# Synthesis and Characterisation of $[N(PPh_3)_2][RuRh_5(CO)_{16}]$† by *X*-Ray Crystallography and by Natural-abundance Carbon-13 Nuclear Magnetic Resonance Spectroscopy

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The synthesis, *X*-ray crystal structure, and spectroscopic studies of a new ruthenium–rhodium mixed-metal cluster $[N(PPh_3)_2][RuRh_5(CO)_{16}]$ are reported. The complex crystallises in the space group *C*2/*c* with $a = 33.62(1)$, $b = 9.729(2)$, $c = 33.72(1)$ Å, $\beta = 94.43(2)$°, and $Z = 8$. The crystal structure is isomorphous with $[N(PPh_3)_2][FeRh_5(CO)_{16}]$. No fluxionality was observed at room temperature by natural-abundance $^{13}C$ n.m.r. spectroscopy, which established the $[Rh_6(CO)_{16}]$-like structure also in solution.

The bimetallic carbonyl clusters of iron with cobalt and rhodium and of ruthenium with cobalt have been studied intensively,[1,2] whereas the analogous compounds between the heavier elements of the iron and cobalt groups are not so well known. Of the anionic clusters there are reports of the pentanuclear coumpunds $[RuRh_4(CO)_{15}]^{2-}$ and $[RuIr_4(CO)_{15}]^{2-}$, but no hexanuclear species have been reported.[3,4] Neutral ruthenium–rhodium clusters of lower nuclearity are also known.[5–9] In this work the synthesis, crystal structure, and spectroscopic studies of $[RuRh_5(CO)_{16}]^-$ are reported.

## Results and Discussion

*Synthesis.*—$[RuRh_5(CO)_{16}]^-$ (**1**) can be easily synthesized by the reaction of $[Rh(CO)_4]^-$ [10] with $[\{Ru(CO)_3Cl_2\}_2]$ in tetrahydrofuran (thf) solution. The reaction first yields a green solution, the components of which we have not yet characterised. Complex (**1**) is then obtained by treatment with phosphoric acid. The behaviour of (**1**) is quite similar to the iron analogue, $[FeRh_5(CO)_{16}]^-$ (**2**), which is found to be relatively stable towards aerial oxidation and protonation.[2]

*X-Ray Crystallography.*—The molecular structure of (**1**) is shown in Figure 1. It is very similar to the structures of isoelectronic clusters $[Rh_6(CO)_{16}]$ [11] and (**2**).[2] The octahedral metal core is symmetric and we were not able to find any evidence of the ruthenium position from the *X*-ray data. As in the crystal structure of $[N(PPh_3)_2][FeRh_5(CO)_{16}]$, where all the metal positions have variable mixed Fe/Rh occupancies, it is plausible that disorder of the metals exists also in the crystal structure of (**1**). The average metal–metal distance (2.769 Å) is longer than the metal–metal bond lengths in (**2**) (av. 2.750 Å) and in $[Fe_2Rh_4(CO)_{16}]^{2-}$ (av. 2.727 Å),[2] but nearly the same as in $[Rh_6(CO)_{16}]$ (av. 2.78 Å). This is reasonable in view of the smaller covalent radius of iron than those of ruthenium and rhodium. The average terminal $M–C_t$ (1.881 Å) and bridging $M–C_{br}$ (2.21 Å) distances are slightly longer than in (**2**) (1.860 and 2.174 Å, respectively), whereas the $C–O_t$ (av. 1.123 Å) and $C–O_{br}$ (av. 1.154 Å) bonds are shorter than in the iron compound (**2**) (1.132 and 1.168 Å). This indicates somewhat weaker metal-to-carbon back-bonding in (**1**).

**Table 1.** $^{13}C-\{^1H\}$ N.m.r. spectrum of $[N(PPh_3)_2][RuRh_5(CO)_{16}]$ in $CDCl_3$ (25 °C)

| | δ/p.p.m. | $^1J(RhC)$/Hz |
|---|---|---|
| $C_a$ | 194.80 | |
| $C_b$* | 186.33 | 68 |
| $C_c$* | 184.68 | 71 |
| $C_d$ | 183.82 | 70 |
| $C_e$ | 255.58 | 14.5 |
| $C_f$ | 237.83 | 30 ($Rh_A–C_f$),<br>25 ($Rh_B–C_f$) |

* May be interchanged.

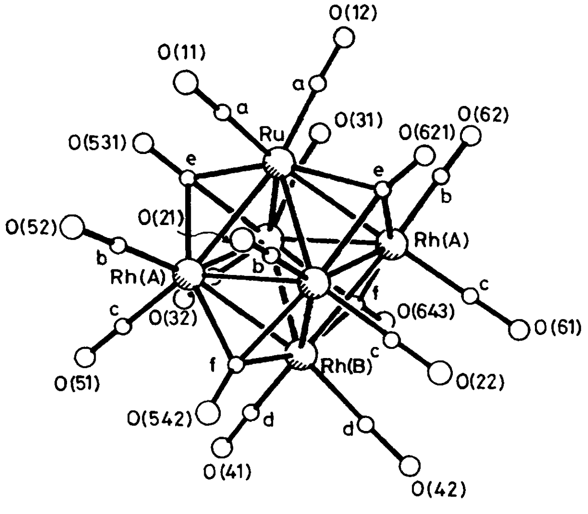

**Figure 1.** The structure and labelling scheme for the $[RuRh_5(CO)_{16}]^-$ anion. The carbonyl lettering (a—f) and metal assignments refer to the $^{13}C$ n.m.r. spectra. The numbering of the carbonyl oxygen refers to the crystal structure; the metal atoms (M) are designated by the first number of their terminal carbonyls

*N.M.R. Spectroscopy.*—The $^{13}C$ n.m.r. spectrum of (**1**) is presented in Figure 2 and in Table 1. Four types of terminal carbonyls (a—d) and two types of face-bridging carbonyls (e and f) are observed in accord with the crystal structure; $^{13}CO$ enrichment was not needed to obtain the spectrum using 9 904 pulses. No fluxionality was observed at room temperature: even the exchange of carbonyls b and c is hindered on the n.m.r. time-scale. Corresponding observations have previously been made for $[Rh_6(CO)_{16}]$ at 70 °C.[12] The coupling of $C_f$ (30 Hz) and $C_e$ (14.5 Hz) to $Rh_A$ is different, which is

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† Bis(triphenylphosphine)iminium 1,2,3; 1,4,5; 2,5,6; 3,4,6-tetra-$\mu_3$-carbonyl-dodecacarbonyl-*octahedro*-pentarhodiumruthenate.

*Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

**Table 2.** Atomic co-ordinates (M = Rh or Ru)

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| M(1) | 0.384 2(1) | 0.193 0(1) | 0.140 2(1) | C(61) | 0.325 2(4) | 0.279 4(15) | 0.020 2(3) |
| M(2) | 0.311 8(1) | 0.317 7(1) | 0.121 6(1) | C(62) | 0.397 9(4) | 0.154 4(13) | 0.037 3(3) |
| M(3) | 0.423 0(1) | 0.414 9(1) | 0.109 0(1) | C(111) | 0.056 3(3) | 0.322 8(11) | 0.075 6(3) |
| M(4) | 0.349 7(1) | 0.539 3(1) | 0.089 8(1) | C(112) | 0.058 8(3) | 0.191 7(12) | 0.063 2(4) |
| M(5) | 0.370 5(1) | 0.457 8(1) | 0.167 4(1) | C(113) | 0.028 3(4) | 0.129 9(15) | 0.039 4(4) |
| M(6) | 0.363 8(1) | 0.276 2(1) | 0.063 1(1) | C(114) | −0.004 3(4) | 0.204 0(15) | 0.026 7(4) |
| P(1) | 0.096 2(1) | 0.400 9(3) | 0.106 2(1) | C(115) | −0.006 9(3) | 0.340 4(14) | 0.037 8(4) |
| P(2) | 0.143 9(1) | 0.195 1(3) | 0.152 3(1) | C(116) | 0.023 5(3) | 0.400 5(12) | 0.061 8(3) |
| O(531) | 0.451 5(2) | 0.321 6(8) | 0.196 9(2) | C(121) | 0.075 6(3) | 0.475 1(10) | 0.148 6(3) |
| O(542) | 0.289 3(3) | 0.608 6(8) | 0.153 0(2) | C(122) | 0.098 6(4) | 0.567 8(12) | 0.171 6(3) |
| O(621) | 0.318 5(2) | 0.017 2(8) | 0.090 4(3) | C(123) | 0.085 0(4) | 0.621 2(14) | 0.206 6(4) |
| O(643) | 0.407 1(3) | 0.511 4(9) | 0.020 9(3) | C(124) | 0.048 5(4) | 0.584 8(16) | 0.217 6(4) |
| O(11) | 0.360 5(3) | 0.028 3(10) | 0.210 4(3) | C(125) | 0.023 5(4) | 0.491 0(16) | 0.195 5(3) |
| O(12) | 0.449 3(2) | 0.001 1(9) | 0.121 6(3) | C(126) | 0.039 0(3) | 0.438 3(11) | 0.160 9(3) |
| O(21) | 0.271 5(3) | 0.172 3(11) | 0.187 5(3) | C(131) | 0.115 7(3) | 0.536 2(11) | 0.078 2(3) |
| O(22) | 0.235 5(2) | 0.364 7(11) | 0.071 1(3) | C(132) | 0.095 7(4) | 0.665 3(13) | 0.074 0(4) |
| O(31) | 0.494 4(3) | 0.268 5(11) | 0.081 6(3) | C(133) | 0.109 4(4) | 0.769 7(15) | 0.050 8(4) |
| O(32) | 0.471 2(3) | 0.671 9(8) | 0.129 1(3) | C(134) | 0.141 8(4) | 0.745 3(16) | 0.031 1(4) |
| O(41) | 0.385 1(3) | 0.820 4(10) | 0.091 7(4) | C(135) | 0.162 2(4) | 0.621 5(18) | 0.033 9(5) |
| O(42) | 0.281 7(3) | 0.626 3(10) | 0.031 8(3) | C(136) | 0.148 7(3) | 0.517 8(13) | 0.057 9(4) |
| O(51) | 0.402 6(3) | 0.732 4(10) | 0.194 4(3) | C(211) | 0.174 5(3) | 0.063 6(10) | 0.133 9(3) |
| O(52) | 0.344 3(3) | 0.372 8(11) | 0.244 6(3) | C(212) | 0.185 6(4) | −0.047 7(14) | 0.159 0(4) |
| O(61) | 0.300 6(3) | 0.295 9(14) | −0.005 2(3) | C(213) | 0.211 7(4) | −0.148 0(15) | 0.144 5(4) |
| O(62) | 0.418 6(3) | 0.086 4(11) | 0.021 6(3) | C(214) | 0.225 8(4) | −0.130 9(16) | 0.108 6(5) |
| N(1) | 0.130 8(2) | 0.293 8(9) | 0.116 0(2) | C(215) | 0.215 5(5) | −0.022 0(17) | 0.085 4(5) |
| C(531) | 0.425 5(3) | 0.338 6(11) | 0.172 9(3) | C(216) | 0.188 8(3) | 0.070 6(12) | 0.098 0(4) |
| C(542) | 0.314 1(3) | 0.536 9(12) | 0.142 5(3) | C(221) | 0.174 0(3) | 0.281 8(10) | 0.190 7(3) |
| C(621) | 0.333 9(3) | 0.122 1(12) | 0.096 9(4) | C(222) | 0.193 9(3) | 0.400 5(12) | 0.181 9(4) |
| C(643) | 0.395 1(3) | 0.468 0(12) | 0.049 1(4) | C(223) | 0.219 6(4) | 0.469 0(13) | 0.209 7(4) |
| C(11) | 0.369 0(3) | 0.090 3(12) | 0.184 7(4) | C(224) | 0.225 1(4) | 0.415 3(14) | 0.246 5(4) |
| C(12) | 0.424 5(3) | 0.071 0(12) | 0.129 4(4) | C(225) | 0.206 6(4) | 0.294 6(14) | 0.256 8(4) |
| C(21) | 0.285 9(3) | 0.228 6(13) | 0.163 5(4) | C(226) | 0.180 6(3) | 0.228 7(13) | 0.228 6(3) |
| C(22) | 0.264 5(3) | 0.344 4(12) | 0.090 2(4) | C(231) | 0.103 3(3) | 0.115 2(12) | 0.174 4(3) |
| C(31) | 0.467 4(3) | 0.322 1(12) | 0.092 0(4) | C(232) | 0.085 6(3) | 0.173 8(13) | 0.206 1(3) |
| C(32) | 0.453 7(3) | 0.572 7(12) | 0.121 0(3) | C(233) | 0.051 4(4) | 0.116 2(16) | 0.220 6(4) |
| C(41) | 0.370 6(4) | 0.712 6(13) | 0.091 8(4) | C(234) | 0.035 8(4) | −0.002 6(18) | 0.202 5(4) |
| C(42) | 0.308 0(3) | 0.589 8(12) | 0.053 2(3) | C(235) | 0.052 3(4) | −0.060 9(15) | 0.172 5(4) |
| C(51) | 0.390 9(4) | 0.628 6(12) | 0.184 7(3) | C(236) | 0.085 8(3) | 0.000 5(13) | 0.158 1(4) |
| C(52) | 0.353 3(3) | 0.407 8(10) | 0.219 2(3) | | | | |

**Table 3.** Bond lengths (Å) in the $[\mathrm{RuRh_5(CO)_{16}}]^-$ cluster

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| M(1)–M(2) | 2.747(1) | M(1)–M(3) | 2.772(1) | M(4)–C(41) | 1.826(13) | M(4)–C(42) | 1.859(10) |
| M(1)–M(5) | 2.785(1) | M(1)–M(6) | 2.759(1) | M(5)–C(531) | 2.179(11) | M(5)–C(542) | 2.154(11) |
| M(1)–C(531) | 2.218(10) | M(1)–C(621) | 2.254(11) | M(5)–C(51) | 1.874(12) | M(5)–C(52) | 1.945(11) |
| M(1)–C(11) | 1.903(13) | M(1)–C(12) | 1.859(11) | M(6)–C(621) | 2.176(12) | M(6)–C(643) | 2.211(12) |
| M(2)–M(4) | 2.762(1) | M(2)–M(5) | 2.769(1) | M(6)–C(61) | 1.868(11) | M(6)–C(62) | 1.905(12) |
| M(2)–M(6) | 2.765(1) | M(2)–C(621) | 2.228(12) | O(531)–C(531) | 1.155(12) | O(621)–C(621) | 1.157(14) |
| M(2)–C(542) | 2.245(11) | M(2)–C(21) | 1.922(14) | O(643)–C(643) | 1.142(16) | O(542)–C(542) | 1.163(14) |
| M(2)–C(22) | 1.861(10) | M(3)–M(4) | 2.778(1) | O(11)–C(11) | 1.111(16) | O(12)–C(12) | 1.135(14) |
| M(3)–M(5) | 2.775(1) | M(3)–M(6) | 2.775(1) | O(21)–C(21) | 1.120(17) | O(22)–C(22) | 1.141(13) |
| M(3)–C(531) | 2.273(10) | M(3)–C(643) | 2.221(12) | O(31)–C(31) | 1.127(15) | O(32)–C(32) | 1.152(14) |
| M(3)–C(31) | 1.871(12) | M(3)–C(32) | 1.876(11) | O(41)–C(41) | 1.155(16) | O(42)–C(42) | 1.152(14) |
| M(4)–M(5) | 2.771(1) | M(4)–M(6) | 2.767(1) | O(51)–C(51) | 1.122(15) | O(52)–C(52) | 0.990(15) |
| M(4)–C(643) | 2.243(12) | M(4)–C(542) | 2.217(11) | O(61)–C(61) | 1.155(15) | O(62)–C(62) | 1.121(16) |

apparently caused by stronger co-ordination of the carbonyl e to Ru than to Rh atoms. The former coupling is larger than the corresponding one in $[\mathrm{Rh_6(CO)_{16}}]$,[12] suggesting that the weak $\mathrm{Rh_A}$–$\mathrm{C_e}$ bonds are balanced by stronger $\mathrm{Rh_A}$–$\mathrm{C_f}$ bonds. The spectrum resembles closely that of (**2**).[2] The largest differences occur in the chemical shifts of the carbons that are co-ordinated to iron or ruthenium [$\mathrm{C_a}$, 211.0; $\mathrm{C_e}$, 256.8 p.p.m. in (**2**)]. Also the $^1J(\mathrm{Rh_AC_e})$, $^1J(\mathrm{Rh_AC_f})$, and $^1J(\mathrm{Rh_BC_f})$ coupling constants of (**2**) are smaller (12.2, 25.9, and 21.4 Hz, respectively).

## Experimental

The reaction was carried out under a nitrogen atmosphere and using deoxygenated solvents up to the recrystallisation step. Infrared spectra were recorded on a Perkin-Elmer 297 spectrophotometer using 0.5-mm NaCl solution cells. $[\mathrm{Rh(CO)_4}]^-$ salts were prepared according to a published procedure.[10] Ruthenium and rhodium analyses were carried out by atomic absorption spectroscopy using a Perkin-Elmer 2380 spectrophotometer. Crystals were grown by evaporation from a saturated hexane–$\mathrm{CH_2Cl_2}$ solution.

**Table 4.** Selected bond angles (°) in the $[RuRh_5(CO)_{16}]^-$ cluster

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| M(2)–M(1)–C(531) | 110.0(3) | M(3)–M(1)–C(531) | 52.8(3) | M(1)–M(5)–C(531) | 51.3(3) | M(2)–M(5)–C(531) | 110.4(3) |
| M(5)–M(1)–C(531) | 50.1(3) | M(6)–M(1)–C(531) | 112.4(3) | M(3)–M(5)–C(531) | 53.0(3) | M(4)–M(5)–C(531) | 112.6(3) |
| M(2)–M(1)–C(621) | 51.8(3) | M(3)–M(1)–C(621) | 110.1(3) | M(1)–M(5)–C(542) | 111.4.3) | M(2)–M(5)–C(542) | 52.5(3) |
| M(5)–M(1)–C(621) | 111.2(3) | M(6)–M(1)–C(621) | 50.2(3) | M(3)–M(5)–C(542) | 111.5(3) | M(4)–M(5)–C(542) | 51.7(3) |
| M(2)–M(1)–C(11) | 97.2(3) | M(5)–M(1)–C(11) | 99.5(4) | M(3)–M(5)–C(51) | 96.7(4) | M(4)–M(5)–C(51) | 95.8(3) |
| M(3)–M(1)–C(12) | 92.9(4) | M(6)–M(1)–C(12) | 97.7(4) | M(1)–M(5)–C(52) | 97.6(3) | M(2)–M(5)–C(52) | 97.4(3) |
| M(1)–M(2)–C(621) | 52.6(3) | M(4)–M(2)–C(621) | 110.2(3) | M(1)–M(6)–C(621) | 52.8(3) | M(2)–M(6)–C(621) | 52.0(3) |
| M(5)–M(2)–C(621) | 112.6(3) | M(6)–M(2)–C(621) | 50.3(3) | M(3)–M(6)–C(621) | 112.5(3) | M(4)–M(6)–C(621) | 111.6(3) |
| M(1)–M(2)–C(542) | 109.8(3) | M(4)–M(2)–C(542) | 51.3(3) | M(1)–M(6)–C(643) | 111.2(3) | M(2)–M(6)–C(643) | 111.5(3) |
| M(5)–M(2)–C(542) | 49.6(3) | M(6)–M(2)–C(542) | 110.8(3) | M(3)–M(6)–C(643) | 51.4(3) | M(4)–M(6)–C(643) | 52.1(3) |
| M(1)–M(2)–C(21) | 94.4(4) | M(5)–M(2)–C(21) | 99.0(4) | M(2)–M(6)–C(61) | 96.3(4) | M(4)–M(6)–C(61) | 96.3(4) |
| M(4)–M(2)–C(22) | 94.0(4) | M(6)–M(2)–C(22) | 100.1(4) | M(1)–M(6)–C(62) | 97.7(3) | M(3)–M(6)–C(62) | 97.3(3) |
| M(1)–M(3)–C(531) | 51.0(3) | M(4)–M(3)–C(531) | 109.3(3) | M(1)–C(531)–O(531) | 131.8(9) | M(3)–C(531)–O(531) | 133.0(8) |
| M(5)–M(3)–C(531) | 49.9(3) | M(6)–M(3)–C(531) | 110.1(3) | M(5)–C(531)–O(531) | 136.6(9) | M(1)–C(621)–O(621) | 133.9(9) |
| M(1)–M(3)–C(643) | 110.4(3) | M(4)–M(3)–C(643) | 51.9(3) | M(2)–C(621)–O(621) | 131.8(9) | M(6)–C(621)–O(621) | 136.7(10) |
| M(5)–M(3)–C(643) | 111.3(3) | M(6)–M(3)–C(643) | 51.5(3) | M(3)–C(643)–O(643) | 133.9(9) | M(4)–C(643)–O(643) | 133.1(9) |
| M(1)–M(3)–C(31) | 98.7(4) | M(6)–M(3)–C(31) | 98.5(4) | M(6)–C(643)–O(643) | 133.9(10) | M(2)–C(542)–O(542) | 131.1(8) |
| M(4)–M(3)–C(32) | 99.0(3) | M(5)–M(3)–C(32) | 95.3(3) | M(4)–C(542)–O(542) | 132.9(9) | M(5)–C(542)–O(542) | 136.5(9) |
| M(2)–M(4)–C(643) | 110.6(3) | M(3)–M(4)–C(643) | 51.2(3) | M(1)–C(11)–O(11) | 178.7(11) | M(1)–C(12)–O(12) | 177.6(11) |
| M(5)–M(4)–C(643) | 110.8(3) | M(6)–M(4)–C(643) | 51.1(3) | M(2)–C(21)–O(21) | 177.4(12) | M(2)–C(22)–O(22) | 178.0(11) |
| M(2)–M(4)–C(542) | 52.2(3) | M(3)–M(4)–C(542) | 109.4(3) | M(3)–C(31)–O(31) | 178.7(11) | M(3)–C(32)–O(32) | 177.2(10) |
| M(5)–M(4)–C(542) | 49.7(3) | M(6)–M(4)–C(542) | 111.6(3) | M(4)–C(41)–O(41) | 177.0(13) | M(4)–C(42)–O(42) | 176.4(11) |
| M(3)–M(4)–C(41) | 93.5(4) | M(5)–M(4)–C(41) | 99.3(5) | M(5)–C(51)–O(51) | 178.3(9) | M(5)–C(52)–O(52) | 174.3(11) |
| M(2)–M(4)–C(42) | 96.8(4) | M(6)–M(4)–C(42) | 99.6(4) | M(6)–C(61)–O(61) | 172.7(13) | M(6)–C(62)–O(62) | 177.7(11) |

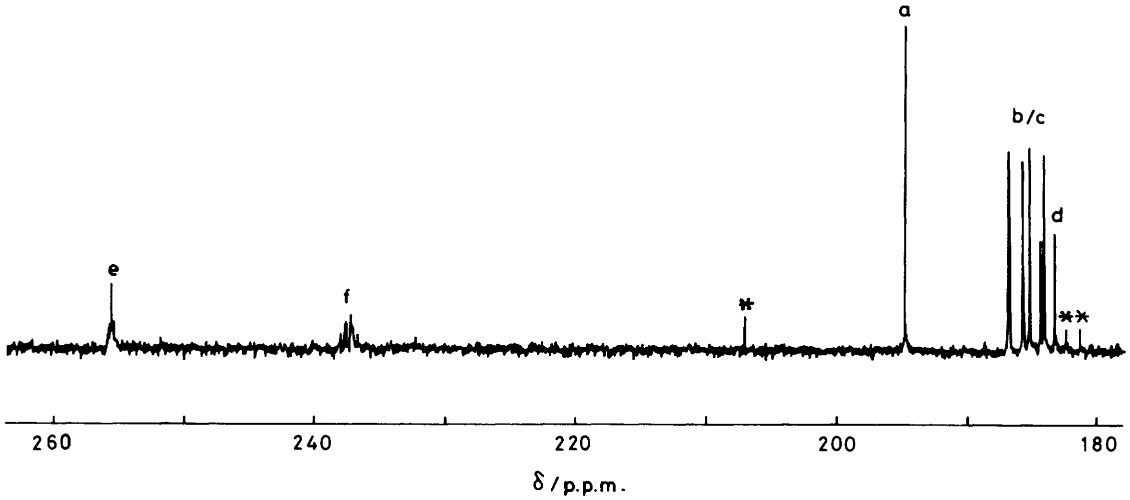

**Figure 2.** The $^{13}C$-{$^1H$} n.m.r. spectrum of (1) in $CDCl_3$ at 25 °C (* = impurity)

*Crystal Data.*—$C_{52}H_{30}NO_{16}P_2Rh_5Ru$, $M = 1\,608.4$, monoclinic, space group $C2/c$, $a = 33.62(1)$, $b = 9.729(2)$, $c = 33.72(1)$ Å, $\beta = 94.43(2)°$, $U = 10\,995$ Å$^3$ (by least-squares refinement on diffractometer angles for 8 automatically centred reflections, $\lambda = 0.710\,69$ Å), $Z = 8$, $D_c = 1.94$ g cm$^{-3}$, $F(000) = 6\,479$, $\mu(\text{Mo-}K_\alpha) = 18.1$ cm$^{-1}$.

*Data Collection and Processing.*—Nicolet R3m diffractometer, graphite-monochromated Mo-$K_\alpha$ radiation, 7 995 reflections measured ($1.5 < \theta < 22.5°$), 7 181 unique [merging $R = 0.0199$ after absorption correction (max., min. transmission factors 0.84, 0.69)], giving 4 175 with $I > 2.5\sigma(I)$.

*Structure Analysis and Refinement.*—The atomic co-ordinates of the isomorphous complex $[N(PPh_3)_2][FeRh_5(CO)_{16}]$ were used for the refinement. Full-matrix least-squares refinement was calculated with non-hydrogen atoms anisotropic except phenyl carbons, which were refined as rigid phenyl groups and hydrogens in calculated positions. Rhodium parameters were used for all the metal atoms in the final refinement. The weighting scheme was $w = 1/[\sigma^2(F) + 0.005F^2]$. The final $R$ and $R'$ values were 0.041 and 0.040. The SHELXTL program package was used.[13] The final atomic co-ordinates are given in Table 2.

*N.M.R. Spectroscopy.*—The $^{13}C$-{$^1H$} n.m.r. spectrum was recorded on a Bruker AM-250 spectrometer in a 10-mm n.m.r. tube using $CDCl_3$ as solvent at 25 °C. The chemical shifts are relative to $SiMe_4$.

*Preparation of* $[N(PPh_3)_2][RuRh_5(CO)_{16}]$.—$[Rh(CO)_4]^-$, prepared from $RhCl_3 \cdot 3H_2O$[10] (500 mg, 1.92 mmol) was extracted by thf from the KOH–$Me_2SO$ media of the $[Rh(CO)_4]^-$ synthesis and added to a thf solution containing $[\{Ru(CO)_3Cl_2\}_2]$ (110 mg, 0.21 mmol). The solution turned green after stirring for 30 min at room temperature. The thf was evaporated and the residue treated with 85% $H_3PO_4$ (2 $cm^3$) to obtain the $[RuRh_5(CO)_{16}]^-$ anion. The crude product was extracted with $CH_2Cl_2$ (10 $cm^3$; *ca.* 20 $cm^3$ of water were added to separate the phases). The $CH_2Cl_2$ was then evaporated and the oily residue ($Me_2SO$ solution) was suspended in methanol (20 $cm^3$) containing excess $N(PPh_3)_2Cl$, and the title compound was precipitated by addition of water. The dark solid was filtered off and dissolved in a small amount of $CH_2Cl_2$ and filtered to remove solid $[Rh_6(CO)_{16}]$. Yield: 485 mg, 72% (Found: Rh, 30.8; Ru, 6.7. Calc. for $C_{52}H_{30}NO_{16}P_2Rh_5Ru$: Rh, 29.5; Ru, 5.8%); $\nu_{max.}$(CO) at 2 084vw, 2 045vs, 2 014m, and 1 780s $cm^{-1}$ ($CH_2Cl_2$).

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