Two New Tetranuclear Ruthenium Complexes: [Ru₂(CO)₅(PPh₂)(C₂PPh₂)]₂ with Two Dinuclear Units Linked by Two Phosphinoacetylide Bridges and [Ru₄(CO)₁₀(PPh)(PhC₂PPh₂)], a Flattened "Butterfly" with a σ-π-Phenyl(diphenylphosphino)ethyne and a μ₄-Phosphinidene Extracted from the Bis(diphenylphosphino)ethyne Reactant

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Syntheses and single-crystal X-ray diffraction studies of two derivatives isolated from the reaction of bis(diphenylphosphino)ethyne with dodecacarbonyltriruthenium are reported. Crystal data for compound I, [Ru₂(CO)₅(PPh₂)(C₂PPh₂)]₂: tetragonal, space group $P4_12_12$, a = 23.13 (2) Å, c = 13.54 (1) Å, R = 0.0581, R_w = 0.0496 for 2181 reflections. Crystal data for compound II, [Ru₄(CO)₁₀(PPh)(PhC₂PPh₂)]: triclinic, space group $P\bar{1}$, a = 12.50 (5) Å, b = 13.28 (5) Å, c = 21.32 (7) Å, α = 137.7 (1)°, β = 107.1 (2)°, γ = 100.1 (2)°, R = 0.0551, R_w = 0.0495 for 3932 reflections. Compound I contains two dinuclear subunits linked by two phosphinoacetylide bridges; each subunit is similar to known σ-π-acetylide bimetallic derivatives with a phosphido bridge. Compound II is a tetranuclear cluster with a flattened "butterfly" geometry capped on one side by a phenyl(diphenylphosphino)ethyne σ-π-bonded to the four ruthenium atoms with its phosphino group making a three-membered $\overline{Ru-P-C}$ ring similar to a phosphirene ring and on the other side by a phosphinidene group extracted from the original bis(diphenylphosphino)ethyne.

Introduction

As part of our continuing synthetic and structural studies in the area of functionalized alkyne–cluster chemistry, we recently reported an unusual tetranuclear complex of ruthenium obtained from the reaction of [Ru₃(CO)₁₂] with 1-(diethylamino)propyne that contained two pentadentate cyclopentadienolato ligands.[1] We then became interested in another functionalized alkyne, bis(diphenylphosphino)ethyne (dppa). Reactions of monophosphinoalkynes RC≡CPR′₂ with metal carbonyls were recently reviewed;[2,3] this chemistry is dominated by the cleavage of the P–C(alkyne) bond and the formation of acetylide-type complexes. Although symmetric phosphinoalkynes might offer the possibility for two P–C(alkyne) bond cleavages, results refer mainly to compounds in which P–C bond rupture does not occur. Carty et al. have reported a compound which consists of two [Fe₂(CO)₃(η-C₅H₅)₂] units linked by a dppa molecule[4] whereas Cotton et al. have isolated tantalum complexes in which the acetylene is dimerized to give a 1,2,3,4-tetraphosphinobut-2-enediyl chain linked to metal atoms through P–C–Ta rings.[5] More recently, Rudler et al. have reported the insertion of this dppa into one of the C–W bonds of a (μ-alkylidene)tungsten compound, followed by a P–C bond rupture.[6]

We report here the syntheses and characterization of two tetranuclear ruthenium complexes: one containing two dinuclear units linked by two phosphinoacetylide bridges

and one tetranuclear cluster exhibiting a rare and unexpected extraction of a phosphinidene group from the bis(diphenylphosphino)ethyne.

Experimental Section

Syntheses. Bis(diphenylphosphino)ethyne [(C₆H₅)₂PC≡C-P(C₆H₅)₂] (432 mg, 1.1 mmol) was dissolved in 30 mL of tetrahydrofuran and slowly added to a solution of [Ru₃(CO)₁₂] (700 mg, 1.1 mmol) in 80 mL of tetrahydrofuran. The solution was stirred and refluxed for 18 h under dry nitrogen. The mixture was evaporated and chromatographed on a 40 × 1.5 cm neutral alumina column. Mixtures of hexane/benzene were used to elute five orange bands. The two first fractions were evaporated, and recrystallizations from hexane yielded three products. (i) Orange-yellow crystals of I: IR ν(CO) 2080 (w), 2030 (vs), 1960 (sh), 1950 (vs), 1910 (w), 1880 (s) cm⁻¹. Anal. Calcd for Ru₄C₆₂H₄₀O₁₀P₄: C, 50.55; H, 2.74. Found: C, 50.48; H, 2.94. (ii) Red crystals of II: IR ν(CO) 2065 (w), 2030 (vs), 1985 (sh), 1980 (s), 1970 (s), 1842 (vs) cm⁻¹. Anal. Calcd for Ru₄C₃₆H₂₀O₁₀P₂: C, 40.08; H, 1.87. Found: C, 40.25; H, 2.0. (iii) Black crystals of III: IR ν(CO) 2050 (s), 2010 (vs), 1980 (sh), 1960 (sh), 1925 (m) cm⁻¹. Anal. Calcd for Ru₅C₃₉H₂₀O₁₃P₂: C, 37.06; H, 1.60. Found: C, 37.92; H, 1.85. This last compound is not discussed here.[7]

X-ray Analyses. For both compounds, preliminary unit cell dimensions and symmetry information were derived from Laue and precession photographs; in the case of compound I, $P4_12_12$ or the enantiomorphous $P4_32_12$ were deduced from the examination of $hk0$ and $h0l$ zero layers and $hk1$, $hk2$, $h1l$, and $h2l$ upper layers. The absolute configuration was not determined. Crystals then were set up on a laboratory-made automatic three-circle diffractometer. Cell dimensions and orientation matrices were obtained from least-squares refinements of nine reflections for which 9° < θ < 12°. A takeoff angle of 3° was used. Crystal data and data collection parameters are listed in Table I. Intensities of two standard reflections were monitored every 100 reflections. These showed no appreciable change during the data collections. In the absence of attenuation filters on the

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Table I. Summary of X-ray Analyses for Complexes I and II

	I	II
A. Crystal Data		
formula	$(Ru_2C_{31}H_{20}P_2O_5)_2$	$Ru_4C_{36}H_{20}P_2O_{10}$
cryst system	$P4_12_12$	$P\bar{1}$
systematic absences	$00l, l = 4n + 1; h00, h = 2n + 1$	
a, Å	23.13 (2)	12.50 (5)
b, Å	23.13 (2)	13.28 (5)
c, Å	13.54 (1)	21.32 (7)
α, deg	90.0	137.7 (1)
β, deg	90.0	107.1 (2)
γ, deg	90.0	100.1 (2)
V, Å^3	7244	1804
Z	4	2
mol wt	1473.2	1078.8
ρ(calcd), g cm^{-3}	1.35	1.99
μ, cm^{-1}	8.99	17.06
B. Data Collection		
diffractometer	laboratory-made, automatic three circle diffractometer	
radiatn	Mo Kα (λ = 0.710 69 Å)	
monochromator	graphite monochromator set in front of the counter	
scan range, deg	$3 < 2\theta < 46$	$4 < 2\theta < 46$
scan type	$\theta - 2\theta$	$\theta - 2\theta$
scan speed, deg min^{-1}	1.25	1.5
scan width, deg in θ	$(1.10 + 0.345 \tan \theta)$	$(0.9 + 0.345 \tan \theta)$
reflctns obsd	2566	4652
criterion	$F > 3\sigma(F)$	$F > 3\sigma(F)$
$F(000)$	2911.92	1043.96
C. Refinement of the Structures		
final no. of variables	173	281
reflectns used	2181	3932
$R = \Sigma \|(F_o - F_c)\|/\Sigma(F_o)$	0.0581	0.0551
$R_w = \{\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2\}^{1/2}$	0.0496	0.0495
weighting scheme $(w = k/\sigma(F_o)^2)$, $k =$	1.06	0.99
GOF	1.59	1.68

diffractometer, intensities were corrected for counting losses when the counting rate exceeded 7000 counts s^{-1}. No absorption corrections were considered to be necessary (μ = 8.99 cm^{-1} and crystal dimensions 0.3 × 0.2 × 0.2 mm for I; μ = 17.06 cm^{-1} and crystal dimensions 0.25 × 0.2 × 0.1 mm for II).

Computations were performed by using SHELX 76[8] on a PDP 11/23 computer for the first stages of calculations and on a GOULD CONCEPT 32/87 for the last full-matrix cycles of refinements. Atomic scattering factors for neutral Ru, P, O, and C were taken from ref 9, those for H were taken from Stewart et al.,[10] and anomalous dispersion terms for Ru were included.[10]

In both compounds, the position of the Ru atoms were determined from a Patterson map. All other non-hydrogen atoms were located on subsequent electron density and difference electron density maps. Phenyl rings were considered as rigid groups and assigned a refineable overall isotropic thermal parameter. Refinements were by full-matrix least squares including isotropic and then anisotropic temperature factors for nongroup atoms. All refinements began with unit weights that were replaced in the final rounds of calculations by a weighting scheme of the form $w = k/\sigma^2(F)$. For the last cycles of refinement, hydrogen atoms were added to the rigid groups (H–C–H = 120°; C–H = 0.95 Å). The criteria for a satisfactory completed analysis were that the ratios of the parameter shifts to standard deviations were all less than 0.04 and that there were no significant features in the final difference maps. The main features of the refinements appear in Table I, part C.

Final positional parameters and their standard deviations, obtained from the last cycle of least-squares refinement, are presented in Tables II and III. Thermal parameters for non-hydrogen atoms and final values of observed and calculated
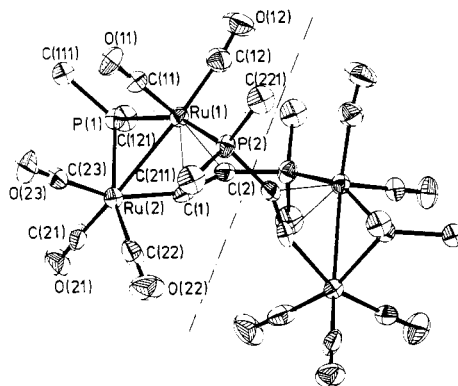
(8) Computer programs used were Sheldrick's SHELX 76, Johnson's ORTEP-2, and locally written routines.

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Figure 1.

structure factors are available as supplementary material.

Results and Discussion

Compound I. A view of the tetranuclear molecule illustrating the atomic numbering scheme is shown in Figure 1. Excluding the distances and angles of phenyl rings, the remaining distances and angles are given in Table IV.

The whole molecule has a twofold axis which relates two dimetallic subunits; each subunit contains a metal–metal bond, a phosphido bridge, and a σ-π-acetylide. The phosphido-bridging group is one of the two phosphino groups formerly attached to the alkyne; such C–P bond cleavage has been described several times and recently reviewed.[2,3] The subunits are connected to each other by a double bridge built up from two (diphenylphosphino)-acetylides. Each bridge is bound to one ruthenium of a first dinuclear Ru$_2$ group by the phosphorus atom of the phosphinoacetylide and to both rutheniums of the second dinuclear Ru$_2$ group by the acetylide part. Although there

Table II. Fractional Atomic Coordinates with Esd's in Parentheses for Compound I

atom	x/a	y/b	z/c	B(iso), Å²
Ru(1)	0.14750 (5)	-0.28795 (6)	0.2127 (1)	
Ru(2)	0.20570 (6)	-0.39100 (6)	0.1672 (1)	
P(1)	0.1320 (2)	-0.3465 (2)	0.0744 (3)	
P(2)	0.1863 (2)	-0.2645 (22)	0.3704 (3)	
C(1)	0.2363 (6)	-0.3082 (9)	0.147(1)	
C(2)	0.2339 (6)	-0.2550 (7)	0.136 (1)	
C(11)	0.0849 (7)	-0.3242 (7)	0.273 (1)	
O(11)	0.0473 (5)	-0.3464 (6)	0.3099 (8)	
C(12)	0.1092 (8)	-0.2173 (9)	0.188 (1)	
O(12)	0.0826 (6)	-0.1789 (7)	0.166 (1)	
C(21)	0.2400 (8)	-0.4383 (8)	0.067 (2)	
O(21)	0.2608 (6)	-0.4663 (6)	0.012 (1)	
C(22)	0.265 (1)	-0.4033 (8)	0.266 (2)	
O(22)	0.3025 (7)	-0.4074 (8)	0.318 (1)	
C(23)	0.1551 (8)	-0.4484 (7)	0.225 (1)	
O(23)	0.1243 (6)	-0.4804 (6)	0.261 (1)	
C(112)	0.2030 (5)	-0.3312 (5)	-0.0904 (8)	6.7 (2)
C(113)	0.2153 (5)	-0.3152 (5)	-0.1875 (8)	6.7 (2)
C(114)	0.1719 (5)	-0.2917 (5)	-0.2468 (8)	6.7 (2)
C(115)	0.1163 (5)	-0.2841 (5)	-0.2091 (8)	6.7 (2)
C(116)	0.1041 (5)	-0.3001 (5)	-0.1119 (8)	6.7 (2)
C(111)	0.1474 (5)	-0.3236 (5)	-0.0526 (8)	6.7 (2)
C(122)	0.0110 (5)	-0.3483 (3)	0.0676 (7)	5.2 (1)
C(123)	-0.0426 (5)	-0.3738 (3)	0.0497 (7)	5.2 (1)
C(124)	-0.0457 (5)	-0.4317 (3)	0.0216 (7)	5.2 (1)
C(125)	0.0048 (5)	-0.4642 (3)	0.0115 (7)	5.2 (1)
C(126)	0.0584 (5)	-0.4387 (3)	0.0294 (7)	5.2 (1)
C(121)	0.0615 (5)	-0.3807 (3)	0.0574 (7)	5.2 (1)
C(212)	0.1494 (5)	-0.3550 (6)	0.487 (1)	8.0 (2)
C(213)	0.1548 (5)	-0.4027 (6)	0.548 (1)	8.0 (2)
C(214)	0.2094 (5)	-0.4193 (6)	0.583 (1)	8.0 (2)
C(215)	0.2583 (5)	-0.3883 (6)	0.555 (1)	8.0 (2)
C(216)	0.2528 (5)	-0.3406 (6)	0.492 (1)	8.0 (2)
C(211)	0.1983 (5)	-0.3240 (6)	0.458 (1)	8.0 (2)
C(222)	0.0889 (6)	-0.2021 (6)	0.4292 (8)	7.7 (2)
C(223)	0.0581 (6)	-0.1658 (6)	0.4926 (8)	7.7 (2)
C(224)	0.0858 (6)	-0.1403 (6)	0.5731 (8)	7.7 (2)
C(225)	0.1443 (6)	-0.1512 (6)	0.5904 (8)	7.7 (2)
C(226)	0.1751 (6)	-0.1875 (6)	0.5271 (8)	7.7 (2)
C(221)	0.1474 (6)	-0.2129 (6)	0.4465 (8)	7.7 (2)

Table III. Fractional Atomic Coordinates with Esd's in Parentheses for Compound II

atom	x/a	y/b	z/c	B(iso), Å²
Ru(1)	0.5473 (1)	0.4942 (1)	0.16459 (9)	
Ru(2)	0.4063 (1)	0.2484 (1)	0.12422 (9)	
Ru(3)	0.4557 (1)	0.5316 (1)	0.35157 (9)	
Ru(4)	0.6603 (1)	0.7707 (1)	0.39918 (9)	
P(1)	0.4060 (3)	0.5210 (4)	0.2318 (3)	
P(2)	0.6287 (3)	0.5270 (4)	0.4245 (3)	
C(1)	0.6502 (8)	0.500 (1)	0.2738 (7)	
C(2)	0.6019 (8)	0.504 (1)	0.3266 (7)	
C(111)	0.2672 (6)	0.5298 (7)	0.1834 (5)	4.96 (8)
C(112)	0.2928 (6)	0.6516 (7)	0.1952 (5)	4.96 (8)
C(113)	0.1878 (6)	0.6664 (7)	0.1656 (5)	4.96 (8)
C(114)	0.0571 (6)	0.5595 (7)	0.1242 (5)	4.96 (8)
C(115)	0.0315 (6)	0.4377 (7)	0.1124 (5)	4.96 (8)
C(116)	0.1366 (6)	0.4229 (7)	0.1420 (5)	4.96 (8)
C(211)	0.7956 (6)	0.7383 (8)	0.5747 (5)	5.46 (9)
C(212)	0.9249 (6)	0.7829 (8)	0.5990 (5)	5.46 (9)
C(213)	1.0510 (6)	0.9505 (8)	0.7182 (5)	5.46 (9)
C(214)	1.0478 (6)	1.0736 (8)	0.8131 (5)	5.46 (9)
C(215)	0.9185 (6)	1.0290 (8)	0.7888 (5)	5.46 (9)
C(216)	0.7924 (6)	0.8613 (8)	0.6696 (5)	5.46 (9)
C(221)	0.6017 (6)	0.3243 (7)	0.3645 (5)	4.95 (8)
C(222)	0.4651 (6)	0.1541 (7)	0.2641 (5)	4.95 (8)
C(223)	0.4418 (6)	-0.0079 (7)	0.2096 (5)	4.95 (8)
C(224)	0.5548 (6)	0.0003 (7)	0.2557 (5)	4.95 (8)
C(225)	0.6915 (6)	0.1705 (7)	0.3561 (5)	4.95 (8)
C(226)	0.7148 (6)	0.3325 (7)	0.4106 (5)	4.95 (8)
C(3)	0.7747 (5)	0.4976 (7)	0.2906 (4)	4.10 (8)
C(4)	0.7757 (5)	0.3669 (7)	0.2659 (4)	4.10 (8)
C(5)	0.8932 (5)	0.3684 (7)	0.2851 (4)	4.10 (8)
C(6)	1.0096 (5)	0.5004 (7)	0.3289 (4)	4.10 (8)
C(7)	1.0085 (5)	0.6310 (7)	0.3536 (4)	4.10 (8)
C(8)	0.8911 (5)	0.6296 (7)	0.3344 (4)	4.10 (8)
C(13)	0.3912 (9)	0.185 (1)	0.0006 (8)	
O(13)	0.3348 (8)	0.0636 (9)	-0.1023 (6)	
C(14)	0.6969 (9)	0.801 (1)	0.3270 (8)	
O(14)	0.7557 (8)	0.9073 (9)	0.3443 (7)	
C(11)	0.661 (1)	0.466 (1)	0.1180 (8)	
O(11)	0.7261 (8)	0.445 (1)	0.0869 (7)	
C(12)	0.448 (1)	0.487 (1)	0.0720 (8)	
O(12)	0.3908 (9)	0.484 (1)	0.0190 (7)	
C(21)	0.4179 (9)	0.058 (1)	0.0653 (7)	
O(21)	0.4109 (8)	-0.0717 (9)	0.0189 (6)	
C(22)	0.215 (1)	0.080 (1)	0.0308 (8)	
O(22)	0.0983 (9)	-0.028 (1)	-0.0262 (8)	
C(31)	0.286 (1)	0.381 (1)	0.2955 (8)	
O(31)	0.1790 (9)	0.279 (1)	0.2585 (8)	
C(32)	0.477 (1)	0.742 (1)	0.4849 (8)	
O(32)	0.497 (1)	0.878 (1)	0.5692 (7)	
C(41)	0.6505 (9)	0.972 (1)	0.4955 (8)	
O(41)	0.6487 (9)	1.096 (1)	0.5536 (7)	
C(42)	0.853 (1)	0.948 (1)	0.5381 (8)	
O(42)	0.9671 (8)	1.064 (1)	0.6249 (7)	

are few examples in which a monophosphinoalkyne behaves as a bridging ligand,[11,12] compound I is a very rare example of a bridging phosphinoacetylide.

Each dinuclear subunit is similar to known σ-π-acetylide bimetallic derivatives with a phosphido bridge resulting from the rupture of a monophosphinoalkyne: [Fe$_2$(CO)$_6(\mu$-PPh$_2)(\mu_2,\eta$-C≡CR)][13] or [Fe$_2$(CO)$_5$(PPh$_3$)$(\mu$-PPh$_2)\mu_2,\eta$-C≡CR)].[14] Several μ_2,η-acetylides of ruthenium have been described. These include binuclear [Ru$_2$(CO)$_6(\mu$-PPh$_2)(\mu_2,\eta$-C≡CR)],[3,15] trinuclear [Ru$_3$(CO)$_6(\mu$-PPh$_2)(\mu$-C≡C-t-Bu)(μ_2,η-C≡C-t-Bu)(Ph$_2$PC≡C-t-Bu)],[16] and tetranuclear [Ru$_4$(CO)$_8(\mu$-PPh$_2)($\mu_2,\eta$-C≡C-$t$-Bu)($\mu_3,\eta$-C≡C-$t$-Bu)(Ph$_2$PC≡C-$t$-Bu)] and [Ru$_4(CO)_{13}(\mu$-PPh$_2)(μ_2,η-C≡C-t-Bu)].[17] Bond distances and angles (Table IV) in the acetylide–metal framework compare favorably with those observed in [Ru$_2$(CO)$_5(\mu$-PPh$_2)($\mu_2,\eta$-C≡C-$i$-Pr)($i$-PrC≡CPPh$_2$)].[3]

The most unusual feature is the coordination about Ru(1). This metal is approximately octahedrally coordi-

nated by two CO ligands, two phosphorus atoms, P(1) of the phosphido bridge and P(2) of the phosphinoacetylide of the second dinuclear unit, Ru(2) and the triple bond of the first phosphinoacetylide. Both phosphorus atoms are approximately trans to each other with a P(1)–Ru(1)–P(2) angle equal to 155.3 (2)°. The Ru(1)–P(2) distance of 2.379 (5) Å appears identical with the Ru–P bond length of 2.356 (1) Å observed in [Ru$_2$(CO)$_5(\mu$-PPh$_2)($\mu_2,\eta$-C≡C-$i$-Pr)($i$-PrC≡CPPh$_2$)][3] or 2.383 (5) Å in [FeRu$_2(\mu$-Cl)$_2$(CO)$_8$-(Ph$_2$PC≡C-t-Bu)].[18]

It is worthy of note that in the diiron compound [Fe$_2$(CO)$_5$(PPh$_3$)$(\mu$-PPh$_2)(\mu_2,\eta$-C≡CPh)][14] as well as in [Ru$_2$(CO)$_5(\mu$-PPh$_2)($\mu_2,\eta$-C≡C-$i$-Pr)($i$-PrC≡CPPh$_2$)][3] the phosphorus atom of the triphenylphosphine or of the acetylene ligand is coordinated to the metal atom σ-bonded to the acetylide whereas in the title compound the phosphorus of the phosphinoacetylide ligand is bound to the

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Table IV. Bond Distances (Å) and Bond Angles (deg) with Esd's in Parentheses for Compound I

Bond Distances

Ru(1)–Ru(2)	2.806 (3)		
Ru(1)–P(1)	2.339 (5)	Ru(2)–P(1)	2.355 (5)
Ru(1)–P(2)	2.379 (5)	Ru(2)–C(1)	2.06 (2)
Ru(1)–C(1)	2.28 (1)	Ru(2)–C(21)	1.92 (2)
Ru(1)–C(2)	2.38 (2)	Ru(2)–C(22)	1.94 (2)
Ru(1)–C(11)	1.86 (2)	Ru(2)–C(23)	1.94 (2)
Ru(1)–C(12)	1.89 (2)		
		C(1)–C(2)	1.24 (3)
C(11)–O(11)	1.13 (2)	P(2)–C(2)	1.74 (2)
C(12)–O(12)	1.12 (3)		
		C(21)–O(21)	1.10 (2)
		C(22)–O(22)	1.12 (3)
		C(23)–O(23)	1.14 (2)

Bond Angles

C(11)–Ru(1)–C(12)	95.9 (8)	C(21)–Ru(2)–C(22)	96.6 (8)
C(11)–Ru(1)–P(1)	88.3 (5)	C(21)–Ru(2)–C(23)	98.4 (8)
C(11)–Ru(1)–P(2)	90.2 (5)	C(21)–Ru(2)–P(1)	99.9 (6)
C(11)–Ru(1)–C(1)	141.0 (7)	C(21)–Ru(2)–C(1)	107.3 (7)
C(11)–Ru(1)–C(2)	171.7 (7)	C(21)–Ru(2)–Ru(1)	147.1 (6)
C(11)–Ru(1)–Ru(2)	95.0 (5)	C(22)–Ru(2)–C(23)	92.6 (8)
C(12)–Ru(1)–P(1)	106.6 (6)	C(22)–Ru(2)–P(1)	160.9 (6)
C(12)–Ru(1)–P(2)	98.0 (6)	C(22)–Ru(2)–C(1)	89.0 (7)
C(12)–Ru(1)–C(1)	122.0 (8)	C(22)–Ru(2)–Ru(1)	108.1 (6)
C(12)–Ru(1)–C(2)	92.2 (7)	C(23)–Ru(2)–P(1)	94.5 (6)
C(12)–Ru(1)–Ru(2)	157.0 (6)	C(23)–Ru(2)–C(1)	153.9 (7)
P(1)–Ru(1)–P(2)	155.3 (2)	C(23)–Ru(2)–Ru(1)	101.7 (5)
P(1)–Ru(1)–C(1)	73.2 (4)	P(1)–Ru(2)–C(1)	76.9 (4)
P(1)–Ru(1)–C(2)	87.9 (4)	P(1)–Ru(2)–Ru(1)	53.0 (1)
P(1)–Ru(1)–Ru(2)	53.6 (1)	C(1)–Ru(2)–Ru(1)	53.4 (4)
P(2)–Ru(1)–C(1)	93.1 (4)		
P(2)–Ru(1)–C(2)	90.2 (4)	Ru(2)–C(21)–O(21)	177.7 (1.7)
P(2)–Ru(1)–Ru(2)	102.1 (2)	Ru(2)–C(22)–O(22)	173.4 (1.9)
C(1)–Ru(1)–C(2)	30.8 (6)	Ru(2)–C(23)–O(23)	177.3 (1.5)
C(1)–Ru(1)–Ru(2)	46.4 (4)		
C(2)–Ru(1)–Ru(2)	76.9 (4)	Ru(2)–C(1)–C(2)	157.4 (1.2)
		C(1)–C(2)–P'(2)	153.2 (1.3)
Ru(1)–C(11)–O(11)	179.3 (1.5)		
Ru(1)–C(12)–O(12)	172.2 (1.8)	Ru(1)–P(2)–C'(2)	113.2 (6)
		Ru(1)–P(2)–C(211)	117.8 (5)
Ru(1)–P(1)–Ru(2)	73.4 (1)	Ru(1)–P(2)–C(221)	118.2 (5)
Ru(1)–P(1)–C(111)	123.6 (4)	C'(2)–P(2)–C(211)	101.3 (7)
Ru(1)–P(1)–C(121)	119.3 (4)	C'(2)–P(2)–C(221)	102.3 (7)
Ru(2)–P(1)–C(111)	119.1 (4)	C(211)–P(2)–C(221)	101.6 (6)
Ru(2)–P(1)–C(121)	121.6 (4)		
C(111)–P(1)–C(121)	100.4 (5)		

Table V. Bond Distances (Å) with Esd's in Parentheses for Compound II

Ru(1)–Ru(4)	2.713 (2)	Ru(2)–Ru(3)	2.912 (2)
Ru(1)–Ru(2)	2.725 (3)	Ru(3)–Ru(4)	2.917 (3)
Ru(1)–Ru(3)	4.171 (3)	Ru(2)–Ru(4)	3.707 (1)
Ru(1)–C(1)	2.24 (2)	Ru(2)–C(2)	2.310 (8)
Ru(2)–C(1)	2.359 (7)	Ru(3)–C(2)	2.06 (1)
Ru(4)–C(1)	2.35 (1)	Ru(4)–C(2)	2.40 (1)
Ru(1)–P(1)	2.500 (6)	Ru(3)–P(1)	2.330 (7)
Ru(2)–P(1)	2.466 (5)	Ru(4)–P(1)	2.443 (3)
Ru(3)–P(2)	2.302 (6)	P(2)–C(2)	1.78 (2)
C(1)–C(2)	1.40 (2)	C(1)–C(3)	1.50 (2)
P(2)–C(211)	1.795 (5)	P(2)–C(221)	1.83 (1)
P(1)–C(111)	1.81 (1)	P(1)–C(2)	2.84 (2)
Ru(1)–C(13)	2.198 (8)	Ru(2)–C(13)	2.02 (2)
Ru(1)–C(14)	2.175 (8)	Ru(4)–C(14)	2.00 (2)
C(13)–O(13)	1.17 (2)	C(14)–O(14)	1.18 (2)
Ru(1)–C(11)	1.90 (2)	Ru(3)–C(31)	1.84 (1)
Ru(1)–C(12)	1.92 (2)	Ru(3)–C(32)	1.87 (1)
Ru(2)–C(21)	1.88 (1)	Ru(4)–C(41)	1.88 (1)
Ru(2)–C(22)	1.85 (1)	Ru(4)–C(42)	1.900 (9)
C(11)–O(11)	1.14 (2)	C(31)–O(31)	1.19 (2)
C(12)–O(12)	1.11 (3)	C(32)–O(32)	1.16 (1)
C(21)–O(21)	1.15 (2)	C(41)–O(41)	1.12 (2)
C(22)–O(22)	1.14 (1)	C(42)–O(42)	1.14 (1)

Table VI. Bond Angles (deg) with Esd's in Parentheses for Compound II

C(11)–Ru(1)–C(12)	89.4 (7)	C(31)–Ru(3)–C(32)	88.1 (6)
C(11)–Ru(1)–C(14)	92.1 (5)	C(31)–Ru(3)–C(2)	137.1 (5)
C(11)–Ru(1)–C(13)	89.5 (5)	C(31)–Ru(3)–P(2)	112.1 (6)
C(11)–Ru(1)–C(1)	94.7 (7)	C(31)–Ru(3)–P(1)	108.1 (6)
C(11)–Ru(1)–P(1)	174.0 (6)	C(31)–Ru(3)–Ru(2)	97.7 (4)
		C(31)–Ru(3)–C(2)	131.1 (4)
C(12)–Ru(1)–C(14)	91.2 (6)	C(32)–Ru(3)–P(2)	106.6 (5)
		C(32)–Ru(3)–P(1)	106.4 (7)
C(12)–Ru(1)–C(1)	175.7 (6)	C(2)–Ru(3)–P(2)	47.8 (5)
C(12)–Ru(1)–P(1)	96.3 (5)	C(2)–Ru(3)–P(1)	80.3 (5)
C(14)–Ru(1)–C(13)	178.2 (6)	P(2)–Ru(3)–P(1)	128.0 (2)
C(14)–Ru(1)–C(1)	89.5 (5)	Ru(2)–Ru(3)–Ru(4)	78.98 (6)
C(14)–Ru(1)–P(1)	89.5 (4)		
C(13)–Ru(1)–C(1)	91.0 (5)	C(41)–Ru(4)–C(14)	93.9 (7)
C(13)–Ru(1)–P(1)	88.9 (4)	C(41)–Ru(4)–P(1)	96.2 (3)
C(1)–Ru(1)–P(1)	76.5 (4)	C(42)–Ru(4)–C(14)	95.8 (7)
Ru(4)–Ru(1)–Ru(2)	85.95 (8)	C(42)–Ru(4)–P(1)	168.2 (7)
		C(14)–Ru(4)–P(1)	95.6 (3)
C(22)–Ru(2)–C(21)	86.5 (6)	Ru(1)–Ru(4)–Ru(3)	95.56 (5)
C(22)–Ru(2)–C(13)	96.3 (7)		
C(22)–Ru(2)–P(1)	95.1 (4)	C(111)–P(1)–Ru(3)	122.8 (5)
C(21)–Ru(2)–C(13)	94.9 (7)	C(111)–P(1)–Ru(4)	130.2 (3)
C(21)–Ru(2)–P(1)	170.6 (5)	C(111)–P(1)–Ru(2)	130.3 (2)
C(13)–Ru(2)–P(1)	94.2 (4)	C(111)–P(1)–Ru(1)	117.7 (5)
Ru(1)–Ru(2)–Ru(3)	95.38 (6)	Ru(3)–P(1)–Ru(4)	75.3 (2)
		Ru(3)–P(1)–Ru(2)	74.7 (2)
C(211)–P(2)–C(221)	109.2 (8)	Ru(3)–P(1)–Ru(1)	119.4 (2)
C(211)–P(2)–Ru(3)	122.3 (4)	Ru(4)–P(1)–Ru(2)	98.1 (2)
C(221)–P(2)–Ru(3)	]25.9 (2)	Ru(4)–P(1)–Ru(1)	66.6 (1)
C(2)–P(2)–C(211)	114.3 (6)	Ru(2)–P(1)–Ru(1)	66.6 (1)
C(2)–P(2)–C(221)	114.6 (5)		
C(2)–P(2)–Ru(3)	59.1 (4)	C(1)–C(2)–P(2)	148 (1)
		C(1)–C(2)–Ru(3)	138 (1)
C(2)–C(1)–C(3)	118 (1)	P(2)–C(2)–Ru(3)	73.1 (6)
C(2)–C(1)–Ru(1)	122.3 (9)	P(2)–C(2)–P(1)	127.0 (6)
C(3)–C(1)–Ru(1)	119 (1)		
		O(11)–C(11)–Ru(1)	178.2 (5)
O(13)–C(13)–Ru(1)	134 (2)	O(12)–C(12)–Ru(1)	180 (1)
O(13)–C(13)–Ru(2)	145 (1)	O(31)–C(31)–Ru(3)	177 (1)
Ru(2)–C(13)–Ru(1)	80.5 (3)	O(32)–C(32)–Ru(3)	176 (2)
O(14)–C(14)–Ru(4)	146.5 (8)	O(21)–C(21)–Ru(2)	172.9 (8)
O(14)–C(14)–Ru(1)	132 (1)	O(22)–C(22)–Ru(2)	177 (2)
Ru(4)–C(14)–Ru(1)	81.0 (6)	O(41)–C(41)–Ru(4)	177 (2)
		O(42)–C(42)–Ru(4)	176 (1)

ruthenium π-bonded to the triple bond. This result is somewhat surprising. Indeed it is known that phosphines and phosphites preferentially attack the α-carbon of the acetylide at room temperature and that a rearrangement occurs on heating. Carty et al. explained in such a way the fact that PPh$_3$ reacts on [Fe$_2$(CO)$_6$(μ-PPh$_2$)(μ_2,η-C≡CR)][13] by substituting eventually a CO bonded to the iron atom σ-bonded to the acetylide. If [Ru$_2$(CO)$_5$(μ-PPh$_2$)(μ_2,η-C≡CPPh$_2$)], i.e., the half unit of the title compound, were to be attacked by the free phosphino group, it might be expected that the same reaction would occur since ruthenium has a lower electronegativity than iron. This is not the case and the expected electronic effect might be overwhelmed by steric constraints since the same ring as in [Fe$_2$(CO)$_6$(Ph$_2$PC≡CPPh$_2$)][11] has been observed. If the phosphino group in the title compound were attached to the ruthenium σ-bonded to the acetylide, not only would a strain occur in the ring but also both acetylides would be nearly parallel and very close to each other. Such an arrangement would be sterically disfavored.

Compound II. The crystal structure of compound II consists of discrete tetranuclear clusters separated by van der Waals distances. A view of the molecule with the labelling scheme is shown in Figure 2. Distances and angles for a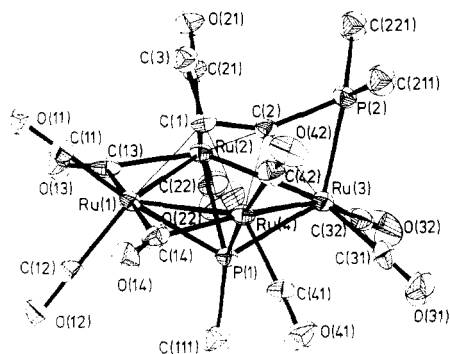ll atoms but the rigid groups are given in Tables V and VI. The geometry presents several interesting features: a flattened "butterfly" arrangement of the four ruthenium atoms, a monophosphinoethyne σ-π bonded to the four Ru atoms with its phosphino group building a triangular ring $\overline{\text{Ru-P-C}}$ on one side of the "butterfly" and

Figure 2.

a phosphinidene group which caps the other side.

In the cluster the four ruthenium–ruthenium bonds make a slightly folded square with two nonbonding diagonals: Ru(1)–Ru(3) = 4.171 (3) Å and Ru(2)–Ru(4) = 3.707 (1) Å. The dihedral angle between the planes defined by Ru(1)–Ru(2)–Ru(3) and Ru(1)–Ru(4)–Ru(2) is 157.1 (9)°. Among the ten carbonyl groups, eight are terminally bonded to ruthenium atoms and two are bridging CO groups. Those two CO groups bridge the two corresponding metal–metal distances (2.725 (3) and 2.713 (2) Å) which have the normal values.[19] The two other Ru–Ru bond lengths are longer but not anomalously long for a nearly square-planar cluster; indeed a flattening of the butterfly geometry and an increase in the nonbonding Ru–Ru distances are accompanied by a lengthening of the ruthenium–ruthenium distances as was noted by Carty et al.[17]

These four ruthenium atoms are capped on one side by the alkyne which might be regarded as σ-bonded to Ru(1) and Ru(3) and π-bonded to Ru(2) and Ru(4). This alkyne is not symmetrically bonded to Ru(1) and Ru(3): Ru-(1)–C(1) = 2.24 (2) Å and Ru(3)–C(2) = 2.06 (1) Å. This last bond looks very short and might be compared to the carbene bond in [(C₅H₅)₂Ru₂(CO)₂(C₂(CH₃)₂CHO)], 2.080 (4) Å.[20] This asymmetry is also reflected in the angle between C(1)–C(2) and Ru(1)–Ru(3) (7.7°). The π-bonded Ru–C distances (mean value 2.36 Å) are longer than the usual 2.27 Å average observed in other ruthenium π-complexes; however, this is not accompanied by a noticeable change in the C(1)–C(2) bond, 1.40 (2) Å, which is in the range of values for μ₄,η-alkynes.[21,22]

The short Ru(3)–C(2) bond involves the carbon atom attached to a phosphino group ligated to the same ruthenium Ru(3). This phosphorus is part of an unusual three-membered metallocyclic rings with an acute Ru-(3)–P(2)–C(2) angle of 59.1 (4)°. Such three-membered rings are rare; as far as we know, there is one documented

example on a P—C=Ta ring.[5] This acute Ru–P–C angle might be compared with the C–P–C anlge of 41.8 (1)° observed by Mathey et al. in the phosphirene ring[23] insofar as that Ru(3)–C(2) is so short that it may be considered as a carbene. It is remarkable that the P(2)–Ru(3) bond length is quite similar within experimental error to the P(1)–Ru(3) bond length coming from the phosphinidene group although these two phosphorus atoms are structurally quite different. It is also remarkable that P(1)–Ru(3) distance is the shortest among the four P(1)–Ru distances. These two electron-donating groups and the electron-deficient C(2) atom might induce back-donation from ruthenium toward the carbon C(2) and explain the formation of the carbene bond.

A striking feature of the structure is the occurrence of the phosphinidene group which can only come from the original bis(diphenylphosphino)ethyne. Examples of the cleavage of all Ph groups from PPh₃ giving phosphides[24] or the cleavage of two P–Ph groups from a μ-PPh₂ giving a phosphide[25] have been described. Rupture of a P–C bond and migration of a phenyl from phosphino groups to a metal atom has been reported,[26-28] and a model for P–C activation and phenyl group transfer has been characterized.[29] Recently there has been a considerable interest in μ-PR groups as stabilizing face-bridging ligands in cluster chemistry;[30] nevertheless tetranuclear clusters incorporating a μ₄-P(C₆H₅) group and a multisite-bound unsaturated ligand are rare.

Although the sequence of reactions leading to this tetranuclear complex has not yet been investigated, one of the first steps might be the formation of a multisite bound acetylide and a phosphido-bridging group; then conversion of this phosphido group to a phosphinidene by phenyl group transfer to the α-carbon of the acetylide would occur. A similar reaction has been described for the multisite-bound acetylide [Ru₅(CO)₁₃(μ-PPh₂)(μ₄,η-C≡CPh)] which on thermolysis yields as a major product the diphenylacetylene compound [Ru₅(CO)₁₃(μ₄-PPh)(μ₃,η-PhC≡CPh)].[5]

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