Cluster Chemistry. Part 32.† Synthesis and X-Ray Crystal Structure of [Ru₅(μ₅-η²-C₂PPh₂-P)(μ-PPh₂)(CO)₁₃], a Complex containing an Alkynyl Ligand in Extended Interaction with an Open Ru₅ Cluster‡

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The radical ion-initiated reaction between $[Ru_3(CO)_{12}]$ and $C_2(PPh_2)_2$ (dppa) (in 2:1 ratio) gives $[\{Ru_3(CO)_{11}\}_2(\mu\text{-dppa})]$ (2), in which the acetylenic bis-tertiary phosphine bridges two monosubstituted Ru_3 clusters. On heating (90 °C, 1 h), complex (2) is converted into $[Ru_5(\mu_5\text{-}\eta^2\text{-}C_2PPh_2\text{-}P)(\mu\text{-}PPh_2)(CO)_{13}]$ (3) in 88% yield, which was characterised by an X-ray study at 295 K. The complex contains a seven-electron donor C_2PPh_2 ligand interacting with all five Ru atoms of an open Ru_5 cluster consisting of three edge-fused Ru_3 triangles (a 'swallow' cluster); the PPh_2 group bridges the non-fused edge of the central triangle. Some comparisons with $[Ru_5(\mu_5\text{-}CNBu^t)(CO)_{14}(CNBu^t)]$ and $[Ru_5(\mu_5\text{-}C_2Ph)(\mu\text{-}PPh_2)(CO)_{14}]$ are made. Crystals of complex (3) are monoclinic, space group $P2_1/n$, with $a = 17.00(1)$, $b = 17.394(9)$, $c = 14.260(7)$ Å, $\beta = 92.89(4)°$, and $Z = 4$; the structure was refined by least-squares methods to a residual of 0.031 for 6 364 independent 'observed' reflections.

There is much current interest in the formation and rearrangement of unsaturated ligands on metal clusters as these reactions may be of relevance to the understanding of the behaviour of such molecules on metal surfaces.[1] While the appropriateness of studies of M_3 cluster complexes in this regard may be questioned, the extended interactions that occur when multiply bonded systems interact with open M_5 clusters suggests that such complexes would be better models. For example we described earlier the complex $[Ru_5(\mu_5\text{-}\eta^2\text{-}CNBu^t)(CO)_{14}(CNBu^t)]$ (1), in which one $CNBu^t$ ligand acts as a six-electron donor to the Ru_5 cluster; further studies of its reactivity have been limited by low yields and its facile decomposition to $[Ru_6C(CO)_{16}(CNBu^t)]$.[2,3]

The decarbonylation of metal carbonyl clusters in the presence of heteronuclear bridging ligands has been shown to be a successful approach to the synthesis of high-nuclearity clusters.[4,5] We have investigated the pyrolysis of complexes of bis(tertiary phosphines), in particular those of $C_2(PPh_2)_2$ (dppa), anticipating that intermolecular condensation of the cluster units to larger metal aggregates would occur in reactions involving the C≡C triple bond, together with one or more P–C bond-cleavage reactions.[6]

Herein we report the synthesis of $[\{Ru_3(CO)_{11}\}_2(\mu\text{-dppa})]$ (2) under mild conditions and its subsequent thermal rearrangement to give $[Ru_5(\mu_5\text{-}\eta^2\text{-}C_2PPh_2\text{-}P)(\mu\text{-}PPh_2)(CO)_{13}]$ (3). While this work was in progress, Carty and his co-workers[7] reported the preparation of $[Ru_5(\mu\text{-}C_2Ph)(\mu\text{-}PPh_2)(CO)_{14}]$ (4), a complex which shows some interesting differences in behaviour from (3).

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† For Part 31, see ref. 9.

‡ 1,1,1,2,2,2,3,3,4,4,5,5,5-Tridecacarbonyl-3,4-μ-diphenylphosphido-μ₅-[diphenylphosphinoethynyl-$C^1(Ru^{1,3,4})C^2(Ru^{1,2})P(Ru^5)$]-cyclopentaruthenium (7Ru–Ru).

Experimental

General experimental conditions were similar to those described in earlier papers. Sodium diphenylketyl solutions were prepared as previously described.[8]

Preparation of $[\{Ru_3(CO)_{11}\}_2(\mu\text{-dppa})]$ (2).—A solution of $[Ru_3(CO)_{12}]$ (150 mg, 0.235 mmol) and dppa (47 mg, 0.119 mmol) in tetrahydrofuran (30 cm³) at room temperature was treated dropwise with a solution of $Na[Ph_2CO]$ in the same solvent until the reaction was complete (t.l.c.). About 10 drops were required, when the solution rapidly darkened. Evaporation and recrystallisation (CH_2Cl_2–hexane) afforded complex (2) as an orange powder (135 mg, 71%), m.p. >150 °C (decomp.) (Found: C, 35.55; H, 0.80. $C_{48}H_{20}O_{22}P_2Ru_6$ requires C, 35.65; H, 1.25%). Infrared (cyclohexane): $\nu(CO)$ 2 102m, 2 068 (sh), 2 052vs, 2 034s, 2 021vs, 2 005 (sh), 1 997w, 1 987 (sh), and 1 970w cm⁻¹. ¹H N.m.r.: $\delta(CDCl_3)$ 7.50 (m, Ph).

Pyrolysis of $[\{Ru_3(CO)_{11}\}_2(\mu\text{-dppa})]$ (2).—A solution of $[\{Ru_3(CO)_{11}\}_2(\mu\text{-dppa})]$ (100 mg, 0.062 mmol) was stirred in toluene (15 cm³) at 90 °C for 1 h, after which time the reaction was adjudged complete [by disappearance of the $\nu(CO)$ band of (2) at 2 102 cm⁻¹]. Evaporation and preparative t.l.c. [silica gel, cyclohexane–acetone (90:10)] gave two bands: (*i*) yellow, containing $[Ru_3(CO)_{12}]$ (6 mg, 15%); (*ii*) black, recrystallised from CH_2Cl_2–MeOH to give black crystals of $[Ru_5(\mu_5\text{-}\eta^2\text{-}C_2PPh_2\text{-}P)(\mu\text{-}PPh_2)(CO)_{13}]$ (3) (69 mg, 88%), m.p. 200—210 °C (Found: C, 36.9; H, 1.00. $C_{39}H_{20}O_{13}P_2Ru_5$ requires C, 37.05; H, 1.60%). Infrared (cyclohexane): $\nu(CO)$ 2 081w, 2 061vs, 2 021s, 1 995w, 1 985vw, and 1 972vw cm⁻¹. ¹H N.m.r.: $\delta(CDCl_3)$ 7.40 (m, Ph).

Crystallography.—*Crystal data.* $C_{39}H_{20}O_{13}P_2Ru_5$, $M = 1 263.9$, monoclinic, space group $P2_1/n$ (C_{2h}^5, no. 14), $a = 17.00(1)$, $b = 17.394(9)$, $c = 14.260(7)$ Å, $\beta = 92.89(4)°$, $U = 4 210(4)$ Å³, $D_m = 1.97(1)$, $D_c(Z = 4) = 1.99$ g cm⁻³, $F(000) = 2 432$, monochromatic Mo-K_α radiation, $\lambda = 0.710 69$ Å, $\mu_{Mo} =$

(1)

(2)

(3)

(4)
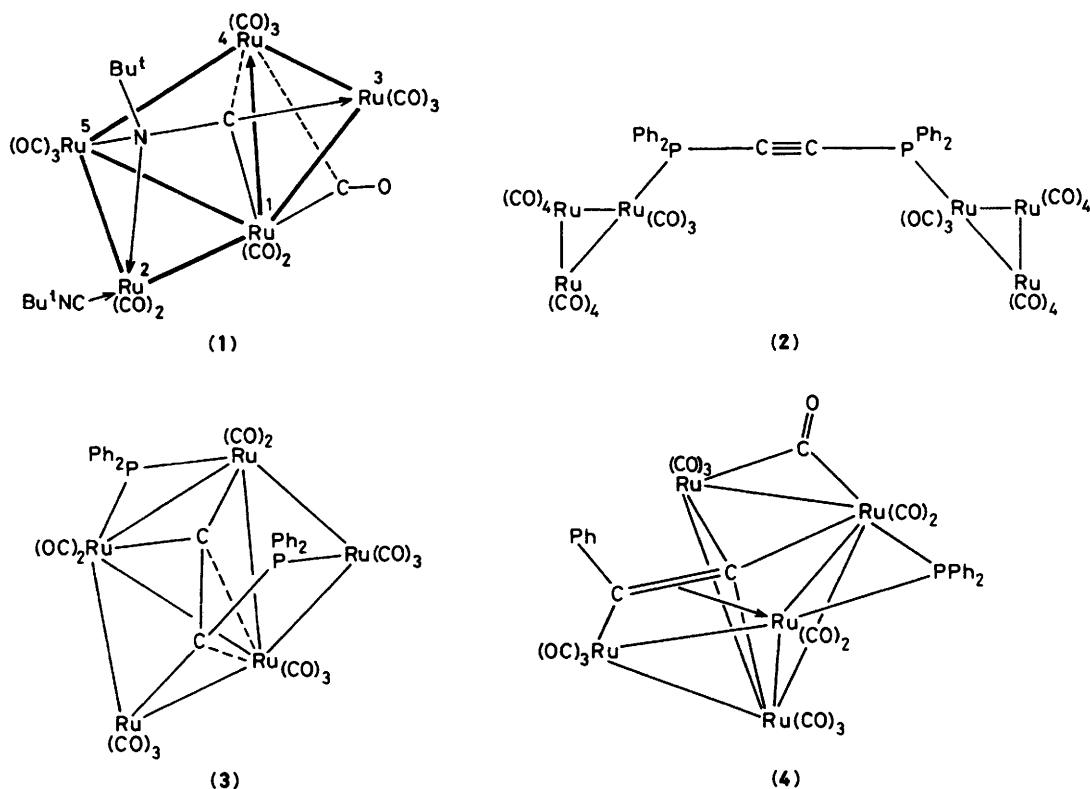
17.4 cm^{-1}. Specimen: $0.38 \times 0.25 \times 0.06$ mm. $T = 295$ K, $2\theta_{max.} = 60°, N = 9\,457, N_o = 6\,364, R = 0.031, R' = 0.038$.

The general procedure for the structure determination follows that outlined in ref. 9.

Results and Discussion

The facile substitution reactions of cluster carbonyls with tertiary phosphines, arsines, and related ligands, which are initiated by addition of small amounts of a radical ion, such as sodium diphenylketyl, have afforded several reactive complexes, whose further reactions have given information concerning the transformation of functional groups on these clusters.[8] Particularly studied have been complexes derived from [Ru$_3$(CO)$_{12}$], and we have considered the reaction where *two* Ru$_3$(CO)$_{11}$ residues may be bonded to two donor atoms separated by an unsaturated carbon chain. By further interaction, either of the Ru$_3$ clusters, or of a second metal substrate, with the unsaturated site, we envisaged that condensation to new, higher-nuclearity clusters might occur.

Accordingly, we have made complex (2) by the radical ion-initiated reaction between [Ru$_3$(CO)$_{12}$] and dppa in 2:1 ratio. The presence of the C≡C triple bond in dppa results in a linear PCCP arrangement and ensures that this ligand cannot chelate one metal atom, or bridge two metal atoms which are bonded together, as found in [Ru$_3$(CO)$_{10}$(dppe)] (dppe = Ph$_2$-PCH$_2$CH$_2$PPh$_2$).[10] The reaction proceeded readily, and good yields of (2) were obtained. This orange complex was identified as the desired hexanuclear complex by elemental analysis, and by the similarity of its i.r. v(CO) spectrum to those of other [Ru$_3$(CO)$_{11}$(PR$_3$)] complexes.[8] The phosphinoalkyne occupies equatorial sites on one ruthenium atom in each cluster, as found for other [Ru$_3$(CO)$_{11}$(PR$_3$)] complexes [PR$_3$ = PPh$_3$[11] or P(C$_6$H$_{11}$)$_3$[12]].

The red solution of complex (2) in toluene rapidly darkens on heating, and after 1 h at 90 °C it is black. Thin-layer

chromatographic (t.l.c.) separation gave the pentanuclear complex (3) in 88% yield, together with small amounts of [Ru$_3$(CO)$_{12}$]. The black crystals of (3) are indefinitely stable in air, and readily soluble in benzene, chloroform, dichloromethane, and acetone; they are only partially soluble in light petroleum, and insoluble in methanol. The solution i.r. spectrum shows only terminal v(CO) bands, and the ^{1}H n.m.r. spectrum contains a multiplet at δ 7.40 from the phenyl protons. No high-field signals from metal-bonded hydrogens were observed. The molecular structure of (3) was determined from a single-crystal X-ray study.

Molecular Structure of Complex (3).—The molecular structure of complex (3) is shown in Figure 1. The five Ru atoms form an open array of three edge-fused triangles, resembling those found earlier in complexes (1) and (4); we have described this as a 'swallow' cluster. The seven Ru–Ru separations fall in the range 2.731(2)—2.932(2) Å. The shortest is between the phosphido-bridged atoms Ru(2) and Ru(3) [2.731(2) Å], while bonds from Ru(1), which bears the phosphine donor atom, to Ru(2) and Ru(5) are respectively, 2.932(2) and 2.921(2) Å, which are rather long for such interactions; we suggest that the presence of the tertiary phosphine ligand simultaneously constrains Ru(1) and lengthens the bonds to the rest of the cluster.

The C$_2$PPh$_2$ group, formed by cleavage of PPh$_2$ from the original dppa ligand, interacts with all five metal atoms. The Ru(1)–P(1) bond [2.373(2) Å] is a conventional two-electron donor interaction of the tertiary phosphine with the metal atom. The acetylenic unit C(131)–C(132) interacts with the other four metal atoms, with C(131) being strongly σ-bonded [2.055(5) Å] to Ru(4), and the Ru(2)Ru(3)Ru(5) face being nearly symmetrically capped by C(132) [2.016(5), 2.024(5), and 2.154(4) Å, respectively]. There is also a much weaker interaction between C(131) and Ru(5) [2.279(4) Å], and the C$_2$ unit can be considered to have an asymmetric η^2 interaction with Ru(5).

Table 1. Non-hydrogen atom co-ordinates

Atom	x	y	z	Atom	x	y	z
Ru(1)	0.962 25(2)	0.168 59(2)	0.072 91(2)	O(53)	0.679 0(3)	0.033 1(2)	0.231 6(3)
Ru(2)	0.915 73(2)	0.235 37(2)	0.250 62(2)	P(1)	0.863 77(8)	0.238 80(7)	−0.014 35(8)
Ru(3)	0.758 20(2)	0.238 73(2)	0.279 84(2)	C(111)	0.879 5(3)	0.341 0(3)	−0.033 6(3)
Ru(4)	0.678 93(2)	0.205 59(2)	0.103 23(3)	C(112)	0.921 5(4)	0.363 5(3)	−0.109 6(4)
Ru(5)	0.817 05(2)	0.120 53(2)	0.157 22(2)	C(113)	0.937 3(4)	0.440 1(3)	−0.124 5(4)
C(11)	0.993 4(3)	0.116 7(3)	−0.035 5(4)	C(114)	0.912 1(4)	0.494 3(3)	−0.064 1(5)
O(11)	1.019 4(3)	0.088 1(3)	−0.099 4(3)	C(115)	0.870 8(4)	0.473 2(3)	0.012 9(5)
C(12)	1.029 6(3)	0.101 7(3)	0.148 2(4)	C(116)	0.854 9(4)	0.396 0(3)	0.027 7(4)
O(12)	1.073 8(3)	0.062 1(3)	0.186 4(3)	C(121)	0.816 6(3)	0.206 3(3)	−0.124 2(3)
C(13)	1.033 6(3)	0.249 8(3)	0.073 3(4)	C(122)	0.825 9(4)	0.132 8(3)	−0.157 7(4)
O(13)	1.079 5(3)	0.298 2(3)	0.071 8(3)	C(123)	0.782 8(4)	0.106 7(4)	−0.237 3(4)
C(21)	0.963 3(3)	0.330 2(3)	0.238 5(3)	C(124)	0.731 7(4)	0.155 9(4)	−0.284 5(4)
O(21)	0.988 6(3)	0.390 1(2)	0.229 5(3)	C(125)	0.721 7(4)	0.230 1(4)	−0.251 5(4)
C(22)	1.008 5(3)	0.195 6(3)	0.314 2(3)	C(126)	0.763 9(3)	0.254 8(3)	−0.173 1(4)
O(22)	1.063 3(2)	0.172 7(2)	0.353 7(3)	C(131)	0.793 0(3)	0.229 1(2)	0.071 0(3)
C(31)	0.718 0(3)	0.336 7(3)	0.295 3(4)	C(132)	0.819 8(3)	0.244 3(2)	0.162 2(3)
O(31)	0.694 5(3)	0.397 6(2)	0.304 3(4)	P(2)	0.855 68(8)	0.240 02(7)	0.395 61(8)
C(32)	0.675 8(4)	0.196 1(3)	0.346 7(4)	C(211)	0.862 8(3)	0.322 9(3)	0.473 0(3)
O(32)	0.625 9(3)	0.168 1(3)	0.385 3(3)	C(212)	0.892 0(5)	0.391 8(3)	0.443 9(4)
C(41)	0.640 7(3)	0.167 4(3)	−0.016 5(4)	C(213)	0.892 2(5)	0.456 0(4)	0.503 2(5)
O(41)	0.613 6(3)	0.146 6(2)	−0.086 3(3)	C(214)	0.865 6(5)	0.450 7(4)	0.589 8(4)
C(42)	0.648 3(3)	0.306 9(3)	0.080 6(4)	C(215)	0.837 2(6)	0.383 8(4)	0.619 2(5)
O(42)	0.633 8(3)	0.369 9(2)	0.067 1(4)	C(216)	0.837 2(5)	0.319 2(4)	0.561 8(4)
C(43)	0.584 0(4)	0.176 3(4)	0.165 3(4)	C(221)	0.871 9(3)	0.159 8(3)	0.475 4(3)
O(43)	0.527 5(3)	0.159 3(4)	0.197 4(3)	C(222)	0.825 5(4)	0.096 2(3)	0.471 1(4)
C(51)	0.829 2(3)	0.046 5(3)	0.058 2(3)	C(223)	0.840 8(5)	0.0333 (3)	0.528 5(4)
O(51)	0.832 3(3)	−0.002 1(2)	0.005 3(3)	C(224)	0.903 9(4)	0.033 5(4)	0.589 6(5)
C(52)	0.882 0(3)	0.063 4(3)	0.245 3(3)	C(225)	0.951 6(4)	0.096 3(5)	0.595 9(5)
O(52)	0.916 8(3)	0.023 9(2)	0.295 1(3)	C(226)	0.935 8(4)	0.159 0(4)	0.539 3(5)
C(53)	0.722 7(4)	0.075 0(3)	0.199 9(4)				
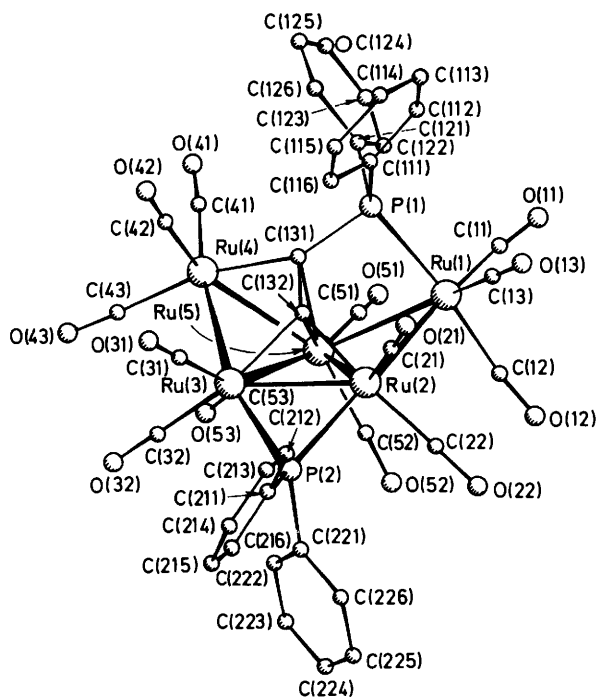
Figure 1. PLUTO plot of [Ru₅(μ₅-η²-C₂PPh₂-P)(μ-PPh₂)(CO)₁₃] (3), showing atom-labelling scheme employed

(5)

The situation in complex (4) is similar, with a further involvement of the C≡C function with the fifth ruthenium atom. The C≡C triple bond has lengthened to 1.383(6) Å in (3), and is comparable with that found in (4) [1.39(1) Å]; both are longer than that found in [Ru₅(μ₄-η²-C₂Ph)(μ-PPh₂)(CO)₁₃] (5), where the alkyne is attached to the square face of the square-pyramidal Ru₅ core.
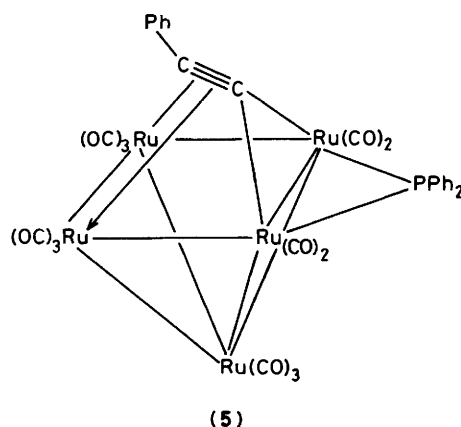
In complex (3) the CO groups are distributed two to each of the phosphido-bridged Ru(2) and Ru(3) atoms, and three each to the other three metal atoms. The electron count shows that the C₂PPh₂ ligand functions as a seven-electron donor to the cluster, which is electron-precise (76e). However, formal electron counts at the individual metal atoms show that Ru(5) is electron-rich (20e), while Ru(4) and either Ru(2) or Ru(3) are electron-deficient (depending on the direction of donation of electrons from the bridging phosphido-ligand). This electron imbalance is partially compensated by the redistribution of electron density over the cluster *via* the semi-bridging CO(53) ligand [Ru(5)–C(53) 1.915(6) and Ru(4)–C(53) 2.741(6) Å].

The μ-PPh₂ ligand bridges the Ru(2)–Ru(3) edge in an

Table 2. Ruthenium, phosphorus, and bridging carbon atom environments. The first column in each matrix is the Ru, P, or C (bridging)–other atom distance (Å). Other entries are the angles (°) subtended at the ruthenium by the relevant atoms at the head of the corresponding row and column. Distances Ru–C <3.0 Å are included

Ru(1)	r	Ru(5)	C(11)	C(12)	C(13)	P(1)
Ru(2)	2.932(2)	59.17(2)	174.6(2)	86.3(2)	84.3(2)	92.03(4)
Ru(5)	2.921(2)		118.5(2)	95.1(2)	141.2(2)	76.99(5)
C(11)	1.889(6)			89.1(2)	98.9(3)	92.0(2)
C(12)	1.922(6)				95.1(3)	171.5(2)
C(13)	1.862(6)					93.1(2)
P(1)	2.373(2)					

Ru(2)	r	Ru(3)	Ru(5)	C(21)	C(22)	C(132)	P(2)
Ru(1)	2.932(1)	116.71(1)	60.23(3)	97.7(2)	90.8(2)	74.6(1)	157.06(3)
Ru(3)	2.731(2)		62.25(3)	115.6(2)	136.7(2)	47.6(1)	52.64(3)
Ru(5)	2.890(1)			145.1(1)	114.5(1)	48.1(1)	99.29(5)
C(21)	1.849(5)				90.8(2)	102.5(2)	105.2(2)
C(22)	1.909(5)					161.3(2)	88.8(2)
C(132)	2.016(5)						100.0(1)
P(2)	2.353(2)						

Ru(3)	r	Ru(4)	Ru(5)	C(31)	C(32)	C(132)	P(2)
Ru(2)	2.731(2)	106.48(4)	61.56(2)	114.1(2)	145.8(2)	47.3(1)	55.13(5)
Ru(4)	2.854(2)		59.22(3)	97.5(2)	92.1(2)	61.3(1)	159.15(5)
Ru(5)	2.909(1)			149.5(2)	108.2(2)	47.7(1)	100.54(4)
C(31)	1.853(6)				90.8(3)	105.3(2)	99.4(2)
C(32)	1.885(6)					150.0(2)	99.7(2)
C(132)	2.024(5)						102.3(1)
P(2)	2.279(2)						

Ru(4)	r	Ru(5)	C(41)	C(42)	C(43)	C(53)	C(131)	C(132)
Ru(3)	2.854(2)	61.35(2)	168.7(1)	94.5(2)	91.0(2)	67.6(1)	75.5(1)	43.3(1)
Ru(5)	2.848(1)		107.4(2)	139.3(2)	115.6(2)	40.0(1)	52.4(1)	46.4(1)
C(41)	1.915(5)			95.4(2)	93.6(2)	103.4(2)	98.6(2)	130.3(2)
C(42)	1.861(6)				95.5(3)	159.8(2)	91.8(2)	93.3(2)
C(43)	1.947(6)					76.4(2)	165.1(2)	134.0(2)
C(53)	2.741(6)						92.4(2)	80.1(2)
C(131)	2.055(5)							32.2(1)
C(132)	2.586(5)							

Ru(5)	r	Ru(2)	Ru(3)	Ru(4)	C(51)	C(52)	C(53)	C(131)	C(132)
Ru(1)	2.921(2)	60.61(3)	111.62(3)	116.23(4)	76.5(2)	87.0(2)	170.9(2)	70.9(1)	73.2(1)
Ru(2)	2.890(1)		56.19(3)	102.52(4)	135.8(2)	75.7(2)	128.0(2)	76.1(1)	44.2(1)
Ru(3)	2.909(1)			59.44(3)	164.7(2)	100.2(2)	77.5(2)	71.4(1)	44.1(1)
Ru(4)	2.848(1)				105.5(2)	152.8(2)	67.0(2)	45.6(1)	60.4(1)
C(51)	1.930(5)					93.1(2)	94.5(2)	100.4(2)	133.5(2)
C(52)	1.909(5)						92.4(2)	150.3(2)	119.2(2)
C(53)	1.915(6)							112.6(2)	114.9(2)
C(131)	2.279(4)								36.2(2)
C(132)	2.154(4)								

P(1)	r	C(111)	C(121)	C(131)	P(2)	r	Ru(3)	C(211)	C(221)
Ru(1)	2.373(2)	118.4(2)	124.2(2)	94.4(1)	Ru(2)	2.353(2)	72.23(5)	122.9(2)	117.8(2)
C(111)	1.820(5)		103.6(2)	108.0(2)	Ru(3)	2.279(2)		118.1(2)	121.9(2)
C(121)	1.814(5)			106.2(2)	C(211)	1.815(5)			103.1(2)
C(131)	1.762(5)				C(221)	1.813(5)			

C(131)	r	Ru(5)	P(1)	C(132)	C(132)	r	Ru(3)	Ru(4)	Ru(5)	C(131)
Ru(4)	2.055(5)	82.0(1)	149.1(2)	95.6(3)	Ru(2)	2.016(5)	85.1(2)	152.8(2)	87.7(2)	142.4(4)
Ru(5)	2.279(4)		110.0(2)	67.0(2)	Ru(3)	2.024(5)		75.4(2)	88.2(2)	127.7(4)
P(1)	1.762(5)			115.3(3)	Ru(4)	2.586(5)			73.2(1)	52.3(2)
C(132)	1.383(6)				Ru(5)	2.154(5)				76.8(2)
					C(131)	1.383(6)				

asymmetric fashion [Ru(2)–P(2) 2.353(2) and Ru(3)–P(2) 2.279(2) Å].

There have now been described three Ru₅ clusters in which a C≡C or C≡N triple bond straddles an open arrangement of metal atoms. Complex (3) is apparently stable towards further rearrangement, whereas the structurally closely related (4)

readily loses CO to reform the nido-Ru₅ cluster (5),[7] while (1) forms a closo-Ru₆C cluster complex on heating.[3] No doubt the presence of the tertiary phosphine ligand in (3) preserves the open nature of this cluster, since ready metal–metal bond formation is no longer possible even if CO were to be lost.

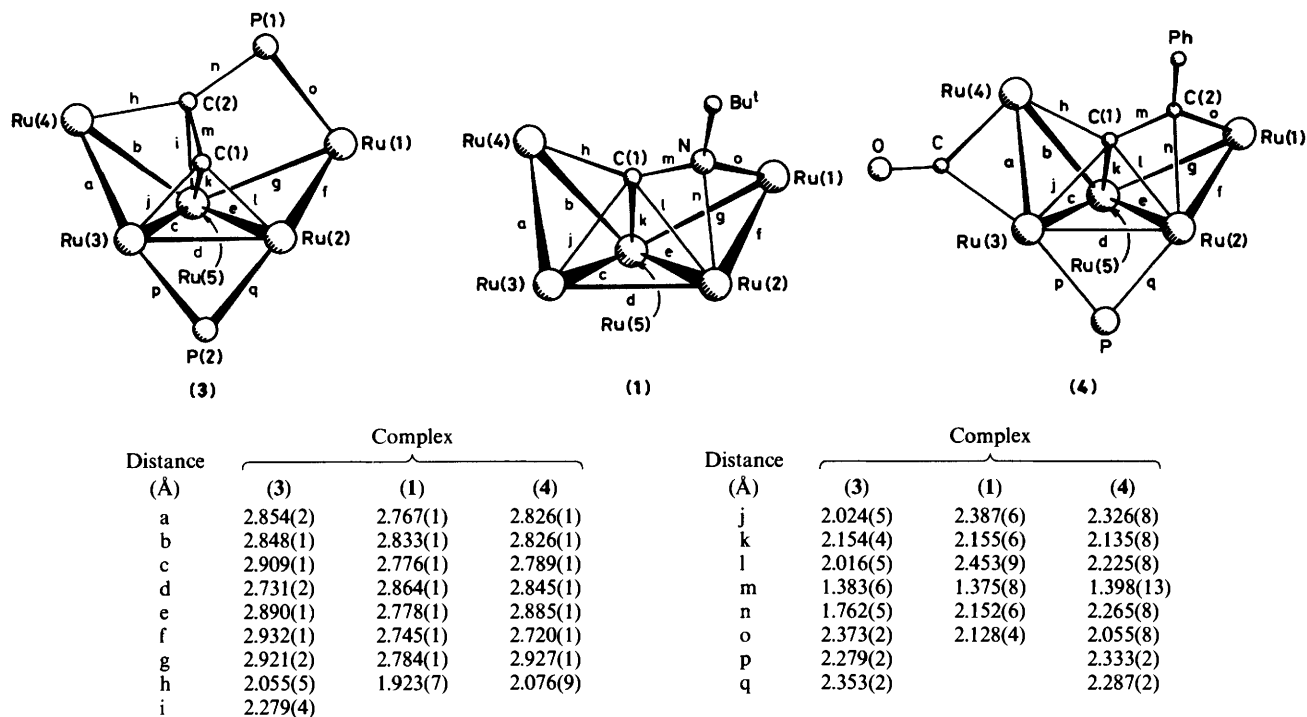Figure 2 shows the heavy atom cores of the three complexes,

Figure 2. Heavy-atom cores of complexes (3), (1), and (4), showing interactions of the phosphinoacetylide [in (3)], isocyanide [in (1)], and acetylide ligands [in (4)] with the Ru_5 moieties

Distance (Å)	Complex (3)	(1)	(4)	Distance (Å)	Complex (3)	(1)	(4)
a	2.854(2)	2.767(1)	2.826(1)	j	2.024(5)	2.387(6)	2.326(8)
b	2.848(1)	2.833(1)	2.826(1)	k	2.154(4)	2.155(6)	2.135(8)
c	2.909(1)	2.776(1)	2.789(1)	l	2.016(5)	2.453(9)	2.225(8)
d	2.731(2)	2.864(1)	2.845(1)	m	1.383(6)	1.375(8)	1.398(13)
e	2.890(1)	2.778(1)	2.885(1)	n	1.762(5)	2.152(6)	2.265(8)
f	2.932(1)	2.745(1)	2.720(1)	o	2.373(2)	2.128(4)	2.055(8)
g	2.921(2)	2.784(1)	2.927(1)	p	2.279(2)		2.333(2)
h	2.055(5)	1.923(7)	2.076(9)	q	2.353(2)		2.287(2)
i	2.279(4)						

Table 3. Carbonyl geometries

Carbonyl	C–O/Å	Ru–C–O/°	Carbonyl	C–O/Å	Ru–C–O/°
11	1.146(8)	173.4(5)	41	1.135(6)	175.7(5)
12	1.138(7)	174.0(5)	42	1.138(7)	176.2(5)
13	1.148(7)	177.6(5)	43	1.124(8)	177.0(5)
21	1.138(7)	176.3(5)	51	1.136(6)	173.1(5)
22	1.136(7)	178.5(5)	52	1.133(6)	173.9(5)
31	1.141(7)	178.8(7)	53*	1.150(7)	162.9(5)
32	1.144(8)	177.7(6)			

* Also: Ru(4)–C 2.741(6) Å, Ru(4)–C–O 123.9(4), and Ru(4)–C–Ru(5) 73.0(2)°.

together with the acetylide or isocyanide ligands, in a manner which details the interaction of the ligands with the Ru_5 skeletons. Atom numbering for complexes (1) and (4) in Figure 2 has been changed from that used in the original papers to simplify the following discussion; in (3), C(131) and C(132) are numbered C(2) and C(1) respectively. The closest similarities are found in (1) and (4), where the isoelectronic $Bu^tN\equiv C$ and $PhC\equiv C^-$ ligands are arranged so that the NC or C_2 moieties have an η^2 interaction with Ru(2), with a strong σ bond from C(1) to Ru(4). This carbon is also bonded to Ru(5), and has much weaker interactions with Ru(2) and Ru(3). In complex (3), on the other hand, the presence of the tertiary phosphine attached to Ru(1) removes the possibility of any interaction of C(1) with this metal atom, the acetylide portion of the ligand now being skewed so that the η^2 interaction occurs with Ru(5). Carbon C(1) now interacts strongly with both Ru(2) and Ru(3), and this, together with the μ-PPh_2 ligand, results in the Ru(2)–Ru(3) separation being the shortest such distance in any of the three complexes. Collectively, these three complexes provide examples of a novel activation of the organic molecules by wrapping a metal cluster around one end of the molecule.

Alternatively, the organic molecule could be considered to 'burrow' into this fragment of a metal surface; in complex (3), the function of the $Ph_2P(1)$ group is to push the acetylide in somewhat deeper, with a closer association with the $Ru(2)Ru(3)Ru(5)/Ru(3)Ru(4)Ru(5)$ faces.

The electron-deficient nature of the μ_4- or μ_5-C–C or μ_5-C–N moiety is clearly shown by the lengthening of these bonds when compared with the normal values found in the free ligands. In the case of the alkynes, this bond-lengthening effect does not differ greatly from that found in a μ_3-η^2-alkyne; in a related complex which was described after submission of this paper, $[Ru_5(\mu_5-\eta^2-C_2Ph)(\mu_3-\eta^2-PhC_2C_2Ph)(\mu-PPh_2)(CO)_{12}]$, the C–C bond of the phenylacetylide unit which interacts with all five metal atoms is 1.340(9) Å,[13] or shorter than that found in (3). Evidently the C–C separation is reflecting a mixture of σ and π interactions of the unsaturated centre with the metal core. Further study of the reactions of these and related complexes will enable the effects of this multicentre bonding on the reactivity of the C–C or C–N units to be gauged; we suggest that such complexes may prove to be better models of similar species adsorbed on (or in) metal surfaces than those involving only a single triangular M_3 face.

It is also of interest to compare the interactions found in these complexes with that found in the product of the reaction between acetylene and the 'bow-tie' cluster $[Os_5(CO)_{19}]$.[14] In this complex the alkyne is bonded to only three metal atoms in the conventional $2\sigma,\eta^2$ mode; the two metal atoms which, with the common central Os, form the second half of the 'bow-tie,' twist to increase the dihedral angle between the two Os_3 planes from that found in the parent carbonyl. It would seem that the lack of any bonding interaction between the two 'basal' edges precludes the extended interaction of the alkyne with four or five Os atoms. It will be interesting to see whether ready CO elimination and Os–Os bond formation, such as might occur on heating or irradiation, will result in more extended interaction of the alkyne with the metal atoms.

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