Crystal and Molecular Structure of Acetatocarbonyl(*N*-*p*-tolylformimidoyl)bis(triphenylphosphine)ruthenium(II)

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The crystal and molecular structure of the title compound has been determined by the heavy-atom method from three-dimensional X-ray data collected by counter methods. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 9.947(4)$, $b = 14.680(4)$, $c = 28.014(5)$ Å, and $\beta = 92.08(2)$°. Block-diagonal least-squares refinement gave R of 0.057 for 2 519 observed reflections. The geometry about the metal is that of a distorted octahedron with carbonyl, N-p-tolylformimidoyl, and bidentate acetate groups forming a plane and the two triphenylphosphine groups occupying the remaining *trans*-positions.

THE reaction of co-ordinated isocyanide in the complex $[Ru(O_2)(CO)(CNR)(PPh_3)_2]$ ($R = p$-tolyl) with ethanol to produce the formimidoyl ligand has recently been reported.[1] The ethanol is believed to react with the molecular oxygen, and a possible mechanism involves the formation of a ruthenium hydride complex as intermediate. Such a hydrogen transfer from a transition metal to the isocyanide ligand has not previously been noted although hydrogen transfers to nitrosyl,[2] acetylene,[3] and ketimido-ligands[4] have been observed, but rarely. Similar compounds are also formed with n-propanol and benzyl alcohol.[1] A crystal-structure analysis of the complex $[Ru(OAc)(p\text{-}MeC_6H_4NCH)(CO)(PPh_3)_2]$ was considered to be particularly appropriate since the ligand N-p-tolylformimidoyl has not previously been characterised by the X-ray method. It was hoped to obtain information on the nature of the metal–formimidoyl bond as well as the *trans*-effect of this ligand.

EXPERIMENTAL

Crystals were pale yellow needles. Unit-cell constants were determined from a least-squares refinement[5] of the setting angles of twelve reflections centred on a Hilger and Watts automatic four-circle diffractometer.

Crystal Data.—$C_{47}H_{41}NO_3P_2Ru$, $M = 830.9$, Monoclinic, $a = 9.947(4)$, $b = 14.680(4)$, $c = 28.014(5)$ Å, $\beta = 92.08(2)$°, $U = 4\,088$ Å^3, $D_m = 1.34$, $Z = 4$, $D_c = 1.35$. Space group $P2_1/c$. Mo-K_α radiation, $\lambda = 0.7107$ Å, μ(Mo-K_α) = 5.0 cm^{-1}. The 2θ–ω scan technique was used to record 2 519 independent reflections for which $I > 2.5\sigma(I)$. Data were processed according to the procedure of Ibers[6] with $p = 0.04$. No absorption corrections were applied since μ was small and the range of absorption factors was only 1.05—1.14.[7]

A 'sharpened' Patterson revealed the site of the ruthenium atom and from the resulting heavy-atom map the two phosphorus atoms were located (R 0.31). A second electron-density synthesis indicated positions for the remaining fifty-one non-hydrogen atoms and inclusion of these in a structure factor calculation reduced R to 0.16. The atomic scattering factors used for the ruthenium atom were taken from ref. 8, and for all other atoms from ref. 9. Four cycles of block-diagonal least-squares refinement assuming isotropic thermal motion lowered the factors R to 0.085 and R' to 0.075 $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$. The weight, w, was given by $4F_o^2/\sigma^2(F_o^2)$; the function minimised was $\Sigma w(|F_o| - |F_c|)^2$. Anisotropic thermal motion was then assumed for all non-hydrogen atoms other than those of the phenyl, p-tolyl, and acetate-methyl groups and after a further three refinement cycles R and R' were 0.079 and 0.069 respectively. Calculated positions for the hydrogen atoms associated with the acetate, phenyl, and p-tolyl groups were included in the structure-factor calculations assuming isotropic thermal

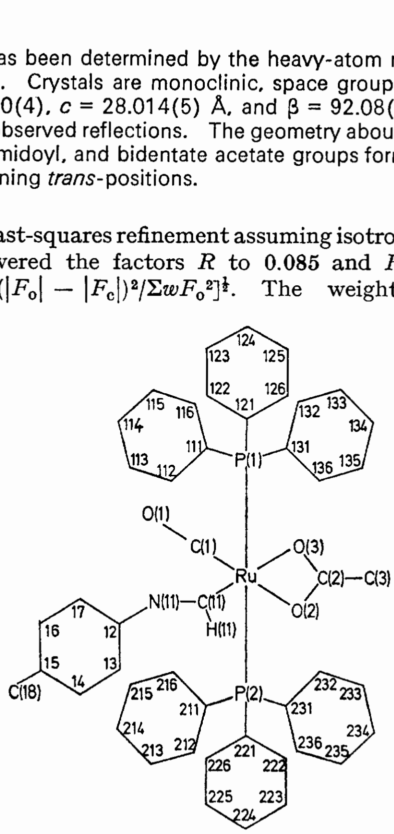

FIGURE 1 The atom numbering system

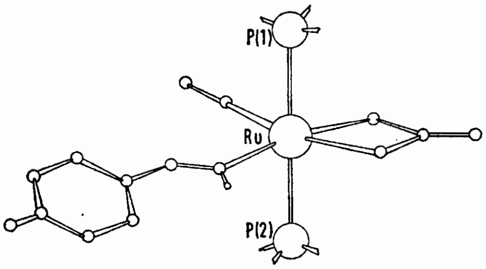

FIGURE 2 The co-ordination about ruthenium

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[1] D. F. Christian, G. R. Clark, W. R. Roper, J. M. Waters, and K. R. Whittle, *J.C.S. Chem. Comm.*, 1972, 458.

[2] K. R. Grundy, C. A. Reed, and W. R. Roper, *Chem. Comm.*, 1970, 1501.

[3] B. E. Mann, B. L. Shaw, and N. I. Tucker, *Chem. Comm.*, 1970, 1333.

[4] B. Cetinkaya, M. F. Lappert, and J. McMeeking, *Chem. Comm.*, 1971, 215.

[5] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1967, **22**, 457.

[6] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

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

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

[9] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

motion with $B = 5.0$ Å^2 (R 0.075). Anisotropic thermal motion was then assumed for all remaining non-hydrogen atoms and after three refinement cycles R and R' were 0.063 and 0.056 respectively. The effects of anomalous dispersion were included in the calculation of F_c, the values of $\Delta f'$ and $\Delta f''$ for ruthenium and phosphorus being those given in ref. 10. Further least-squares refinement gave R 0.057 and R' 0.056. A final difference map showed a region of positive electron density suitable for a hydrogen-atom site near carbon atom C(11) [C–H 0.91 Å, Ru–C(11)–H 96°], but this could not be identified with certainty as the formimidoyl hydrogen, since peaks of comparable height appeared elsewhere on the map.

Table 1

Atomic co-ordinates with standard deviations in parentheses

Atom	x/a	y/b	z/c
Ru	0.176 03(9)	0.234 97(6)	0.381 82(3)
P(1)	0.0571(3)	0.1166(2)	0.3410(1)
P(2)	0.3011(3)	0.3497(2)	0.4243(1)
O(1)	−0.0640(9)	0.3530(6)	0.3826(3)
O(2)	0.3374(8)	0.1364(6)	0.3922(3)
O(3)	0.1981(9)	0.1514(6)	0.4502(3)
N(11)	0.1769(10)	0.3214(7)	0.2857(3)
C(1)	0.0289(12)	0.3073(8)	0.3821(4)
C(2)	0.3046(15)	0.1130(10)	0.4349(5)
C(3)	0.3821(16)	0.0452(10)	0.4620(5)
C(11)	0.2328(11)	0.2806(8)	0.3199(4)
C(12)	0.2487(13)	0.3335(9)	0.2424(4)
C(13)	0.1855(15)	0.3094(12)	0.1988(5)
C(14)	0.2519(18)	0.3157(14)	0.1574(6)
C(15)	0.3803(16)	0.3501(11)	0.1561(5)
C(16)	0.4403(16)	0.3754(12)	0.1987(6)
C(17)	0.3753(14)	0.3678(10)	0.2420(5)
C(18)	0.4481(23)	0.3606(16)	0.1107(7)
C(111)	0.0416(11)	0.0158(9)	0.3781(4)
C(112)	−0.0372(15)	0.0219(10)	0.4188(5)
C(113)	−0.0469(17)	−0.0519(12)	0.4488(5)
C(114)	0.0172(19)	−0.1301(12)	0.4395(6)
C(115)	0.0933(19)	−0.1392(12)	0.4004(7)
C(116)	0.1043(16)	−0.0661(11)	0.3685(6)
C(121)	−0.1144(11)	0.1431(8)	0.3195(4)
C(122)	−0.2255(13)	0.0884(9)	0.3275(5)
C(123)	−0.3512(12)	0.1112(11)	0.3099(5)
C(124)	−0.3686(12)	0.1902(10)	0.2840(5)
C(125)	−0.2632(11)	0.2453(10)	0.2749(4)
C(126)	−0.1317(12)	0.2224(9)	0.2922(4)
C(131)	0.1316(11)	0.0716(8)	0.2868(4)
C(132)	0.0502(11)	0.0253(9)	0.2535(4)
C(133)	0.1072(13)	−0.0117(11)	0.2131(5)
C(134)	0.2392(13)	−0.0017(10)	0.2070(5)
C(135)	0.3211(12)	0.0408(10)	0.2319(5)
C(136)	0.2675(11)	0.0757(8)	0.2804(4)
C(211)	0.3412(11)	0.4530(8)	0.3923(4)
C(212)	0.2447(13)	0.4926(9)	0.3618(5)
C(213)	0.2726(16)	0.5745(10)	0.3396(6)
C(214)	0.3958(17)	0.6175(11)	0.3457(5)
C(215)	0.4883(15)	0.5768(11)	0.3758(5)
C(216)	0.4659(13)	0.4957(10)	0.3987(5)
C(221)	0.4661(11)	0.3078(8)	0.4465(4)
C(222)	0.5532(12)	0.2767(9)	0.4136(4)
C(223)	0.6756(12)	0.2410(11)	0.4283(5)
C(224)	0.7120(13)	0.2387(13)	0.4763(5)
C(225)	0.6256(13)	0.2691(13)	0.5082(5)
C(226)	0.5033(14)	0.3047(10)	0.4944(5)
C(231)	0.2211(11)	0.3922(8)	0.4773(4)
C(232)	0.2457(13)	0.4797(9)	0.4945(4)
C(233)	0.1855(15)	0.5099(9)	0.5354(5)
C(234)	0.1073(15)	0.4554(10)	0.5613(5)
C(235)	0.0858(18)	0.3710(12)	0.5445(6)
C(236)	0.1394(15)	0.3386(10)	0.5028(5)

Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21433 (28 pp., 1 microfiche),* together with thermal parameters, details of planes, and root-mean-square amplitudes of vibration. In Figure 1 the numbering system for the molecule is given and in Figure 2 the co-ordination about the ruthenium is shown. Final atomic positional parameters are listed in Table 1 with their standard deviations, calculated positions for hydrogen atoms in Table 2, and bond lengths and angles, with their standard deviations, in Tables 3 and 4.

Table 2

Calculated hydrogen positions (numbered according to the carbon atoms to which they are attached)

Atom	x/a	y/b	z/c
H(11)	0.331	0.270	0.314
H(13)	0.089	0.284	0.198
H(14)	0.213	0.293	0.125
H(16)	0.535	0.402	0.198
H(17)	0.420	0.390	0.273
H(31)	0.470	0.070	0.473
H(32)	0.397	−0.013	0.441
H(33)	0.319	0.016	0.488
H(181)	0.506	0.418	0.109
H(182)	0.493	0.300	0.100
H(183)	0.377	0.377	0.084
H(112)	−0.086	0.080	0.426
H(113)	−0.107	−0.051	0.478
H(114)	0.005	−0.180	0.463
H(115)	0.141	−0.197	0.395
H(116)	0.159	−0.071	0.338
H(122)	−0.211	0.029	0.347
H(123)	−0.430	0.074	0.318
H(124)	−0.461	0.206	0.273
H(125)	−0.278	0.301	0.254
H(126)	−0.051	0.263	0.285
H(132)	−0.048	0.019	0.259
H(133)	0.048	−0.047	0.189
H(134)	0.279	−0.027	0.177
H(135)	0.422	0.047	0.234
H(136)	0.325	0.108	0.305
H(212)	0.153	0.462	0.356
H(213)	0.201	0.606	0.318
H(214)	0.420	0.675	0.328
H(215)	0.578	0.608	0.382
H(216)	0.541	0.468	0.420
H(222)	0.526	0.280	0.378
H(223)	0.739	0.217	0.404
H(224)	0.802	0.213	0.486
H(225)	0.652	0.268	0.544
H(226)	0.442	0.330	0.519
H(232)	0.308	0.521	0.476
H(233)	0.201	0.575	0.546
H(234)	0.067	0.481	0.590
H(235)	0.023	0.330	0.564
H(236)	0.123	0.274	0.492

RESULTS AND DISCUSSION

The crystal structure is built up of monomeric units. The five ligands about the ruthenium adopt a distorted octahedral arrangement with the two triphenylphosphine groups occupying the *trans*-positions (see Figure 2); the distortion is caused by the acetate group, which is bonded in an asymmetric bidentate manner.

This is the first structural analysis of an *N*-*p*-tolyl formimidoyl ligand, and hence its molecular dimensions are of particular interest. It is bound to ruthenium *via* a carbon at a distance [Ru–C(11) 1.96(1) Å] which is only a

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1974, Index issue.

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

TABLE 3

Bond lengths (Å), with standard deviations in parentheses

Ru–P(1)	2.373(3)	C(121)–C(122)	1.39(2)
Ru–P(2)	2.386(3)	C(121)–C(126)	1.40(2)
Ru–O(2)	2.173(8)	C(122)–C(123)	1.37(2)
Ru–O(3)	2.279(8)	C(123)–C(124)	1.37(2)
Ru–C(1)	1.81(1)	C(124)–C(125)	1.36(2)
Ru–C(11)	1.96(1)	C(125)–C(126)	1.42(2)
P(1)–C(111)	1.82(1)	C(131)–C(132)	1.39(2)
P(1)–C(121)	1.83(1)	C(131)–C(136)	1.37(2)
P(1)–C(131)	1.84(1)	C(132)–C(133)	1.40(2)
P(2)–C(211)	1.81(1)	C(133)–C(134)	1.34(2)
P(2)–C(221)	1.84(1)	C(134)–C(135)	1.34(2)
P(2)–C(231)	1.82(1)	C(135)–C(136)	1.39(2)
O(1)–C(1)	1.14(1)	C(211)–C(212)	1.39(2)
O(2)–C(2)	1.30(2)	C(211)–C(216)	1.40(2)
O(3)–C(2)	1.29(2)	C(212)–C(213)	1.39(2)
N(11)–C(11)	1.24(1)	C(213)–C(214)	1.38(2)
N(11)–C(12)	1.44(2)	C(214)–C(215)	1.36(2)
C(2)–C(3)	1.46(2)	C(215)–C(216)	1.38(2)
C(12)–C(13)	1.40(2)	C(221)–C(222)	1.37(2)
C(12)–C(17)	1.36(2)	C(221)–C(226)	1.38(2)
C(13)–C(14)	1.36(2)	C(222)–C(223)	1.38(2)
C(14)–C(15)	1.38(2)	C(223)–C(224)	1.38(2)
C(15)–C(16)	1.37(2)	C(224)–C(225)	1.34(2)
C(15)–C(18)	1.47(3)	C(225)–C(226)	1.37(2)
C(16)–C(17)	1.40(2)	C(231)–C(232)	1.39(2)
C(111)–C(112)	1.41(2)	C(231)–C(236)	1.35(2)
C(111)–C(116)	1.39(2)	C(232)–C(233)	1.38(2)
C(112)–C(113)	1.38(2)	C(233)–C(234)	1.35(2)
C(113)–C(114)	1.34(3)	C(234)–C(235)	1.34(2)
C(114)–C(115)	1.36(3)	C(235)–C(236)	1.39(2)
C(115)–C(116)	1.40(2)		

little shorter than that estimated for Ru–C(sp^2) (2.00 Å),[11] and which suggests a bond order close to one. It thus appears that in this complex at least, the formimidoyl ligand has little or no π-bonding capacity.

The bond length C(11)–N(11) [1.24(1) Å] is shorter than that expected for a double bond and may indicate a slight increase in bond order. The Ru–C(11)–N(11) angle [135.3(9)°] is considerably greater than the expected value of 120° and probably arises because of the steric interaction between N(11) and H(126); the distance between these two atoms is 2.42 Å. The N(11)–C(12) distance [1.44(2) Å] and C(11)–N(11)–C(12) angle [119.1(1.0)°] are as expected for a nitrogen–carbon single bond and trigonal nitrogen atom. The mean bond length within the phenyl rings is 1.38(2) Å which is a normal value; the associated bond angles do not differ significantly from 120°. The bond length C(15)–C(18) [1.47(3) Å] is not significantly different from that expected for a single C–C bond. The C(14)–C(15)–C(18) [121(2)°] and C(16)–C(15)–C(18) [122(2)°] angles are also normal. The plane of best fit through the phenyl ring of the *N*-*p*-tolylformimidoyl group shows that this ligand is approximately planar but that it makes a dihedral angle of 65.5° with that of atoms C(1), C(11), O(2), O(3). This angle results from a rotation about the bond N(11)–C(12) as well as a bend at atom C(11), and is apparently caused by steric interaction between phenyl rings C(121′)—(126′), C(131)—(136) and the *N*-*p*-tolylformimidoyl ligand. Figure 3 shows the formimidoyl group sandwiched between these two phenyl rings.

TABLE 4

Bond angles (°), with standard deviations in parentheses

P(1)–Ru–P(2)	177.8(1)
P(1)–Ru–O(2)	86.0(2)
P(1)–Ru–O(3)	92.4(2)
P(1)–Ru–C(1)	92.4(4)
P(1)–Ru–C(11)	88.7(3)
P(2)–Ru–O(2)	92.0(2)
P(2)–Ru–O(3)	85.9(2)
P(2)–Ru–C(1)	89.5(4)
P(2)–Ru–C(11)	92.2(3)
O(2)–Ru–O(3)	58.7(3)
O(2)–Ru–C(11)	96.3(4)
O(3)–Ru–C(1)	111.5(4)
C(1)–Ru–C(11)	93.6(5)
Ru–P(1)–C(111)	111.8(4)
Ru–P(1)–C(121)	116.5(4)
Ru–P(1)–C(131)	116.9(4)
Ru–P(2)–C(211)	117.7(4)
Ru–P(2)–C(221)	112.0(4)
Ru–P(2)–C(231)	114.4(4)
C(111)–P(1)–C(121)	105.3(5)
C(111)–P(1)–C(131)	103.0(5)
C(121)–P(1)–C(131)	101.8(5)
C(211)–P(2)–C(221)	103.7(5)
C(211)–P(2)–C(231)	103.1(5)
C(221)–P(2)–C(231)	104.5(5)
Ru–O(2)–C(2)	95.2(8)
Ru–O(3)–C(2)	90.6(8)
O(2)–C(2)–O(3)	115.4(1.2)
O(2)–C(2)–C(3)	121.1(1.3)
O(3)–C(2)–C(3)	123.5(1.3)
Ru–C(1)–O(1)	179.6(1.0)
Ru–C(11)–N(11)	135.3(9)
C(11)–N(11)–C(12)	119.1(1.0)
N(11)–C(12)–C(13)	119.0(1.2)
N(11)–C(12)–C(17)	122.7(1.2)
C(13)–C(12)–C(17)	118.4(1.3)
C(12)–C(13)–C(14)	120.7(1.5)
C(13)–C(14)–C(15)	122.0(1.7)
C(14)–C(15)–C(16)	116.9(1.6)
C(14)–C(15)–C(18)	121.2(1.6)
C(16)–C(15)–C(18)	121.9(1.6)
C(15)–C(16)–C(17)	122.3(1.5)
C(12)–C(17)–C(16)	119.6(1.4)
P(1)–C(111)–C(112)	118.2(1.0)
P(1)–C(111)–C(116)	123.1(1.0)
P(1)–C(121)–C(122)	124.0(9)
P(1)–C(121)–C(126)	116.8(8)
P(1)–C(131)–C(132)	119.2(9)
P(1)–C(131)–C(136)	121.4(9)
P(2)–C(211)–C(212)	119.6(9)
P(2)–C(211)–C(216)	121.5(9)
P(2)–C(221)–C(222)	117.6(9)
P(2)–C(221)–C(226)	123.0(9)
P(2)–C(231)–C(232)	121.6(9)
P(2)–C(231)–C(236)	121.3(1.0)
C(112)–C(111)–C(116)	119(1)
C(111)–C(112)–C(113)	120(1)
C(112)–C(113)–C(114)	121(2)
C(113)–C(114)–C(115)	122(2)
C(114)–C(115)–C(116)	120(2)
C(111)–C(116)–C(115)	120(1)
C(122)–C(121)–C(126)	119(1)
C(121)–C(122)–C(123)	121(1)
C(122)–C(123)–C(124)	120(1)
C(123)–C(124)–C(125)	121(1)
C(124)–C(125)–C(126)	120(1)
C(121)–C(126)–C(125)	118(1)
C(132)–C(131)–C(136)	119(1)
C(131)–C(132)–C(133)	119(1)
C(132)–C(133)–C(134)	119(1)
C(133)–C(134)–C(135)	123(1)
C(134)–C(135)–C(136)	119(1)
C(131)–C(136)–C(135)	120(1)
C(212)–C(211)–C(216)	119(1)
C(211)–C(212)–C(213)	120(1)
C(212)–C(213)–C(214)	122(1)

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[11] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 3rd edn., 1960.

Table 4 (*Continued*)

C(213)–C(214)–C(215)	117(1)
C(214)–C(215)–C(216)	123(1)
C(211)–C(216)–C(215)	119(1)
C(222)–C(221)–C(226)	119(1)
C(221)–C(222)–C(223)	120(1)
C(222)–C(223)–C(224)	120(1)
C(223)–C(224)–C(225)	119(1)
C(224)–C(225)–C(226)	122(1)
C(221)–C(226)–C(225)	119(1)
C(232)–C(231)–C(236)	117(1)
C(231)–C(232)–C(233)	121(1)
C(232)–C(233)–C(234)	122(1)
C(233)–C(234)–C(235)	117(1)
C(234)–C(235)–C(236)	124(2)
C(231)–C(236)–C(235)	120(1)

The asymmetric bidentate acetate group has ruthenium–oxygen distances of 2.173(8) and 2.279(8) Å whereas the O–Ru–O angle is 58.7(3)°. These values suggest that the acetate group is loosely held and is comparable with the acetate group in [RuH(OAc)$(PPh_3)_3$] where the corresponding values are 2.256(10), 2.208(10) Å, and 57.5(4)°.[12] The *N-p*-tolylformimidoyl ligand is opposite the longer Ru–O bond and it appears that this ligand has a greater *trans*-effect than carbonyl which is opposite the shorter Ru–O bond. The two C–O distances [1.30(2) and 1.29(2) Å] are identical but the Ru–O–C angles [95.2(8) and 90.6(8)°] are not, the difference arising from the asymmetric binding to ruthenium. The O–C–O angle [115.4(1.2)°] differs slightly from the expected trigonal value due to the formation of the four-membered chelate ring. The foregoing values can be compared with similar ones in the complex acetato-*C*-*rac*-(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane)nickel(II) perchlorate where values of 1.25(2) and 1.25(2) Å and 88.2(8), 87.8(8), and 121.6(1.4)° were found.[13] The C(2)–C(3) bond length [1.46(2) Å] is slightly shorter than a normal C–C single bond but in view of the common underestimation of standard deviations[14] it is unlikely that this difference is meaningful. The two O–C–C angles [121.1(1.3) and 123.5(1.3)°] are normal.

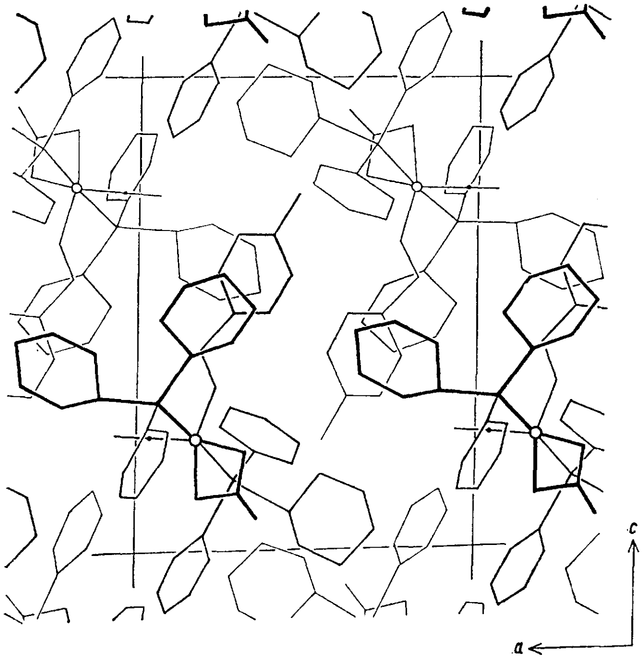

Figure 3 The packing of the molecules in the unit cell

The carbonyl group is bonded linearly with Ru–C and C–O bond lengths of 1.81(1) and 1.14(1) Å; Ru–C–O is 180(1)°. These values can be compared with the appropriate distances and angles in $Ru_3(CO)_{12}$,[15] where Ru–C distances range from 1.83(2) to 1.99(2) Å and the mean C–O distance is 1.14(2) Å. In the present complex the carbonyl appears to be a better π-acceptor than in $Ru_3(CO)_{12}$, no doubt since it is only competing with the acetate group for π-electrons.

The mean Ru–P bond length [2.379(9) Å] compares well with previous values.[12,16] The mean P–C bond length is 1.83(1) Å and mean Ru–P–C, C–P–C, and P–C–C angles are 115(3), 104(1), and 121(2)° [*cf.* P–C 1.848(5) Å and C–P–C 101.6(1.0)° in $RuCl_2(PPh_3)_3$].[16] The mean C–C bond length is 1.38 Å with an estimated standard deviation of 0.02 Å calculated from a statistical spread of values and no angles within the phenyl rings deviate significantly from 120°. The phenyl rings are approximately planar.

As already mentioned, the geometry of the complex can be described as a distorted octahedron with the bulky triphenylphosphine ligands lying mutually *trans* and the distortion arising from chelation of the acetate group. The angles O(2)–Ru–O(3), O(3)–Ru–C(1), C(1)–Ru–C(11), and O(2)–Ru–C(11) are 58.7(3), 111.5(4), 93.6(5), and 96.3(4)°. There are a number of intermolecular contacts involving the carbonyl oxygen O(1) (none <3.20 Å) and it appears that the effect of these has been lessened by the O(3)–Ru–C(1) angle increasing from the expected angle of *ca.* 100° to 111.5(4)°. The C(1)–Ru–C(11) and O(2)–Ru–C(11) angles have apparently decreased slightly to accommodate this change. The plane of best fit through atoms O(2), O(3), C(1), and C(11) shows that the three ligands forming the plane of the octahedron are in fact non-planar with the *trans*-atoms O(2) and C(1)

Table 5

Intermolecular distances ⩽3.40 Å (excluding hydrogen atoms)

	Symmetry position *	Translation	Distance
O(1) · · · C(133)	$(\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z)$	(0,0,0)	3.35
O(1) · · · C(233)	(x,y,z)	$(\bar{1},0,0)$	3.36
O(1) · · · C(233)	$(\bar{x},\bar{y},\bar{z})$	(0,1,1)	3.32
O(1) · · · C(234)	$(\bar{x},\bar{y},\bar{z})$	(0,1,1)	3.26
C(3) · · · C(3)	$(\bar{x},\bar{y},\bar{z})$	(1,0,1)	3.38
C(113) · · · C(113)	$(\bar{x},\bar{y},\bar{z})$	(0.0,1)	3.35

* Of second atom.

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below this plane by 0.05 and 0.04 Å respectively and O(3) and C(11) above it by 0.05 and 0.04 Å respectively.

The packing of the molecules is illustrated in Figure 3. Intermolecular distances $\leqslant$3.40 Å (except for hydrogen contacts which are $\leqslant$2.90 Å) are listed in Tables 5 and 6 and non-bonded intramolecular distances (excluding the C–C distances within a phenyl ring) $\leqslant$3.75 Å are listed in Table 7. The more important intermolecular contacts involve the oxygen of the carbonyl group and carbons of the phenyl rings. Two of the O · · · H distances are less than the sum of the van der Waals radii (2.6 Å)[17] but it is unlikely that hydrogen bonding occurs since the C–H · · · O angles are less than 140° and the C · · · O distances are too long. These close contacts appear to be the result of the crystal packing.

TABLE 6

Intermolecular distances involving hydrogen atoms $\leqslant$2.90 Å

	Symmetry position *	Translation	Distance
O(1) · · · H(133)	$(\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z)$	(0,0,0)	2.50
O(1) · · · H(223)	(x,y,z)	$(\bar{1},0,0)$	2.88
O(1) · · · H(233)	$(\bar{x},\bar{y},\bar{z})$	(0,1,1)	2.67
O(1) · · · H(234)	$(\bar{x},\bar{y},\bar{z})$	(0,1,1)	2.56
O(3) · · · H(113)	$(\bar{x},\bar{y},\bar{z})$	(0,0,1)	2.67
C(3) · · · H(31)	$(\bar{x},\bar{y},\bar{z})$	(1,0,1)	2.85
C(18) · · · H(32)	$(\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z)$	(1,0,0)	2.84
C(122) · · · H(223)	(x,y,z)	$(\bar{1},0,0)$	2.88

* Of second atom.

TABLE 7

Some non-bonded intramolecular distances (Å)

P(1) · · · O(2)	3.10	P(2) · · · H(11)	3.33
P(1) · · · O(3)	3.36	O(1) · · · N(11)	3.72
P(1) · · · C(1)	3.04	O(2) · · · O(3)	2.18
P(1) · · · C(11)	3.04	O(2) · · · C(11)	3.08
P(1) · · · H(11)	3.63	O(2) · · · H(11)	2.94
P(2) · · · O(2)	3.28	O(3) · · · C(1)	3.39
P(2) · · · O(3)	3.18	N(11) · · · C(1)	3.13
P(2) · · · C(1)	2.98	C(1) · · · C(11)	2.75
P(2) · · · C(11)	3.15		

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