	−0.191 7(4)	0.141 3(3)
C(72)	0.078 7(4)	−0.314 6(5)	0.142 7(5)
C(81)	−0.038 0(2)	−0.139 3(4)	0.001 2(4)
C(82)	−0.069 4(3)	−0.253 7(6)	0.019 5(5)
C(91) *	0.096 4(2)	−0.209 6(3)	−0.057 4(3)
C(92)	0.164 8(2)	−0.228 8(4)	−0.043 8(3)
C(93)	0.201 3(3)	−0.294 6(4)	−0.105 4(4)
C(94)	0.170 0(3)	−0.341 2(4)	−0.183 1(4)
C(95)	0.103 1(3)	−0.321 3(5)	−0.198 5(4)
C(96)	0.065 9(2)	−0.256 7(4)	−0.136 6(3)

* Phenyl carbon atoms are numbered (C*mn*) where *m* is ring no. and *n* is the atom no. in the ring; *n* is such that C(*m*1) is attached to P and other atoms are numbered in succession such that C(*m*4) is *para* to C(*m*1).

Table 1 lists the final fractional co-ordinates of the non-hydrogen atoms with their estimated standard deviations.* The coefficients in the expression for the anisotropic Debye-Waller factor $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 +$

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* The least-squares program CRYLSQ uses large partial matrices. The standard deviations thus obtained are more realistic than those from a simple block-diagonal program such as BLOKLS,[10] but may still be a slight underestimate of the true deviations.

[8] F. L. Phillips and A. C. Skapski, *J.C.S. Chem. Comm.*, 1975, 49.

[9] F. H. Allen, D. Rogers, and P. G. H. Troughton, *Acta Cryst.*, 1971, **B27**, 1325.

[10] ' X-Ray '63 ' system of programs, J. M. Stewart, University of Maryland, Technical Report TR 64 6, version of July 1970, eds. J. M. Stewart, F. A. Kundell, and J. C. Baldwin.

[11] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

[12] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.

[13] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

[14] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[15] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[16] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

$2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$, and the root-mean-square amplitudes of vibration along the principal axes of the thermal ellipsoid, are listed in Table 2. Unrefined co-ordinates of the hydrogen atoms are given in Table 3. Observed and the calculated structure amplitudes are listed in Supplementary Publication No. SUP 21656 (13 pp., 1 microfiche).†

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Figure 1 is a stereoscopic illustration of the molecular structure, and also shows the thermal vibration ellipsoids of the non-hydrogen atoms.[17] A phosphine-iminato-ligand ($PhEt_2P{:}N^-$), two phosphorus atoms from *trans* PEt_2Ph groups, and three chlorine atoms in a *mer*-arrangement constitute the slightly distorted octahedral environment of the ruthenium atom. The Ru–N distance is 1.841 Å, the Ru–P bond lengths are almost identical (2.424 and 2.426 Å), while the three Ru–Cl distances lie within a narrow range (2.382—2.397 Å). A full list of the more important interatomic distances, both bonded and non-bonded, is given in Table 4, while bond angles are listed in Table 5.

TABLE 2

Anisotropic thermal parameters and root-mean-square amplitudes of vibration (Å)

Atom	10^4U_{11}	10^4U_{22}	10^4U_{33}	10^4U_{12}	10^4U_{13}	10^4U_{23}	Min.	Inter.	Max.
Ru(1)	231(2)	301(2)	283(2)	−3(1)	18(1)	−1(1)	0.150	0.170	0.174
Cl(1)	533(6)	527(5)	439(5)	−80(5)	217(4)	−63(5)	0.163	0.219	0.275
Cl(2)	294(4)	557(6)	498(5)	24(4)	−63(4)	34(5)	0.165	0.224	0.239
Cl(3)	464(5)	453(5)	567(6)	1(4)	−194(5)	79(5)	0.173	0.213	0.270
P(1)	358(5)	385(5)	345(5)	29(4)	77(4)	−3(4)	0.164	0.195	0.209
P(2)	291(4)	297(4)	379(5)	−5(4)	−9(4)	−25(4)	0.168	0.172	0.197
P(3)	375(4)	315(4)	384(5)	−60(4)	37(4)	−12(4)	0.166	0.189	0.209
	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}			
N(1)	37(2)	43(2)	49(2)	1(2)	6(2)	4(2)	0.185	0.204	0.231
C(11)	33(2)	62(3)	53(2)	−4(2)	7(2)	−4(2)	0.175	0.229	0.255
C(12)	48(3)	82(4)	124(6)	8(3)	−4(3)	25(4)	0.211	0.272	0.368
C(21)	57(3)	47(2)	44(2)	−6(2)	10(2)	−8(2)	0.191	0.212	0.258
C(22)	80(4)	70(3)	82(4)	−4(3)	−30(3)	−7(3)	0.221	0.269	0.333
C(31)	48(2)	38(2)	40(2)	0(2)	5(2)	0(2)	0.193	0.195	0.226
C(32)	60(3)	57(3)	63(3)	0(2)	18(2)	11(2)	0.199	0.239	0.287
C(33)	75(3)	61(3)	65(3)	−14(3)	11(3)	13(3)	0.203	0.277	0.291
C(34)	89(4)	40(2)	56(3)	−7(3)	−8(3)	8(2)	0.191	0.236	0.304
C(35)	65(3)	45(2)	55(3)	10(2)	−3(2)	5(2)	0.195	0.239	0.264
C(36)	51(2)	47(2)	45(2)	3(2)	1(2)	2(2)	0.208	0.217	0.230
C(41)	47(2)	48(2)	44(2)	−4(2)	1(2)	−9(2)	0.191	0.215	0.238
C(42)	73(3)	56(3)	58(3)	−6(2)	−7(2)	−24(2)	0.176	0.274	0.285
C(51)	40(2)	43(2)	65(3)	10(2)	−5(2)	−2(2)	0.177	0.222	0.259
C(52)	42(2)	75(3)	86(4)	21(2)	4(3)	−8(3)	0.175	0.284	0.302
C(61)	30(2)	38(2)	46(2)	−2(1)	−1(2)	0(2)	0.172	0.196	0.214
C(62)	36(2)	49(2)	56(2)	−4(2)	−6(2)	3(2)	0.185	0.219	0.243
C(63)	34(2)	51(2)	76(3)	−2(2)	−6(2)	−2(2)	0.182	0.226	0.278
C(64)	39(2)	60(3)	69(3)	−14(2)	1(2)	−8(3)	0.177	0.247	0.274
C(65)	57(3)	58(3)	65(3)	−22(2)	−0(2)	16(3)	0.177	0.248	0.294
C(66)	42(2)	47(2)	54(2)	−9(2)	−9(2)	10(2)	0.186	0.201	0.266
C(71)	80(3)	43(2)	40(2)	−8(2)	2(2)	8(2)	0.181	0.220	0.285
C(72)	119(5)	49(3)	76(4)	3(3)	28(4)	21(3)	0.187	0.273	0.367
C(81)	35(2)	56(3)	76(3)	−11(2)	7(2)	−6(2)	0.174	0.238	0.282
C(82)	69(3)	76(4)	96(5)	−36(3)	11(2)	−7(4)	0.190	0.297	0.341
C(91)	46(2)	34(2)	40(2)	−2(2)	−1(2)	1(2)	0.184	0.199	0.217
C(92)	50(2)	44(2)	48(2)	6(2)	0(2)	0(2)	0.201	0.219	0.233
C(93)	58(3)	55(3)	62(3)	11(2)	6(2)	−4(2)	0.206	0.253	0.261
C(94)	77(3)	54(3)	60(3)	13(3)	11(3)	−14(2)	0.190	0.267	0.290
C(95)	81(4)	58(3)	53(3)	4(3)	−9(3)	−18(2)	0.193	0.260	0.295
C(96)	56(2)	48(2)	52(2)	1(2)	−9(2)	−10(2)	0.195	0.227	0.256

The mean (2.425 Å) for the two Ru–P bonds is towards the long end of the range of literature values. This is to be expected, since a mutual *trans*-influence would operate on these bonds, and any steric crowding between the ligands would also tend to push the phosphorus atoms outwards. Although there are no Ru^{IV}–P (*cis* to P) distances available for comparison, those for Ru^{II} are appreciably shorter, *e.g.* a mean of 2.326 in $[Ru(pyS)_2(PPh_3)_2]$ [18] and 2.346 Å in $[Ru(HCS_2)_2(PPh_3)_2]$.[19]

Compared to Ru–Cl bond distances in other Ru^{IV} complexes, *e.g.* 2.364 and 2.367 Å in $K_3[Ru_2NCl_8(H_2O)_2]$,[20] and 2.370 and 2.391 Å in $[NH_4]_3[Ru_2NCl_8(H_2O)_2]$,[21] those in the title complex are on average slightly longer. A mean of 2.388 Å is found for Ru–Cl (*trans* to Cl), while Ru–Cl (*trans* to N) is 2.397 Å. Were the Ru–Cl and Ru–P bonds to lengthen slightly to ease any crowding of the ligands around ruthenium, this would tend to mask any difference in the Ru–Cl bond lengths arising from a *trans*-influence. The intramolecular contact distances between chlorine and phosphorus atoms range from 3.127 to 3.525 Å, of which the shortest is Cl(1) ··· P(3).

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† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

[17] C. K. Johnson, ORTEP thermal ellipsoid plotting program, Oak Ridge National Laboratory, 1965, Report ORNL 3794.

[18] S. R. Fletcher and A. C. Skapski, *J.C.S. Dalton*, 1972, 635.

[19] R. O. Harris, L. S. Sadavoy, S. C. Nyburg, and F. H. Pickard, *J.C.S. Dalton*, 1973, 2646.

[20] M. Ciechanowicz and A. C. Skapski, *Chem. Comm.*, 1969, 574; *J. Chem. Soc. (A)*, 1971, 1792.

TABLE 3

Fractional co-ordinates of the hydrogen atoms. The atoms are labelled such that the first two digits are those of the carbon atoms to which they are attached. The two calculated positions are given in square brackets

	x	*y*	*z*
H(111)	0.298	0.075	−0.200
H(112)	0.291	0.140	−0.111
H(121)	0.350	−0.038	−0.088
[H(122)	0.283	−0.009	−0.016]
H(123)	0.287	−0.097	−0.120
H(211)	0.193	−0.050	−0.310
H(212)	0.153	−0.088	−0.218
H(221)	0.069	−0.021	−0.226
H(222)	0.081	−0.085	−0.334
H(223)	0.090	0.050	−0.338
H(32)	0.267	0.208	−0.295
H(33)	0.250	0.398	−0.388
H(34)	0.148	0.488	−0.353
H(35)	0.060	0.420	−0.255
H(36)	0.078	0.250	−0.168
H(411)	0.082	0.250	0.223
H(412)	0.156	0.228	0.223
H(421)	0.180	0.425	0.205
H(422)	0.143	0.413	0.298
H(423)	0.115	0.450	0.203
H(511)	0.050	0.363	−0.040
H(512)	0.078	0.460	0.035
H(521)	−0.003	0.400	0.145
H(522)	−0.042	0.438	0.048
H(523)	−0.050	0.300	0.075
H(62)	0.253	0.230	0.145
H(63)	0.358	0.270	0.066
H(64)	0.375	0.388	−0.063
H(65)	0.272	0.474	−0.133
H(66)	0.170	0.438	−0.070
H(711)	0.102	−0.146	0.174
[H(712)	0.020	−0.178	0.182]
H(721)	0.039	−0.347	0.109
H(722)	0.074	−0.349	0.205
H(723)	0.113	−0.344	0.107
H(811)	−0.045	−0.120	−0.072
H(812)	−0.065	−0.086	0.038
H(821)	−0.067	−0.275	0.100
H(822)	−0.115	−0.252	0.008
H(823)	−0.043	−0.316	−0.020
H(92)	0.186	−0.188	0.013
H(93)	0.258	−0.313	−0.095
H(94)	0.193	−0.388	−0.226
H(95)	0.090	−0.325	−0.255
H(96)	0.017	−0.250	−0.148

TABLE 4

Selected interatomic distances (Å), with estimated standard deviations in parentheses

Ru(1)–N(1)	1.841(3)	Ru(1)–Cl(1)	2.397(2)
Ru(1)–P(2)	2.426(2)	Ru(1)–Cl(2)	2.393(2)
Ru(1)–P(3)	2.424(2)	Ru(1)–Cl(3)	2.382(2)
	N(1)–P(1)	1.586(3)	
P(1)–C(11)	1.829(4)	P(2)–C(51)	1.835(4)
P(1)–C(21)	1.804(5)	P(2)–C(61)	1.824(4)
P(1)–C(31)	1.801(4)	P(3)–C(71)	1.849(5)
P(2)–C(41)	1.836(5)	P(3)–C(81)	1.827(4)
	P(3)–C(91)	1.818(4)	
		Mean C–C	
Ring (3*n*)	1.384(8)	Ring (9*n*)	1.384(8)
Ring (6*n*)	1.385(7)	Ethyl	1.508(9)
N(1) · · · Cl(2)	3.021(3)	Cl(1) · · · Cl(2)	3.337(2)
N(1) · · · Cl(3)	3.038(4)	Cl(1) · · · Cl(3)	3.394(2)
N(1) · · · P(2)	3.131(4)	Cl(1) · · · P(2)	3.324(2)
N(1) · · · P(3)	3.261(4)	Cl(1) · · · P(3)	3.127(2)
Cl(2) · · · P(2)	3.525(2)	Cl(3) · · · P(2)	3.305(2)
Cl(2) · · · P(3)	3.443(2)	Cl(3) · · · P(3)	3.328(2)

This suggests, therefore, that any *trans*-influence exerted by the phosphineiminato-ligand is, at best, only marginal.

There are few Ru^{IV}–N distances with which to compare that found in the title complex. For two Ru^{IV} compounds in which the nitrogen plays a bridging role, the Ru–N bond lengths are 1.720 {in $K_3[Ru_2NCl_8(H_2O)_2]$ [20]} and 1.725 Å {in $[NH_4]_3[Ru_2NCl_8(H_2O)_2]$ [21]}: these linkages can be at most double bonds. No Ru^{IV}–N single-bond distances are available for comparison, but those of Ru^{II} and Ru^{III} are generally >2.1 Å, *e.g.* 2.144 in $[Ru(NH_3)_6]I_2$,[22] 2.105 in $[Ru(NH_3)_6][BF_4]_3$,[22] and 2.11 Å in $[Ru(en)_3]Cl_3$.[23] Thus the present value (1.841 Å) seems short for a simple single bond.

TABLE 5

Bond angles (°), with estimated standard deviations in parentheses

N(1)–Ru(1)–Cl(1)	178.36(10)	Ru(1)–N(1)–P(1)	174.9(3)
N(1)–Ru(1)–Cl(2)	90.07(10)	N(1)–Ru(1)–P(2)	93.37(12)
N(1)–Ru(1)–Cl(3)	91.07(10)	N(1)–Ru(1)–P(3)	98.79(12)
Cl(1)–Ru(1)–Cl(2)	88.34(3)	Cl(1)–Ru(1)–P(2)	87.11(4)
Cl(1)–Ru(1)–Cl(3)	90.51(4)	Cl(1)–Ru(1)–P(3)	80.88(4)
Cl(2)–Ru(1)–P(2)	94.02(4)	Cl(3)–Ru(1)–P(2)	86.85(4)
Cl(2)–Ru(1)–P(3)	91.26(4)	Cl(3)–Ru(1)–P(3)	87.65(4)
Cl(2)–Ru(1)–Cl(3)	178.53(4)	P(2)–Ru(1)–P(3)	166.74(4)
N(1)–P(1)–C(11)	111.4(2)	C(11)–P(1)–C(21)	109.8(2)
N(1)–P(1)–C(21)	111.4(2)	C(11)–P(1)–C(31)	105.6(2)
N(1)–P(1)–C(31)	112.7(2)	C(21)–P(1)–C(31)	105.6(2)
Ru(1)–P(2)–C(41)	111.8(2)	C(41)–P(2)–C(51)	104.2(2)
Ru(1)–P(2)–C(51)	117.3(2)	C(41)–P(2)–C(61)	102.5(2)
Ru(1)–P(2)–C(61)	115.1(2)	C(51)–P(2)–C(61)	104.4(2)
Ru(1)–P(3)–C(71)	112.5(2)	C(71)–P(3)–C(81)	105.0(2)
Ru(1)–P(3)–C(81)	112.9(2)	C(71)–P(3)–C(91)	104.4(2)
Ru(1)–P(3)–C(91)	114.8(2)	C(81)–P(3)–C(91)	106.5(2)
	Mean $P–CH_2–CH_3$	115.9(4)	

An essentially linear geometry is found for the Ru–N–P system, although the angle (174.9°) at the nitrogen atom represents a small, though statistically significant, deviation from linearity. The P–N bond length (1.586 Å) lies in the range (1.51—1.61 Å) found for a large number of phosphonitrilic compounds, and is quite similar to the mean (1.575 Å) observed in five salts containing the non-cyclic but bent bis(triphenylphosphine)iminium cation $[(Ph_3P)_2N]^+$ (ref. 24). A P–N single bond is commonly accepted to be *ca.* 1.77 Å, as found in the phosphoramidate ion,[25] while values (refs. 26 and 27) of 1.57 and 1.49 Å (ref. 28) have been cited for P∶N and P⋮N bonds respectively. Although there is now a large body of structural data about P–N bond distances, there is no clear consensus as to the nature of the bonding involved and the correlations between bond length and bond order.

We suggest the following bonding scheme to account for the geometry observed in the Ru–N–P system.

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[21] R. J. Gee and H. M. Powell, *J. Chem. Soc. (A)*, 1971, 1795.

[22] B. R. Davis and J. A. Ibers, *Inorg. Chem.*, 1970, **9**, 2768.

[23] H. J. Peresie and J. A. Stanko, *Chem. Comm.*, 1970, 1674.

[24] L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1970, **92**, 7327.

[25] D. W. J. Cruickshank, *Acta Cryst.*, 1964, **17**, 671.

[26] M. J. E. Hewlins, *J. Chem. Soc. (B)*, 1971, 942.

[27] A. F. Wells, ' Structural Inorganic Chemistry,' 3rd edn., Clarendon Press, Oxford, 1962, p. 660.

[28] *Chem. Soc. Special Publ.*, 1965, No. 18, p. S 9s.

At the phosphorus atom, sp^3 hybrid orbitals are involved in four σ-bonds, three to the phenyl and ethyl groups, and the fourth to nitrogen. This leaves an electron in a d orbital. Nitrogen, on the other hand, utilizes linear sp hybrid orbitals for two σ-bonds, one to phosphorus and the other to ruthenium, leaving three electrons to be accommodated thus: $\{2p_x\}^2\{2p_y\}^1$. A d_π–p_π overlap of the type described by Cruickshank [29] for $[PO_4]^{3-}$ is then possible between $N\{2p_y\}^1$ and $P\{3d_{z^2}\}^1$ (Figure 2). For this interaction, a slight movement of P(1) in the y direction would tend to equalize the degree of overlap experienced by the positive and the negative lobes of the d_{z^2} orbital. Such a displacement is in fact the major component of the distortion which is observed, and may be a reason for the slight deviation from linearity at N(1). Steric interactions may, of course, also be a contributing factor. [The alternative orbital on P(1) which could be involved is $3d_{x^2-y^2}$; however, none of the three possible orientations of its lobes is correctly disposed to interact with the nitrogen $2p_y$ or $2p_x$ orbitals.]

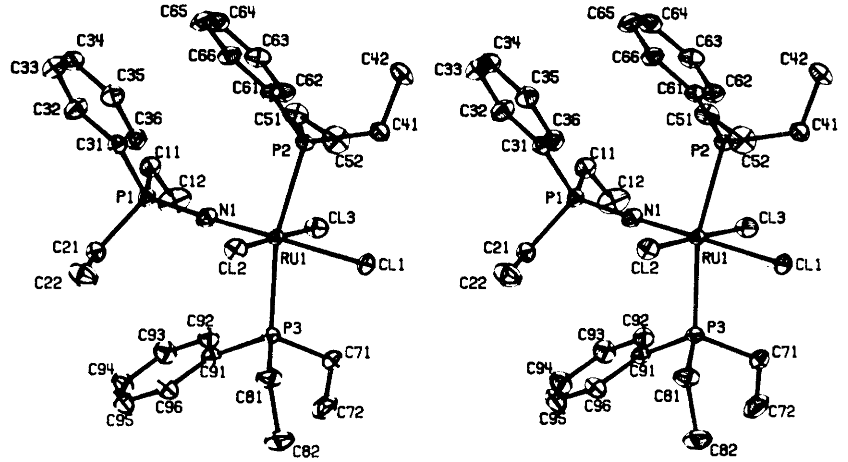

FIGURE 1 A stereoscopic view of the molecular structure of $[Ru(NPEt_2Ph)Cl_3(PEt_2Ph)_2]$. Thermal vibration ellipsoids are scaled to enclose 20% probability

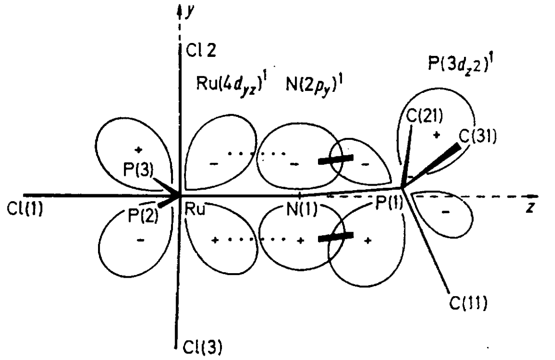

FIGURE 2 A schematic representation of the orbitals used in the π-bonding within the Ru–N–P system. For clarity, the Ru($4d_{xz}$) and N($2p_x$) orbitals have been omitted. *N.B.* The system of axes refers to ruthenium only

Taking into account the observed paramagnetism of the title complex and its effective magnetic moment of 2.8 B.M.,[7] the electron configuration at ruthenium should be $[Kr]^{36}\{4d_{xy}\}^2\{4d_{yz}\}^1\{4d_{xz}\}^1$, with $d_{x^2-y^2}d_{z^2}\,sp^3$ hybridized orbitals involved in the octahedral co-ordination. The overall angular mismatch between the $Ru\{4d_{yz}\}$ orbital and the positive lobe of $P\{3d_{z^2}\}$, as calculated from the disposition of the ligands at Ru(1) and P(1), is only *ca.* 11°, with the $N\{p_y\}$ orbital presumably at an optimum orientation between the two. While the juxtaposition of $Ru\{4d_{xz}\}^1$ and $N\{2p_x\}^2$ is not conducive to bond formation [hence the bending of P(2) and P(3) away from N(1)], that of $Ru\{4d_{yz}\}^1$ and $N\{2p_y\}^1$ is suitable for π-bonding. However, this would imply competition between Ru(1) and P(1) for the $N\{2p_y\}$ electron. Any overlap would be further weakened by the departure from coplanarity of the relevant orbitals. A contribution from the ylide form, $Ru–N^-–P^+$ with two lone pairs on the nitrogen, would also reduce the opportunity for Ru–N π-bonding to take place, but then one might expect the *trans*-chlorine atoms to bend away from N(1) in the same way as P(2) and P(3).

The overall picture, therefore, is one in which the Ru–N bond has a bond order somewhat >1, while that for P–N is correspondingly <2. The same change in bond order will, of course, have a much larger effect on a single-bond distance than on a double bond (see Figure 4 of ref. 30), in line with what is observed in the Ru–N–P system.

Individual P–C distances lie in the range 1.801—1.849 Å, similar to that found in many transition-metal complexes. However, there are small variations between these bonds and the bond angles at phosphorus, which may be related to the degree of distortion from ideal tetrahedral geometry, and the different substituents at the phosphorus atom. Thus at P(1), where the mean N–P–C and C–P–C angles are 111.8 and 107.0° respectively, the mean P–C distance is 1.810 Å, while for the two $PPhEt_2$ groups directly bonded to the metal, the distortion is greater (mean Ru–P–C 114.1 and C–P–C

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[29] D. W. J. Cruickshank, *J. Chem. Soc.*, 1961, 5486.
[30] F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 867.

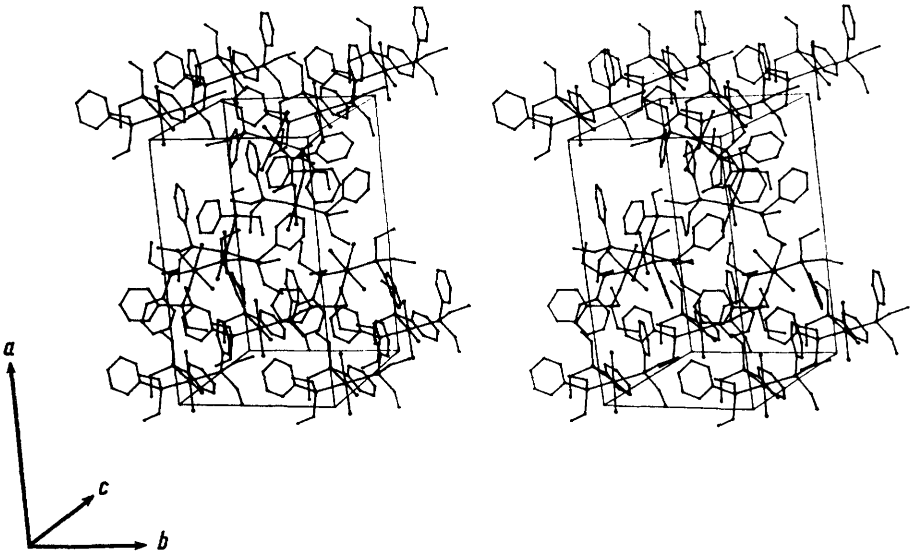

FIGURE 3 A stereoscopic view of the packing of [Ru(NPEt$_2$Ph)Cl$_3$(PEt$_2$Ph)$_2$] molecules

104.5°), and the mean P–C distance is 1.833 Å. Similarly, there may be a small difference between P–C(Ph) distances (mean 1.817 Å) and P–CH_2 distances (mean 1.829 Å). These trends may be compared with the situation in a less-distorted tetrahedral environment found in the benzyltriphenylphosphonium ion [31] where the mean P–C(Ph) distance is 1.790 and P–CH_2 is 1.811 Å.

TABLE 6

Planarity of the phenyl groups. The equations of planes are expressed as $Px + Qy + Rz = S$ in direct space, and deviations (Å) of relevant atoms from the planes are given in square brackets

Plane	P	Q	R	S
Ring (3)	8.63	5.81	10.75	0.22
[C(31) 0.013, C(32) −0.009, C(33) 0.001, C(34) 0.003, C(35) 0.002, C(36) −0.010, P(1) 0.037]				
Ring (6)	0.32	9.07	9.22	3.15
[C(61) −0.001, C(62) −0.009, C(63) 0.011, C(64) −0.004, C(65) −0.006, C(66) 0.008, P(2) −0.081]				
Ring (9)	4.45	9.73	−7.58	−1.17
[C(91) −0.007, C(92) 0.008, C(93) −0.002, C(94) −0.006, C(95) 0.007, C(96) −0.001, P(3) 0.011]				

A least-squares calculation shows that the three phenyl rings are satisfactorily planar. Details of these planes are given in Table 6. There is relatively little bending at the C(*m*1) atoms of these rings in that each phosphorus atom lies reasonably close to the least-squares plane through its phenyl ring, the maximum deviation being 0.08 Å. The main cohesive forces between the molecules are of the van der Waals type and the packing arrangement is shown in Figure 3 as a pair of stereoscopic drawings.[17]

We thank Dr. W. P. Griffith and Dr. D. Pawson for providing the crystals and for discussions, Dr. G. J. Buist for the use of his Atomic Orbital Program ATOM5, Professor D. Rogers for discussions and for the use of a diffractometer, and the University of Ghana for a Postgraduate Scholarship (to F. L. P.).

[5/2019 *Received*, 15*th October*, 1975]

[31] A. C. Skapski and F. A. Stephens, *J. Cryst. Mol. Struct.*, 1974, **4**, 77.