Cyclopentadienyl-ruthenium and -osmium Chemistry. Part 15.‡ Some Cyanocarbon and Cyanonitrogen Complexes: Crystal and Molecular Structures of $[Ru\{N{=}C{=}C(CN)C(CN){=}C(CN)_2\}\{P(OMe)_3\}(PPh_3)(\eta\text{-}C_5H_5)]$ §

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A series of cyanocarbon and cyanonitrogen derivatives $[RuR(PPh_3)_2(\eta\text{-}C_5H_5)]$ {R = $CH(CN)_2$, $C(CN)_3$, $N(CN)_2$, $C_3(CN)_5$, and $N[C_2(CN)_3]_2$} have been prepared from reactions between $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ and the appropriate cyano-substituted anion. The R groups are probably attached *via* Ru–N bonds, *i.e.* they are keteniminato-complexes; this was confirmed for R = $C_3(CN)_5$ by an *X*-ray diffraction study of the complex $[Ru\{N{=}C{=}C(CN)C(CN){=}C(CN)_2\}\{P(OMe)_3\}(PPh_3)(\eta\text{-}C_5H_5)]$. Crystals are monoclinic, space group *C2/c*, a = 18.845(8), b = 20.967(6), c = 19.336(7) Å, β = 118.54(3)°, and Z = 8, the structure being refined to a residual of 0.042 for 3 646 'observed' reflections. The ruthenium atom is pseudo-octahedrally co-ordinated by the cyclopentadienyl ring [Ru–C 2.160(12)—2.236(6) Å], the two phosphine ligands [$Ru{-}PPh_3$ 2.322(2), $Ru{-}P(OMe)_3$ 2.239(2) Å], and the ligand nitrogen atom [Ru–N 2.033(6) Å].

REPLACEMENT of H by F in σ-bonded transition-metal alkyls increases thermal stability, and decreases the M–C bond lengths; [1] experimental ESCA shifts of $[Mn(CH_3)(CO)_5]$ and $[Mn(CF_3)(CO)_5]$ show that the electron density at the C atom is considerably higher in the CH_3 than in the CF_3 compounds.[2] Calculations on a series of $Mn(CO)_5$ compounds using an extended CNDO formalism support observations that electron-withdrawing groups decrease reaction rates.[3] The experimental observations are not limited to σ-bonded groups; transition-metal complexes containing olefins, dienes, and arenes bearing electron-withdrawing groups, and particularly polysubstituted molecules, as ligands show significant differences in structure and reactivity from their hydrocarbon analogues. The most commonly studied compounds have F or CF_3 groups in place of H in the ligands; a growing number of reports are concerned with poly-methoxycarbonyl-substituted ligands, often derived from $C_2(CO_2Me)_2$, and with ligands containing several cyano-groups. Both substituents can conjugate with unsaturated centres also present in the ligand, facilitating electron delocalisation, and a similar situation would be expected with cyano-substituted ligands.

Many studies of tricyanomethanide, $C(CN)_3$, and tetracyanoethylene, $C_2(CN)_4$, complexes have appeared.[4,5] It is pertinent to note King's [6] studies of the reactions of chlorocyanocarbons with metal carbonyl anions which have given polycyanovinyl complexes, and *via* subsequent reactions and transformations, derivatives containing dicyanomethylene and dicyanovinylidene ligands, as well as various cyanoalkyl complexes obtained by insertion of tetracyanoethylene into M–H or M–C bonds,[7] and also by oxidative addition of chloroacetonitrile and related compounds to suitable electron-rich transition metal complexes.[8] Also of interest is the work of Köhler *et al.*[9] on the preparation of simple salts containing many simple substituted cyanocarbon, cyanonitrogen, and related pseudo-halide ions.

Ligands containing more than two carbons bearing cyano-substituents are rare. Reactions of $[MCl(CO)(PPh_3)_2]$ (M = Rh or Ir) with the tetracyanoethylene radical anion affords $[\{M(CO)(PPh_3)_2\}_2\{C_4(CN)_6\}]$ (1) containing a $\mu\text{-}(NC)_2C{=}C(CN)C(CN){=}C(CN)_2$ ligand,[10,11] while pentacyanobutadienyl complexes were obtained from several metal carbonyl anions and $ClC(CN){=}C(CN)C(CN){=}C(CN)_2$.[12] Complexes containing cyclic polycyano-ligands appear to be limited to the complexes of $\eta\text{-}C_5H_{5-n}(CN)_n^-$ (n = 1, 2, 3, and 5) with manganese and rhenium,[13] and the silver and iron derivatives of pentacyanocyclopentadienide, $C_5(CN)_5^-$, obtained by Webster.[14] The iron(II) complex decacyanoferrocene is an insoluble brown solid, thought to be polymeric *via* bridging CN groups.

Cyanocarbon acids are among the strongest organic acids; the original paper describing these intriguing compounds reports the preparation of several simple salts of these anions with transition-metal cations.[15] However, we are not aware of any compounds containing these anions and organometallic residues, and we have commenced a study of these derivatives with a survey of some reactions with the versatile complex $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$. The resulting complexes, together with some related derivatives containing smaller cyanocarbon and cyanonitrogen ligands, and the crystal and molecular structures of $[Ru\{C_3(CN)_5\}\{P(OMe)_3\}(PPh_3)(\eta\text{-}C_5H_5)]$, are described in this paper.

RESULTS AND DISCUSSION

We have described previously the cationic complexes $[Ru(NCMe)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ and $[Ru(NCCH_2CN)(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$, obtained directly from $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ and the nitrile in the presence of $[NH_4][PF_6]$; [16] the $NCCH_2CN$ complex is readily deprotonated by strong bases, such as $K[OBu^t]$, to give the

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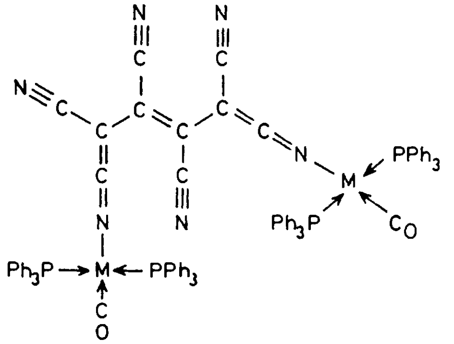
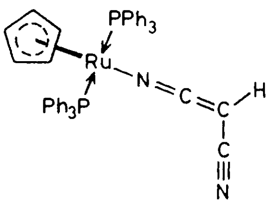
‡ For Part 14 see ref. 20.

§ 1—5-η-Cyclopentadienyl(2,3,4,4-tetracyanobutadienylideneamido)(trimethyl phosphite)(triphenylphosphine)ruthenium.



(1a) M = Rh

(1b) M = Ir



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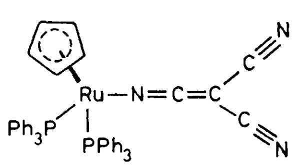

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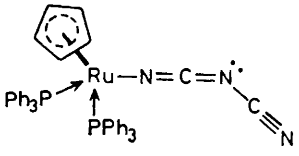

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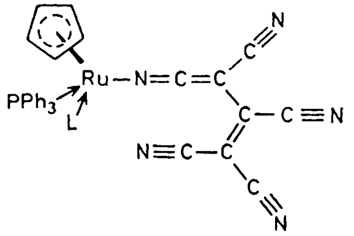
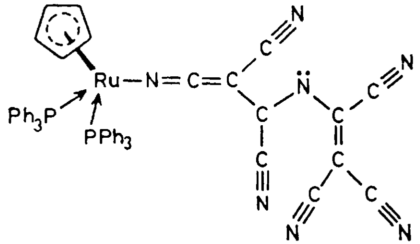


(5a) L = PPh_3

(5b) L = $P(OMe)_3$



(6)

neutral dicyanomethanide complex (2) as orange crystals. This complex has now also been obtained directly from $Na[CH(CN)_2]$ and $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ and yellow crystals of the analogous tricyanomethanide (3) and dicyanamide (4) complexes were similarly prepared from $K[C(CN)_3]$ or $Na[N(CN)_2]$; these complexes were characterised by elemental analysis and spectroscopic methods, although the cyanocarbon ligand was only detected by the characteristic ν(CN) bands around 2 200 cm^{-1} in the i.r. spectra.

Reactions between $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ and other cyanocarbon anions such as 1,1,2,3,3-pentacyanopropenide and 1,1,2,4,5,5-hexacyano-3-azapentadienide have been shown to yield the intensely red $[Ru\{C_3(CN)_5\}(PPh_3)_2(\eta\text{-}C_5H_5)]$ (5a) and deep purple $[Ru\{NC_4(CN)_6\}(PPh_3)_2(\eta\text{-}C_5H_5)]$ (6) complexes. The identities of these complexes have again been deduced from the manner of synthesis, elemental analyses, and the presence of ν(CN) bands in the i.r. spectra; we were unable to identify any ^{13}C n.m.r. resonances which might be assigned to the cyanocarbon ligands, in spite of long accumulation times, delayed pulse techniques, or the addition of a variety of paramagnetic relaxation reagents. Some C-bonded complexes have resonances in the region 100—120 p.p.m.[17]

Many organometallic complexes containing cyanocarbon ligands have been shown to contain the ligand attached *via* the nitrogen of a cyano-group, the ligand thus assuming the keteniminato resonance form. Structurally characterised examples include $[Ir\{N{=}C{=}C(CN)\text{-}CH(CN)_2\}(tcne)(CO)(PPh_3)]$ [18] (tcne = tetracyanoethylene) and the hexacyanobutenedi-iderhodium complex mentioned above, while in several cases it has been possible to deduce the presence of the N-bonded form of the ligand by characteristic ν(C=N) bands, which appear at *ca.* 2 050—2 150 cm^{-1} rather than at the higher frequency of *ca.* 2 250 cm^{-1} usually associated with the CN group. Similar structures have also been found for complexes obtained from insertion reactions of tetracyanoethylene with metal–carbon bonds, although the products from carbonylmetal anions and chlorocyanoethylenes contain C-bonded cyanocarbon ligands. In the spectra of complexes (2)—(6), ν(CN) bands occur in the range 2 137—2 266 cm^{-1}; no well defined separation of bands which could be due to cyano-groups and keteniminato-fragments has been found, although in the best spectra some fine structure was observed in the ν(CN) bands. Since no examples of metal complexes of the $C_3(CN)_5$ ligand have been described, we decided to determine the structure of the pentacyanopropenide complex to clarify further the mode of attachment of the cyanocarbon ligand. In the event, no suitable crystals of (5a) were obtained, but simple exchange of one PPh_3 ligand for $P(OMe)_3$ in decalin afforded $[Ru\{C_3(CN)_5\}\{P(OMe)_3\}(PPh_3)(\eta\text{-}C_5H_5)]$ (5b), whose structure was readily determined by *X*-ray diffraction methods.

The structure of complex (5b) is shown in Figure 1 and important bond distances and angles are listed in Tables 2—4. The crystal structure consists of monomeric molecules, of which one forms the asymmetric unit. The structure determination confirms that the pentacyanopropenide group is N-bonded to ruthenium, as the cyano(tricyanovinyl)keteniminato-ligand. Other ligands attached to ruthenium are the η^5-cyclopentadienyl ring, with Ru–C distances 2.160(12)—2.236(6) Å, the triphenylphosphine ligand [Ru–P 2.322(2) Å], and the trimethyl phosphite ligand [Ru–P 2.239(2) Å]. The angles of ruthenium accord with the more or less distorted octahedral co-ordination found for other complexes containing the $Ru(PR_3)_2(\eta\text{-}C_5H_5)$ moiety [*e.g.* P–Ru–P 91.2(1), Ph_3P–Ru–N(11) 90.1(1), $(MeO)_3P$–Ru–N(11) 90.1(1)°], with the $\eta\text{-}C_5H_5$ group formally occupying three co-ordination positions.

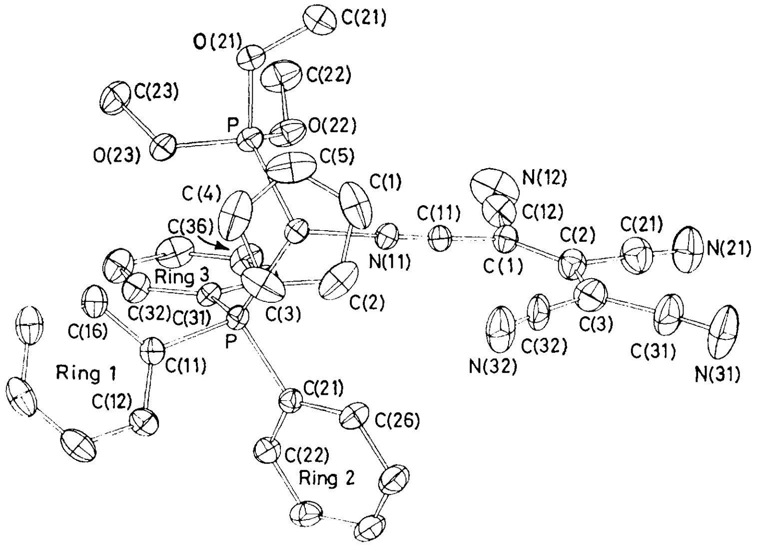


FIGURE 1 Projection of the molecule down the axis of the cyclopentadienide ring through the ruthenium, showing the atom labelling and non-hydrogen atoms as 20% thermal ellipsoids

In the triphenylphosphine ligand, the Ru–P distance is similar to that found in $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ [2.335(1) Å].[19] The ligand geometry is also similar to that found in other metal–PPh_3 complexes, with distorted tetrahedral geometry at phosphorus [*e.g.* C(11)–P–Ru 112.4(2), C(21)–P–Ru 115.1(2), C(31)–P–Ru 119.9(1)°], and the slightly opened intra-ring angle at the phenyl carbon which is attached to phosphorus. In the trimethyl phosphite ligand the Ru–P distance is close to that found in $[\overline{Ru\{NHC(CF_3)=NC(CF_3)N}H\}\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ [2.219(2) Å] with other bond parameters also similar.[20]

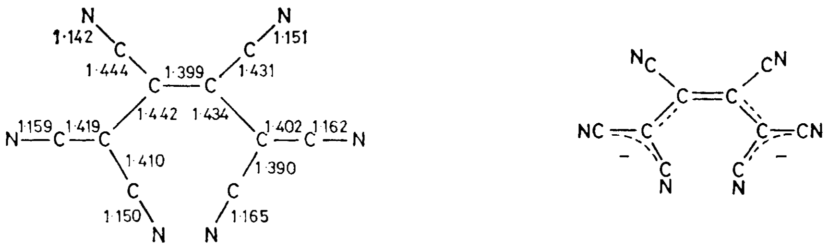
In the cyclopentadienyl ligand, although the C_5 ring is a regular pentagon within experimental error, there is some evidence for differing *trans* influences of the various ligands present as shown by the Ru–C distances [*e.g.* Ru–C(1,2) 2.220(8), 2.236(6) Å, approximately *trans* to P; Ru–C(4) 2.160(12) Å, approximately *trans* to N]. This is the trend expected if the cyanocarbon ligand is a better π-donor than the phosphorus ligands and this phenomenon is also present in the compound $[\overline{Ru\{NHC(CF_3)=NC(CF_3)N}H\}\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$.[20]

In the $C_3(CN)_5$ ligand of (5b), the Ru–N distance [2.033(6) Å] is close to that found in complex (8), and the bond distances in the ketenimine fragment [C–N 1.142(9), C–C 1.423(10) Å] confirm the multiple order of these bonds. The unco-ordinated C–N bond lengths are in the range 1.106(11)—1.152(14) Å, with bond angles at the cyano-carbon atom of 169.3(11)—179.1(8)°, both parameters indicating that these are normal cyano-groups. These are attached to the carbon skeleton with C–CN distances which are scattered between 1.385(12) and 1.511(13) Å. The C(1)–C(2)–C(3) system shows evidence for considerable multiple bonding between the three carbons, with C–C separations of 1.331(10) and 1.366(9) Å. For a least-squares plane, calculated through the ligand atoms, σ is 0.10 Å with individual atom deviations being respectively C(1) 0.01, C(11) 0.10, N(11), 0.19, C(12) −0.05, N(12), −0.11, C(2) 0.00, C(21) 0.00, N(21) 0.01, C(3) 0.00, C(31) 0.05, N(31) 0.10, C(32) −0.10, N(32) −0.20 Å, *i.e.* the notably deviant atoms are N(11) and N(32). The ruthenium deviation is 0.43 Å.

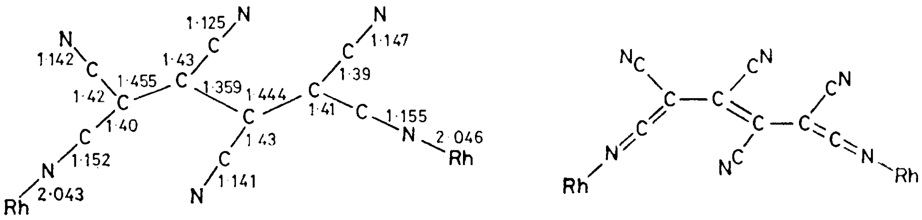
Although the pentacyanopropenide anion has previously been structurally characterised in $[Fe(CO)_2(PPh_3)(\eta\text{-}C_5H_5)][C_3(CN)_5]$,[21] disorder problems prevented a precise measurement of its bond parameters. Accordingly, the geometry of potassium *cis*-hexacyanobutenenedi-ide,[22] K_2[hcbd], is given in Figure 2 for comparison with that of the present structure.

In the hcbd dianion, as in complex (1), the 'single' bonds are shorter than those normally found in conjugated systems. The central C=C double-bond length in (1) is similar to that found in tetracyanoethylene [cubic, 1.344(3);[23] monoclinic, 1.339(9) Å[24]]; that in the hcbd dianion is considerably longer, at 1.399(9) Å, and is in accord with the extensive delocalisation predicted by extended Hückel calculations. In (5b), the bond distances within the carbon skeleton suggest a considerable degree of delocalisation over the three carbons, and the slight opening of this system [C(1)–C(2)–C(3) 131.2(8)°] supports this tendency to formation of an allenic group.

The results of this structure determination suggest that *cis*-Hexacyanobutenedi-ide (ref. 22)



trans-Hexacyanobutenedi-ide (ref. 11)



Pentacyanopropenide (this work)

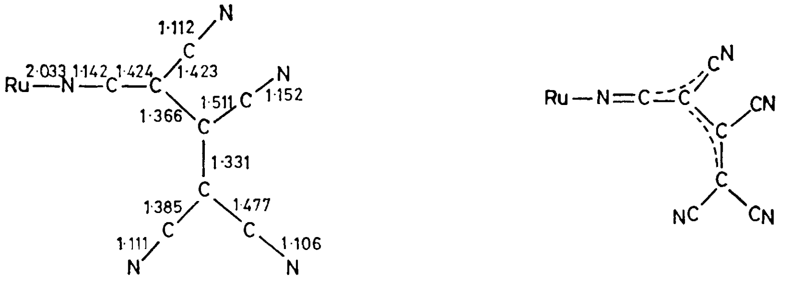


FIGURE 2 Comparative geometry of the co-ordinated pentacyanopropenide ligand with some related species

the degree of conjugation in the cyanocarbon ligand is intermediate between the fully delocalised allylic system, and the formal $(NC)_2C=C(CN)\bar{C}(CN)_2$ arrangement. Comparison of the three structures discussed above suggests that delocalisation of charge occurs largely over the dicyanomethylene and carbon skeleton; attachment of a metal atom to one of the terminal cyano-nitrogens results in little modification of the system, with the exception of a slight lengthening of the C=C double bond which is conjugated with the M–N=C=C group.

EXPERIMENTAL

General experimental conditions were similar to those described in previous papers in this series. Cyanocarbon derivatives $[NMe_4][C_3(CN)_5]$ and $[NEt_4][N\{C(CN)=C(CN)_2\}_2]$ were prepared as described in the literature;[15] sodium dicyanamide was purchased from the Aldrich Chemical Company.

Reactions of $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$.—(*a*) *With sodium dicyanomethanide*. A mixture of $Na[CH(CN)_2]$ [prepared *in situ* from malononitrile (33 mg, 0.5 mmol) and sodium (12 mg, 0.5 mmol) in ethanol (40 cm^3) at 0 °C] and $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ (363 mg, 0.5 mmol) was stirred at room temperature (15 h). Removal of solvent and recrystallisation of the residue from dichloromethane–diethyl ether gave orange *crystals* of $[Ru\{N=C=CH(CN)\}(PPh_3)_2(\eta\text{-}C_5H_5)]$ (2) (260 mg, 69%), m.p. >110 °C (decomp.) (Found: C, 69.4; H, 4.9; N, 3.9. $C_{44}H_{36}N_2P_2Ru$ requires C, 69.9; H, 4.8; N, 3.7%). I.r. spectrum (Nujol): ν(CN) 2 231vw, 2 161(sh), 2 137s cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ (p.p.m.) 4.24 (s, 5 H, C_5H_5), 7.24 (m, 30 H, PPh_3).

(*b*) *With potassium tricyanomethanide*. A mixture of $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ (726 mg, 1.0 mmol) and $K[C(CN)_3]$ (130 mg, 1.0 mmol) was heated in refluxing methanol (40 cm^3) for 3 h. On cooling, fine yellow crystals deposited. Recrystallisation (dichloromethane–diethyl ether) afforded yellow *crystals* of the dichloromethane solvate of [Ru-

TABLE 1

Atomic fractional cell co-ordinates

Atom	*x*	*y*	*z*
Ru	0.190 51(3)	0.115 51(2)	0.211 97(2)
(*a*) Cyclopentadienide ligand			
C(0)	0.155 1(−)	0.050 2(−)	0.254 3(−)
C(1)	0.218 9(4)	0.027 0(3)	0.283 2(5)
H(1)	0.272(−)	0.011(−)	0.310(−)
C(2)	0.155 0(5)	0.013 3(3)	0.208 3(4)
H(2)	0.156(−)	−0.017(−)	0.172(−)
C(3)	0.092 3(4)	0.051 4(4)	0.199 1(4)
H(3)	0.039(−)	0.050(1)	0.152(−)
C(4)	0.117 0(5)	0.087 4(3)	0.264 9(5)
H(4)	0.077(−)	0.119(−)	0.266(−)
C(5)	0.193 2(5)	0.071 6(4)	0.316 5(4)
H(5)	0.217(−)	0.095(−)	0.366(−)
(*b*) Pentacyanopropenyl ligand			
C(1)	0.401 2(3)	0.098 1(2)	0.156 5(3)
C(11)	0.334 3(3)	0.104 4(2)	0.171 2(3)
N(11)	0.281 8(2)	0.110 3(2)	0.184 4(2)
C(12)	0.439 5(4)	0.155 9(3)	0.154 1(4)
N(12)	0.470 0(4)	0.200 6(3)	0.151 8(4)
C(2)	0.428 6(4)	0.040 7(3)	0.145 4(3)
C(21)	0.503 8(5)	0.043 7(4)	0.136 3(5)
N(21)	0.561 1(4)	0.043 3(3)	0.129 2(5)
C(3)	0.401 1(4)	−0.018 3(3)	0.142 3(4)
C(31)	0.444 8(5)	−0.073 5(3)	0.133 6(5)
N(31)	0.469 0(5)	−0.120 2(3)	0.128 2(6)
C(32)	0.329 8(4)	−0.030 3(3)	0.144 1(4)
N(32)	0.272 6(4)	−0.044 7(2)	0.143 2(5)
(*c*) Trimethyl phosphite ligand			
P	0.237 92(9)	0.209 41(7)	0.271 41(8)
O(1)	0.282 7(2)	0.213 1(2)	0.365 2(2)
C(1)	0.359 4(4)	0.182 4(4)	0.410 9(4)
H(1A)	0.354(−)	0.138(−)	0.401(−)
H(1B)	0.397(−)	0.200(−)	0.396(−)
H(1C)	0.378(−)	0.190(−)	0.466(−)
O(2)	0.298 5(3)	0.241 6(2)	0.247 9(2)
C(2)	0.350 0(5)	0.295 6(9)	0.281 7(4)
H(2A)	0.319(−)	0.332(−)	0.277(−)
H(2B)	0.385(−)	0.286(−)	0.335(−)
H(2C)	0.381(−)	0.303(−)	0.255(−)
O(3)	0.167 0(2)	0.257 8(2)	0.254 5(2)
C(3)	0.175 6(4)	0.321 9(3)	0.283 7(4)
H(3A)	0.201(−)	0.322(−)	0.339(−)
H(3B)	0.207(−)	0.345(−)	0.266(−)
H(3C)	0.123(−)	0.341(−)	0.264(−)
(*d*) Triphenylphosphine ligand			
P	0.109 51(8)	0.165 92(6)	0.092 91(8)
(*e*) Phenyl ring 1			
C(11)	0.004 3(3)	0.172 3(2)	0.072 1(3)
C(12)	−0.058 0(3)	0.142 2(3)	0.009 5(3)
H(12)	−0.047(−)	0.117(−)	−0.026(−)
C(13)	−0.137 3(4)	0.147 5(3)	−0.003 6(4)
H(13)	−0.181(−)	0.125(−)	−0.047(−)
C(14)	−0.153 7(4)	0.183 1(3)	0.046 3(4)
H(14)	−0.209(−)	0.187(−)	0.037(−)
C(15)	−0.092 2(4)	0.212 3(3)	0.110 2(4)
H(15)	−0.104(−)	0.238(−)	0.146(−)
C(16)	−0.012 9(3)	0.207 0(3)	0.124 3(3)
H(16)	0.031(−)	0.227(−)	0.170 1(−)
(*f*) Phenyl ring 2			
C(21)	0.101 7(3)	0.125 1(2)	0.005 9(3)
C(22)	0.067 0(3)	0.155 2(3)	−0.066 4(3)
H(22)	0.047(−)	0.200(−)	−0.071(−)
C(23)	0.059 6(4)	0.124 4(3)	−0.132 5(3)
H(23)	0.035(−)	0.147(−)	−0.183(−)
C(24)	0.087 9(4)	0.062 7(3)	−0.126 8(4)
H(24)	0.082(−)	0.041(−)	−0.173(−)
C(25)	0.122 1(4)	0.032 1(3)	−0.056 2(4)
H(25)	0.142(−)	−0.012(−)	−0.053(−)
C(26)	0.129 0(4)	0.063 5(3)	0.010 1(3)
H(26)	0.153(−)	0.042(−)	0.061(−)
(*g*) Phenyl ring 3			
C(31)	0.134 5(3)	0.247 0(2)	0.075 5(3)
C(32)	0.088 7(4)	0.300 1(3)	0.069 0(3)
H(32)	0.039(−)	0.294(−)	0.072(−)
C(33)	0.113 4(4)	0.360 6(3)	0.060 2(4)
H(33)	0.079(−)	0.398(−)	0.055(−)
C(34)	0.184 6(4)	0.367 6(3)	0.056 7(4)
H(34)	0.201(−)	0.410(−)	0.050(−)
C(35)	0.229 7(4)	0.315 4(3)	0.062 0(4)
H(35)	0.279(−)	0.322(−)	0.059(−)
C(36)	0.205 5(3)	0.254 9(3)	0.071 6(3)
H(36)	0.238(−)	0.218(−)	0.075(−)

$\{N{=}C{=}C(CN)_2\}(PPh_3)_2(\eta\text{-}C_5H_5)]$ (3) (680 mg, 79%), m.p. 207—210 °C (Found: C, 64.1; H, 4.4; N, 5.1; P, 7.3. $C_{45}H_{35}N_3P_2Ru{\cdot}CH_2Cl_2$ requires C, 63.8; H, 4.3; N, 4.9; P, 7.2%). I.r. spectrum (Nujol): ν(CN) 2 175vs cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ (p.p.m.) 4.29 (s, 5 H, C_5H_5), 5.30 (s, CH_2Cl_2), 7.21, 7.30 (m, 30 H, PPh_3). ^{13}C N.m.r. ($CDCl_3$): δ (p.p.m.) 82.8 (s, C_5H_5), 128.5—136.4 (m, PPh_3).

(*c*) *With sodium dicyanamide.* A similar reaction to (*b*) used $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ (726 mg, 1.0 mmol) and $Na[N(CN)_2]$ (89 mg, 1.0 mmol) in refluxing 1,2-dimethoxyethane (60 cm^3) for 14 h. The turbid yellow-brown solution was filtered and evaporated and the residue was chromatographed on alumina, a yellow band being eluted with dichloromethane. Crystallisation (dichloromethane–methanol) gave yellow *crystals* of $[Ru\{N{=}C{=}N(CN)\}(PPh_3)_2(\eta\text{-}C_5H_5)]$ (4) (150 mg, 20%), m.p. >160 °C (decomp.) (Found: C, 67.4; H, 4.7; N, 5.3. $C_{43}H_{35}N_3P_2Ru$ requires C, 68.3; H, 4.7; N, 5.6%). I.r. spectrum (Nujol): ν(CN) 2 266m, 2 228m, 2 161s cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ (p.p.m.) 4.20 (s, 5 H, C_5H_5), 7.23 (m, 30 H, PPh_3). ^{13}C N.m.r. ($CDCl_3$): δ (p.p.m.) 82.0 (s, C_5H_5), 128.2—137.0 (m, PPh_3).

(*d*) *With tetramethylammonium* 1,1,2,3,3-*pentacyanopropenide.* (*i*) A mixture of $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ (500 mg, 0.69 mmol) and $[NMe_4][C_3(CN)_5]$ (166 mg, 0.69 mmol) was heated in refluxing methanol (40 cm^3) for 30 min. A red *precipitate* formed, which was collected, washed with methanol, and dried to give pure $[Ru\{C_3(CN)_5\}(PPh_3)_2(\eta\text{-}C_5H_5)]$ (5a) (510 mg, 86%), m.p. >225 °C (decomp.) (Found: C, 67.8; H, 4.1; N, 7.9. $C_{49}H_{35}N_5P_2Ru$ requires C, 68.7; H, 4.1; N, 8.2%). I.r. spectrum (Nujol): ν(CN) 2 199s; ν(C=N) 1 500s cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ (p.p.m.) 4.44 (s, *ca.* 2 H, ?), 4.52 (s, 5 H, C_5H_5), 7.07—7.34 (m, 30 H, PPh_3). ^{13}C N.m.r. ($CDCl_3$): δ (p.p.m.) 83.7 (s, C_5H_5), 128.7—135.7 (m, PPh_3).

(*ii*) Complex (5a) (216 mg, 0.25 mmol) was heated with $P(OMe)_3$ (120 mg, 0.97 mmol) in refluxing decalin (40 cm^3) for 15 min. The cooled solution was then chromatographed directly on alumina, the decalin and excess $P(OMe)_3$ being washed out with light petroleum (b.p. 40—60 °C). A yellow band was then eluted with diethyl ether. Crystallisation (diethyl ether–light petroleum) then afforded red *crystals* of $[Ru\{C_3(CN)_5\}\{P(OMe)_3\}(PPh_3)(\eta\text{-}C_5H_5)]$ (5b) (105 mg, 72%), m.p. 170—174 °C (Found: C, 56.8; H, 4.0; N, 9.6%; *M* (mass spectrometry) 719. $C_{34}H_{29}N_5P_2O_3Ru$ requires C, 56.8; H, 4.1; N, 9.8%; *M* 719). I.r. spectrum (Nujol): ν(CN) 2 204m, 2 193m; ν(C=N) 1 502w; ν(PO) 1 046m, 1 011m cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ (p.p.m.) 3.53 [d, 9 H, $P(OMe)_3$, *J*(HP) 11.5], 4.71 [d, *ca.* 1 H, ? *J*(HP) 0.7], 4.77 [d, 5 H, C_5H_5, *J*(HP) 0.7 Hz], 7.45, 7.55 (m, 15 H, PPh_3). ^{13}C N.m.r.

TABLE 2

Ruthenium atom environment *

	r_{Ru-L}	P(c)	N(11)	C(1)	C(2)	C(3)	C(4)	C(5)	C(0)
P(d)	2.322(2)	91.19(6)	90.1(1)	147.8(2)	111.1(2)	92.7(2)	109.1(2)	144.8(2)	124.3(–)
P(c)	2.239(2)		90.1(1)	119.9(2)	154.0(2)	134.6(2)	100.7(2)	93.9(2)	123.8(–)
N(11)	2.033(6)			97.7(3)	102.6(3)	135.1(2)	157.5(2)	124.6(3)	126.7(–)

* r_{Ru-L} is the ruthenium–ligand distance (Å). The other entries in the matrix are the angles (°) subtended at the ruthenium by the atoms at the head of the respective rows and columns; C(0) is the ' dummy ' atom at the centre of the cyclopentadienide ring.

($CDCl_3$): δ (p.p.m.) 52.7 [d, 9 H, P(O*Me*)$_3$, *J*(CP) 8 Hz], 83.2 (s, C_5H_5), 128.6—135.3 (m, PPh_3).

(*e*) *With tetraethylammonium* 1,1,2,4,5,5-*hexacyano*-3-*aza-penta*-1,4-*dienide*. A mixture of $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ (340 mg, 0.47 mmol) and $[NEt_4][N\{C(CN)=C(CN)_2\}_2]$ (163 mg, 0.47 mmol) was heated in refluxing methanol (40 cm^3) for 1 h. Removal of the solvent and recrystallisation of the residue from dichloromethane–diethyl ether gave a deep purple *precipitate* of $[Ru\{NC_4(CN)_6\}(PPh_3)_2(\eta\text{-}C_5H_5)]$ (6) (315 mg, 74%), m.p. >95 °C. Satisfactory analyses were not obtained. I.r. spectrum (Nujol): ν(CN) 2 215s, 2 199(sh); ν(C=N) 1 500s cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ (p.p.m.) 4.49 (s, *ca.* 2 H, ?), 4.45 (s, 5 H, C_5H_5), 7.07—7.35 (m, 30 H, PPh_3). ^{13}C N.m.r. ($CDCl_3$): δ (p.p.m.) 84.4 (s, C_5H_5), 128.8—135.4 (m, PPh_3).

Crystallography.—Crystal data. $C_{34}H_{29}N_5O_3P_2Ru$, M = 718.7, Monoclinic, a = 18.845(8), b = 20.967(6), c = 19.336(7) Å, β = 118.54(3)°, U = 6 712(4) Å^3, $F(000)$ = 2 928, D_m = 1.42(1), Z = 8, D_c = 1.42 g cm^{-3}, space group $C2/c$ (C^6_{2h}, no. 15). Monochromatic Mo-K_α radiation, λ = 0.7106$_9$ Å, μ = 5.7 cm^{-1}, specimen size 0.20 × 0.19 × 0.28 mm, T = 295(1) K.

Structure determination. A unique data set was measured within the limit $2\theta_{max.}$ = 50° using a Syntex $P2_1$ four-circle diffractometer in conventional θ—2θ scan mode, yielding 5 947 independent reflections, 3 646 with $I > 3\sigma(I)$ being considered ' observed ' and used in the structure solution (heavy-atom method) and refinement after absorption correction. Block diagonal (9 × 9) least-squares methods were used, anisotropic thermal parameters being employed for the non-hydrogen atoms. Aromatic hydrogen atoms were included at calculated trigonal positions as invariants with U_H set at 1.25 $\langle U_{ii}$(parent atom)$\rangle$; those of the methyl groups were idealised after location in difference maps and treated similarly with U set at 1.5$\langle \bar{U}_{ii}$(parent carbon)$\rangle$. Final residuals (R,R',S) were 0.042, 0.050, 1.3 respectively, reflection weights being $[\sigma^2(F_o) + 0.000\ 5(F_o)^2]^{-1}$. Neutral-atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f',f'').[25-27] Computation was carried out using the X-RAY '76 program system,[28] implemented by S. R. Hall on a Perkin-Elmer 8/32 computer. Structure-factor amplitudes, thermal parameters, hydrogen-atom geometries, and least squares planes are listed in Supplementary Publication No. SUP 23190 (28 pp.).*

TABLE 3

Triphenylphosphine ligand non-hydrogen geometry

	Ring 1	Ring 2	Ring 3
Distances (Å)			
P–C(1)	1.831(6)	1.831(6)	1.838(5)
Angles (°)			
Ru–P–C(1)	112.4(2)	115.1(2)	119.9(1)
P–C(1)–C(2)	122.8(5)	120.5(4)	124.1(5)
P–C(1)–C(6)	118.6(3)	121.3(4)	117.4(4)

Other angles: C(11)–P–C(21) 103.2(2), C(21)–P–C(31) 100.4(3), C(31)–P–C(11) 103.8(2).

TABLE 4

Other ligand non-hydrogen atom geometry

Distances (Å)

(*a*) Cyclopentadienide ligand

C(1)–C(2)	1.401(9)	C(4)–C(5)	1.342(11)
C(2)–C(3)	1.366(12)	C(5)–C(1)	1.348(13)
C(3)–C(4)	1.356(12)		

(*b*) Pentacyanopropenyl ligand

C(1)–C(2)	1.366(9)	C(2)–C(21)	1.511(13)
C(1)–C(11)	1.424(10)	C(21)–N(21)	1.152(14)
C(1)–C(12)	1.423(9)	C(3)–C(31)	1.477(12)
C(11)–N(11)	1.142(9)	C(3)–C(32)	1.385(12)
C(12)–N(12)	1.112(10)	C(31)–N(31)	1.106(11)
C(2)–C(3)	1.331(10)	C(32)–N(32)	1.111(11)

(*c*) Trimethyl phosphite ligand

P–O(1)	1.595(4)	O(1)–C(1)	1.437(8)
P–O(2)	1.570(6)	O(2)–C(2)	1.429(8)
P–O(3)	1.583(4)	O(3)–C(3)	1.435(7)

Angles (°)

(*a*) Cyclopentadienide ligand

C(5)–C(1)–C(2)	107.9(7)	C(3)–C(4)–C(5)	109.0(8)
C(1)–C(2)–C(3)	106.1(7)	C(4)–C(5)–C(1)	108.5(7)
C(2)–C(3)–C(4)	108.4(6)		

(*b*) Pentacyanopropenyl ligand

Ru–N(11)–C(11)	176.3(4)	C(3)–C(2)–C(21)	113.5(7)
N(11)–C(11)–C(1)	178.5(5)	C(2)–C(21)–N(21)	177.2(9)
C(11)–C(1)–C(2)	123.3(6)	C(2)–C(3)–C(31)	120.6(8)
C(11)–C(1)–C(12)	116.1(5)	C(2)–C(3)–C(32)	121.9(7)
C(2)–C(1)–C(12)	120.6(7)	C(31)–C(3)–C(32)	117.5(7)
C(1)–C(12)–N(12)	179.1(8)	C(3)–C(31)–N(31)	169.3(11)
C(1)–C(2)–C(3)	131.2(8)	C(3)–C(32)–N(32)	174.3(8)
C(1)–C(2)–C(21)	115.3(6)		

(*c*) Trimethyl phosphite ligand

Ru–P–O(1)	119.4(2)	O(2)–P–O(3)	108.9(2)
Ru–P–O(2)	113.4(2)	P–O(1)–C(1)	120.5(5)
Ru–P–O(3)	111.5(1)	P–O(2)–C(2)	129.6(6)
O(1)–P–O(2)	104.2(3)	P–O(3)–C(3)	126.4(4)
O(1)–P–O(3)	98.0(2)		

Non-hydrogen atom numbering is given in Figure 1. Hydrogen atoms are labelled according to the parent carbon, suffixed A, B, C where necessary for distinguishing purposes (as is the case of the methyl groups).

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

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