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Synthesis and Reactivity of Ruthenium Hydride Complexes of Chelating Triphosphines. 7. X-ray Structures of *syn-mer*-RuCl(η^3-PhC$_3$CHPh)(Cyttp)·$^1/_2$C$_6$H$_6$, *anti-mer*-RuCl(η^3-PhC$_3$CHPh)(Cyttp), and *mer*-Ru(C≡CPh)(η^3-PhC$_3$CHPh)(Cyttp)[1]

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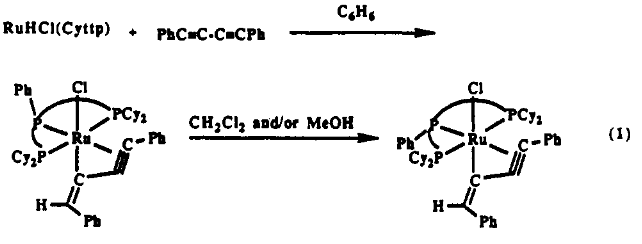
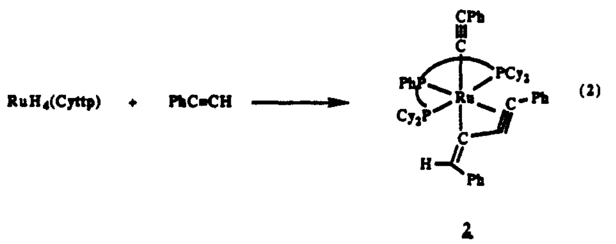
The structures of *syn-mer*-RuCl(η^3-PhC$_3$CHPh)(Cyttp) (**1A**) (Cyttp = PhP(CH$_2$CH$_2$CH$_2$P(C$_6$H$_{11}$)$_2$)$_2$), *anti-mer*-RuCl(η^3-PhC$_3$CHPh)(Cyttp) (**1B**), and *mer*-Ru(C≡CPh)(η^3-PhC$_3$CHPh)(Cyttp) (**2**) have been determined by X-ray diffraction. **1A** crystallizes in space group $P2_1/c$ with cell constants a = 11.218 (3) Å, b = 21.911 (3) Å, c = 20.252 (3) Å; β = 91.09 (2)°; V = 4977 Å^3; Z = 4; and $R(F)$ = 0.030 and $R_w(F)$ = 0.037 for the 6731 intensities with $F_o^2 > 3\sigma(F_o^2)$ and the 542 variables. **1B** crystallizes in space group $P\bar{1}$ with cell constants a = 12.131 (1) Å, b = 18.715 (2) Å, c = 11.495 (1) Å; α = 103.91 (1)°, β = 105.06 (1)°, γ = 99.13 (1)°; V = 2377 Å^3; Z = 2; and $R(F)$ = 0.035 and $R_w(F)$ = 0.042 for the 6080 intensities with $F_o^2 > 3\sigma(F_o^2)$ and the 536 variables. **2** crystallizes in space group $P\bar{1}$ with cell constants a = 11.566 (3) Å, b = 12.532 (3) Å, c = 19.328 (7) Å; α = 90.49 (3)°, β = 102.42 (3)°, γ = 108.03 (3)°; V = 2593 (1) Å^3; Z = 2; and $R(F)$ = 0.038 and $R_w(F)$ = 0.043 for the 6540 intensities with $F_o > 5\sigma(F_o)$ and the 533 variables. The geometry of the coordination sphere of the compounds about the ruthenium atom is roughly octahedral, and all the compounds contain an η^3-PhC$_3$CHPh ligand. The triphosphine is meridional around ruthenium. The phenyl group on the central phosphorus atom P(2) is on the same side of the Cyttp ligand as the chloride in **1A** and on the same side of the Cyttp as the vinyl group in **1B** and **2**. The acetylenic group is more strongly bound to ruthenium in **1B** and **2** than in **1A**.

Introduction

In the previous paper,[3] we reported that two isomers of RuCl(η^3-PhC$_3$CHPh)(Cyttp) (Cyttp = PhP(CH$_2$CH$_2$CH$_2$P(C$_6$H$_{11}$)$_2$)$_2$) were obtained from the reaction of RuHCl (Cyttp) and 1,4-diphenylbutadiyne (PhC≡CC≡CPh) (eq 1) and that Ru(C≡CPh)(η^3-PhC$_3$CHPh)(Cyttp) was produced from the reaction of RuH$_4$(Cyttp) and excess phenylacetylene (eq 2). The spectroscopic data alone for the new complexes did not provide enough information to define their structures. Thus, X-ray diffraction studies were carried out on *syn-mer*-RuCl(PhC$_3$CHPh)(Cyttp) (**1A**), *anti-mer*-RuCl(PhC$_3$CHPh)(Cyttp) (**1B**), and Ru(C≡CPh)(PhC$_3$CHPh)(Cyttp) (**2**). These compounds contain the novel ligand η^3-PhC$_3$CHPh. The only X-ray-characterized compounds for this type of complex that we are aware of is [Os(η^3-PhC$_3$CHPh)(PMe$_3$)$_4$]PF$_6$, which was produced from the reaction of *cis*-Os(C≡CPh)$_2$(PMe$_3$)$_4$ with AgPF$_6$.[4] We herein report the structural studies of the ruthenium complexes.



1A **1B**



2

Experimental Section

Crystallographic Analysis of *syn-mer*-RuCl(η^3-PhC$_3$CHPh)(Cyttp)·$^1/_2$C$_6$H$_6$ (1A). X-ray-quality crystals of the compound were obtained by slow diffusion of Et$_2$O into a saturated benzene solution of *syn-mer*-RuCl(η^3-PhC$_3$CHPh)(Cyttp).[3] The clear crystal used for data collection was red and had well-formed faces. It was coated with a thin layer of epoxy as a precaution against possible air sensitivity. Examination of the diffraction pattern on a Rigaku AFC5 diffractometer revealed a monoclinic crystal system with a uniquely determined space group, $P2_1/c$. The cell constants a = 11.218 (3) Å, b = 21.911 (3) Å, c = 20.252 (3) Å, and β = 91.09 (2)° were determined by a least-squares fit of the diffractometer setting angles for 25 reflections in the 2θ range 29–30° with Mo Kα radiation.

Intensities were measured by the ω–2θ scan method. Six standard reflections were measured after every 150 reflections and indicated that the crystal was stable during the course of data collection. Data reduction and all subsequent calculations were done with the TEXSAN package of crystallographic programs.[5]

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[1] Part 6: Jia, G., Meek, D. W. Submitted for publication in *Inorg. Chem.*

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[3] Jia, G.; Meek, D. W. *Organometallics*, in press.

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Table I. Crystallographic Details for the Ru(Cyttp) Complexes

	1A	1B	2
formula	$C_{52}H_{72}ClP_3Ru\cdot{}^1/_2C_6H_6$	$C_{52}H_{72}ClP_3Ru$	$C_{60}H_{77}P_3Ru$
fw	965.64	926.59	992.26
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a, Å	11.218 (3)	12.131 (1)	11.566 (3)
b, Å	21.911 (3)	18.715 (2)	12.532 (3)
c, Å	20.252 (3)	11.495 (1)	19.328 (7)
α, deg		103.91 (1)	90.49 (3)
β, deg	91.09 (2)	105.06 (1)	102.42 (3)
γ, deg		99.13 (1)	108.03 (3)
V, Å^3	4977	2377	2593 (1)
Z	4	2	2
d_{calcd}, g/cm^3	1.29	1.29	1.23
cryst size, mm	0.38 × 0.42 × 0.42	0.15 × 0.23 × 0.38	0.22 × 0.29 × 0.36
radiation	Mo Kα with graphite monochromator	Mo Kα with graphite monochromator	Mo Kα with graphite monochromator
linear abs coeff, cm^{-1}	4.91	5.11	4.2
T, °C	22	23	23
scan type	ω–2θ	ω–2θ	ω–2θ
2θ limits, deg	$4 \le 2\theta \le 50$	$4 \le 2\theta \le 50$	$4 \le 2\theta \le 48$
scan speed, deg min^{-1}	4 in ω, max of 4 scans/ref	8 in ω, max of 4 scans/ref	variable, 7–20
scan range	$(0.95 + 0.35 \tan\theta)°$ in ω	$(1.20 + 0.35 \tan\theta)°$ in ω	
data collected	$+h,+k,\pm l$	$+h,\pm k,\pm l$	$\pm h,\pm k,+l$
no. of unique data	9031	8373	8142
no. of data used in refinement	6731 ($F_o^2 > 3\sigma(F_o^2)$)	6080 ($F_o^2 > 3\sigma(F_o^2)$)	6540 ($F_o > 5\sigma(F_o)$)
final no. of variables	542	536	533
$R(F)$[a]	0.030	0.035	0.038
$R_w(F)$[b]	0.037	0.042	0.043
goodness of fit	1.42	1.29	1.27

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F) = [\sum_w(|F_o| - |F_c|)^2/\sum_w|F_o|^2]^{1/2}$ with $w = 1/\sigma^2(F_o)$.

Since the crystal is approximately equidimensional and the absorption coefficient is small, no absorption correction was added to the data.

The position of the Ru atom was located by Patterson methods. This Ru atom was then used as a phasing model in the DIRDIF procedure,[6] and a major portion of the rest of the molecule was located on an electron density map. The remainder of the missing atoms were located by standard Fourier methods. During the course of isotropic refinement it was discovered that a benzene solvent molecule had cocrystallized with the Ru complex. With a crystallographic inversion center located at its center, there is half of a benzene molecule in the asymmetric unit. After the benzene molecule was introduced into the model and refined isotropically, the difference electron density map revealed peaks with substantial electron density located approximately at the midpoints of the C–C bonds. This was interpreted as an alternate position for the benzene and was then included in the model with the two positions each assigned an occupancy factor of 0.5. This disorder model for the benzene, with the two molecules labeled as C(53A), C(54A), C(55A) and C(53B), C(54B), C(55B), is kept at the isotropic level for the remainder of the least-squares refinements. After a cycle of anisotropic refinement of the ruthenium complex, most of the hydrogen atoms were located on a difference electron density map, including the hydrogen atom bonded to C(4). The hydrogen atoms of the ruthenium complex were included in the model as fixed contributions in their calculated positions with d(C–H) = 0.98 Å and $B_H = 1.2B_{C(eq)}$. In the final stages of refinement the H(1) atom bonded to C(4) was allowed to refine isotropically. No hydrogen atoms were added to the disordered benzene solvent molecule. The final refinement cycle for the 6731 intensities with $F_o^2 > 3\sigma(F_o^2)$, and the 542 variables yielded agreement indices of $R(F)$ = 0.030 and $R_w(F)$ = 0.037. The final difference electron density map contains maximum and minimum peak heights of 0.36 and –0.32 e/Å^3. Scattering factors for neutral atoms, including terms for anomalous scattering, are from the usual sources.[7] Further crystallographic details are given in Table I. Final atomic coordinates and selected bond lengths and bond angles are presented in Tables II and III, respectively.

Crystallographic Analysis of *anti-mer*-RuCl(η^3-PhC$_3$CHPh)(Cyttp) (1B). X-ray-quality crystals of the compound were obtained by slow evaporation of solvents from a saturated CH_2Cl_2/MeOH solution of RuCl(η^3-PhC$_3$CHPh)(Cyttp).[3] The crystal used for data collection was a clear, orange-red rod with well-formed faces. The crystal system is triclinic, and the space group possibilities are $P1$ or $P\bar{1}$. The cell constants a = 12.131 (1) Å, b = 18.715 (2) Å, c = 11.495 (1) Å, α = 103.91 (1)°, β = 105.06 (1)°, and γ = 99.13 (1)° were determined by a least-squares fit of the diffractometer setting angles for 25 reflections in the 2θ range 20–30° with Mo Kα radiation.

Intensities were measured by the ω–2θ scan method. Six standard reflections were measured after every 150 reflections and indicated that the crystal was stable throughout data collection. Data reduction and all subsequent calculations were done with the TEXSAN package of crystallographic programs.[5] No absorption correction was applied to the data.

The structure was solved and refined in the space group $P\bar{1}$. The position of the Ru atom was located by Patterson methods. The Ru atom was used as a phasing model in the DIRDIF procedure,[6] and most of the rest of the molecule was located in the electron density map. The missing atoms, which are five carbon atoms from one cyclohexyl ring, were subsequently located by standard Fourier methods. During the course of isotropic refinement it was discovered that this cyclohexyl ring is disordered. Atoms C(35), C(37), C(38), and C(40) of this ring essentially lie in a plane, and since the ring is in the chair form, atom C(36) can be considered to be above this plane with C(39) lying below it.

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(5) TEXSAN, TEXRAY Structure Analysis Package, version 2.1, Molecular Structure Corp., College Station, TX 1987.

(6) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; Van der Hark, Th. E. M.; Prick, P. A. J.; Noordik, J. H.; Beurskens, G.; Parthasarathi, V.; Haltiwanger, R. C.; Bruins Slot, H. J. DIRDIF: Direct Methods for Difference Structures—an Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors. Technical Report 1984/1; Crystallography Laboratory: Toernooiveld, 6525 Ed Nijmegen, The Netherlands.

(7) Scattering factors for the non-hydrogen atoms and anaomalous dispersion terms are from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 71 and 148. The scattering factor for the hydrogen atom is from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters for 1A[a]

atom	x	y	z	B(eq), Å^2
Ru	0.60471 (2)	0.06581 (1)	0.25005 (1)	2.33 (1)
Cl	0.79503 (6)	0.07977 (3)	0.31316 (4)	3.44 (3)
P(1)	0.69886 (6)	0.00259 (3)	0.16822 (3)	2.51 (3)
P(2)	0.52726 (6)	−0.02041 (3)	0.29292 (4)	2.92 (3)
P(3)	0.52022 (7)	0.12263 (3)	0.34083 (4)	2.94 (3)
C(1)	0.6411 (3)	0.1596 (1)	0.1780 (1)	3.4 (1)
C(2)	0.5453 (2)	0.1335 (1)	0.1741 (1)	2.6 (1)
C(3)	0.4636 (2)	0.0864 (1)	0.1891 (1)	2.5 (1)
C(4)	0.3524 (3)	0.0779 (1)	0.1663 (1)	3.0 (1)
C(5)	0.6102 (3)	−0.0627 (1)	0.1379 (1)	3.5 (1)
C(6)	0.5565 (3)	−0.1047 (1)	0.1887 (2)	4.0 (2)
C(7)	0.4637 (3)	−0.0731 (1)	0.2309 (2)	3.5 (1)
C(8)	0.3962 (3)	−0.0086 (1)	0.3442 (2)	3.8 (1)
C(9)	0.4236 (3)	0.0191 (2)	0.4118 (2)	4.6 (2)
C(10)	0.5106 (3)	0.0732 (1)	0.4146 (1)	3.8 (1)
C(11)	0.7347 (2)	0.0381 (1)	0.0872 (1)	2.7 (1)
C(12)	0.6207 (3)	0.0538 (1)	0.0475 (1)	3.4 (1)
C(13)	0.6487 (3)	0.0937 (2)	−0.0112 (1)	4.1 (2)
C(14)	0.7309 (3)	0.0602 (2)	−0.0573 (1)	4.5 (2)
C(15)	0.8426 (3)	0.0386 (2)	−0.0209 (2)	4.7 (2)
C(16)	0.8157 (3)	0.0019 (2)	0.0411 (1)	3.8 (1)
C(17)	0.8392 (2)	−0.0317 (1)	0.2020 (1)	2.9 (1)
C(18)	0.9457 (2)	0.0115 (1)	0.1994 (1)	3.3 (1)
C(19)	1.0452 (3)	−0.0112 (2)	0.2455 (2)	4.4 (2)
C(20)	1.0831 (3)	−0.0753 (2)	0.2270 (2)	5.1 (2)
C(21)	0.9779 (3)	−0.1188 (2)	0.2240 (2)	5.4 (2)
C(22)	0.8769 (3)	−0.0953 (1)	0.1786 (2)	4.3 (2)
C(23)	0.6140 (3)	−0.0743 (1)	0.3453 (2)	3.5 (1)
C(24)	0.7188 (3)	−0.0578 (1)	0.3761 (2)	4.2 (2)
C(25)	0.7827 (3)	−0.0991 (2)	0.4148 (2)	5.3 (2)
C(26)	0.7441 (4)	−0.1569 (2)	0.4231 (2)	5.7 (2)
C(27)	0.6410 (4)	−0.1747 (2)	0.3925 (3)	7.8 (3)
C(28)	0.5752 (4)	−0.1341 (2)	0.3543 (2)	7.0 (2)
C(29)	0.5992 (3)	0.1916 (1)	0.3759 (1)	3.5 (1)
C(30)	0.6901 (3)	0.1785 (2)	0.4322 (2)	4.6 (2)
C(31)	0.7537 (4)	0.2367 (2)	0.4551 (2)	5.6 (2)
C(32)	0.8135 (3)	0.2694 (2)	0.3987 (2)	5.6 (2)
C(33)	0.7234 (3)	0.2843 (2)	0.3444 (2)	4.7 (2)
C(34)	0.6594 (3)	0.2272 (1)	0.3206 (1)	3.7 (1)
C(35)	0.3646 (3)	0.1508 (1)	0.3288 (1)	3.4 (1)
C(36)	0.2950 (3)	0.1628 (2)	0.3921 (2)	4.9 (2)
C(37)	0.1647 (3)	0.1778 (2)	0.3754 (2)	6.3 (2)
C(38)	0.1539 (3)	0.2318 (2)	0.3294 (2)	6.3 (2)
C(39)	0.2255 (3)	0.2226 (2)	0.2674 (2)	5.2 (2)
C(40)	0.3552 (3)	0.2073 (1)	0.2841 (2)	3.9 (1)
C(41)	0.2880 (3)	0.1135 (1)	0.1149 (1)	3.1 (1)
C(42)	0.1642 (3)	0.1113 (2)	0.1116 (2)	4.4 (2)
C(43)	0.1001 (3)	0.1429 (2)	0.0634 (2)	5.6 (2)
C(44)	0.1576 (4)	0.1761 (2)	0.0168 (2)	5.6 (2)
C(45)	0.2801 (3)	0.1792 (2)	0.0190 (2)	4.8 (2)
C(46)	0.3447 (3)	0.1484 (1)	0.0677 (2)	3.9 (1)
C(47)	0.7277 (3)	0.2062 (1)	0.1646 (1)	3.2 (1)
C(48)	0.6908 (3)	0.2608 (2)	0.1366 (2)	4.4 (2)
C(49)	0.7715 (4)	0.3067 (2)	0.1236 (2)	5.4 (2)
C(50)	0.8897 (4)	0.2985 (2)	0.1380 (2)	5.3 (2)
C(51)	0.9274 (3)	0.2452 (2)	0.1656 (2)	5.6 (2)
C(52)	0.8479 (3)	0.1994 (2)	0.1799 (2)	4.4 (2)
C(53A)	0.964 (1)	0.0478 (4)	0.4567 (7)	5.1 (2)*
C(53B)	0.999 (1)	0.0301 (5)	0.4399 (4)	4.3 (2)*
C(54A)	0.897 (1)	0.0410 (6)	0.5125 (8)	6.6 (3)*
C(54B)	0.920 (1)	0.0433 (5)	0.4884 (8)	6.0 (3)*
C(55A)	1.063 (1)	0.0095 (7)	0.4442 (5)	6.0 (2)*
C(55B)	0.9174 (9)	0.0168 (7)	0.5518 (6)	5.8 (2)*
H(1)	0.309 (2)	0.046 (1)	0.185 (1)	2.6 (6)*

[a] $B(\mathrm{eq}) = {}^{8}/_{3}\pi^2\sum_i\sum_j U_{ij}a_i^*a_j^*a_i{\cdot}a_j$. Starred atoms were refined isotropically.

Table III. Selected Bond Lengths and Angles for 1A[a]

Bond Lengths (Å)

Ru–P(1)	2.4180 (8)	Ru–P(2)	2.2559 (8)	Ru–P(3)	2.4279 (8)
Ru–Cl	2.4863 (8)	Ru–C(1)	2.558 (3)	Ru–C(2)	2.229 (3)
Ru–C(3)	2.040 (3)	C(1)–C(2)	1.220 (4)	C(1)–C(47)	1.439 (4)
C(2)–C(3)	1.416 (4)	C(3)–C(4)	1.335 (4)	C(4)–H(1)	0.94 (3)
C(4)-C(41)	1.477 (4)				

Bond Angles (deg)

C(3)–Ru–C(2)	38.4 (1)	P(2)–Ru–P(3)	88.81 (3)
C(3)–Ru–P(2)	96.78 (8)	P(2)–Ru–Cl	103.77 (3)
C(3)–Ru–P(1)	93.21 (8)	P(1)–Ru–P(3)	174.04 (3)
C(3)–Ru–P(3)	92.02 (8)	P(1)–Ru–Cl	92.34 (3)
C(3)–Ru–Cl	158.90 (8)	P(3)–Ru–Cl	83.76 (3)
C(2)–Ru–P(2)	135.15 (7)	C(2)–C(1)–C(47)	156.7 (3)
C(2)–Ru–P(1)	92.11 (7)	C(1)–C(2)–C(3)	154.3 (3)
C(2)–Ru–P(3)	93.77 (7)	C(1)–C(2)–Ru	90.9 (2)
C(2)–Ru–Cl	121.04 (7)	C(3)–C(2)–Ru	63.5 (1)
C(1)–Ru–C(2)	28.48 (9)	C(4)–C(3)–C(2)	129.2 (3)
C(1)–Ru–C(3)	66.9 (1)	C(4)–C(3)–Ru	152.6 (2)
C(1)–Ru–P(1)	89.61 (7)	C(2)–C(3)–Ru	78.0 (2)
C(1)–Ru–P(2)	163.28 (7)	C(3)–C(4)–C(41)	127.7 (3)
C(1)–Ru–P(3)	95.08 (7)	C(3)–C(4)–H(1)	117 (2)
C(1)–Ru–Cl	92.83 (7)	C(41)–C(4)–H(1)	115 (2)
P(2)–Ru–P(1)	87.73 (3)		

[a] Estimated standard deviations in the least significant figure are given in parentheses.

The disorder occurs as a result of C(36) having an alternate position below the plane with C(39) then having an alternate position above the plane, such that two different orientations of the cyclohexyl ring are present in the crystal. The disorder model is set up such that the occupancy factor of C(36A), α, is tied to that of its alternate position C(36B), $1-\alpha$. A separate occupancy factor for C(39A), β, is tied to that of C(39B), $1-\beta$. When the refinement of these occupancy factors settled, the average value of α and β, 0.51 (2), was chosen as the final occupancy factor for C(36A) and C(39A) and fixed at that value. The occupancy factors for C(36B) and C(39B) were then fixed at 0.49 each. After a cycle of anisotropic refinement, hydrogen atoms were added as fixed contributions in calculated positions with the assumptions C–H = 0.98 Å and $B_H = 1.2B_{eq}$ (attached carbon atom). One hydrogen atom bonded to C(4) was located on the PhC≡CC═CHPh ligand in a difference electron density map. In the final stages of refinement this hydrogen atom, H(1), was allowed to refine isotropically. The final refinement cycle for the 6080 intensities with $F_o^2 > 3\sigma(F_o^2)$ and the 536 variables resulted in agreement indices of $R(F) = 0.035$ and $R_w(F) = 0.042$. The final difference electron density map contains maximum and minimum peak heights of 0.51 and −0.31 e/Å^3. Scattering factors for neutral atoms, including terms for anomalous scattering, are from the usual sources.[7] Further crystallographic details are given in Table I. Final atomic coordinates and selected bond lengths and bond angles are presented in Tables IV and V, respectively.

Crystallographic Analysis of *mer*-Ru(C≡CPh)(η^3-PhC$_3$CHPh)(Cyttp) (2). X-ray-quality crystals of the compound were obtained by slow evaporation of solvents from a saturated CH_2Cl_2/MeOH solution of *mer*-Ru(C≡CPh)(η^3-PhC$_3$CHPh)(Cyttp).[3] The crystal used for data collection was deep red-orange and was mounted on the end of a glass fiber with epoxy cement. The crystal system is triclinic. The cell constants a = 11.566 (3) Å, b = 12.532 (3) Å, c = 19.328 (7) Å, α = 90.49 (3)°, β = 102.42 (3)°, and γ = 108.03 (3)° were determined by the least-squares fit of 25 reflections ($20° \le 2\theta \le 25°$).

Intensities were measured with use of ω scans. Three standard reflections measured every 197 reflections showed insignificant variation (<1%) in intensity. No absorption correction was applied to the data set (well-shaped crystal, μ = 4.17 cm^{-1}, T_{max}/T_{min} = 1.043).

E statistics suggested the centrosymmetric space group $P\bar{1}$, and this was confirmed by the chemically sensible results of the refinement.

The structure was solved by direct methods that located the ruthenium atom. The remaining non-hydrogen atoms were found through subsequent least-squares and difference Fourier syntheses. All hydrogen atoms were included as idealized isotropic contributions (d(C–H) = 0.960 Å; $U_H = 1.2U_C$ for attached C), and phenyl rings were fixed as rigid hexagons (d(C–C) = 1.345 Å). All non-hydrogen atoms were refined with anisotropic thermal parameters. The final refinement cycle for the 6540 intensities with $F_o > 5\sigma(F_o)$ and 533 variables resulted in agreement indices of $R(F) = 0.0376$ and $R_w(F) = 0.0429$. In the final difference electron density map, the largest peaks (0.50–0.67 e/Å^3) are in the vicinity of carbon atoms 13, 14, and 15 of the cyclohexyl ring. The largest negative peak is −0.39 e/Å^3.

Table IV. Positional Parameters and Equivalent Isotropic Thermal Parameters for 1B[a]

atom	x	y	z	B(eq), Å^2
Ru	0.21267 (3)	0.20234 (2)	0.80788 (3)	2.50 (1)
Cl	0.20663 (9)	0.11658 (5)	0.59983 (8)	3.79 (3)
P(1)	0.00543 (8)	0.14846 (5)	0.77145 (8)	2.98 (3)
P(2)	0.26545 (8)	0.10391 (5)	0.88104 (9)	3.00 (3)
P(3)	0.41550 (8)	0.25645 (5)	0.83695 (9)	2.92 (3)
C(1)	0.1500 (3)	0.2985 (2)	0.7339 (3)	3.1 (1)
C(2)	0.1764 (3)	0.3139 (2)	0.8510 (3)	2.7 (1)
C(3)	0.2154 (3)	0.2913 (2)	0.9587 (3)	2.7 (1)
C(4)	0.2343 (3)	0.3276 (2)	1.0806 (3)	3.1 (1)
C(5)	−0.0380 (3)	0.0448 (2)	0.7286 (4)	3.8 (1)
C(6)	0.0368 (4)	0.0090 (2)	0.8176 (4)	4.1 (1)
C(7)	0.1591 (3)	0.0119 (2)	0.8074 (4)	3.8 (1)
C(8)	0.3888 (3)	0.0709 (2)	0.8392 (4)	3.6 (1)
C(9)	0.5052 (3)	0.1283 (2)	0.8865 (4)	3.9 (1)
C(10)	0.5091 (3)	0.1884 (2)	0.8171 (4)	3.8 (1)
C(11)	−0.1033 (3)	0.1679 (2)	0.6428 (3)	3.6 (1)
C(12)	−0.0832 (3)	0.1408 (2)	0.5143 (3)	4.0 (1)
C(13)	−0.1599 (4)	0.1691 (2)	0.4170 (4)	5.0 (2)
C(14)	−0.2901 (4)	0.1427 (3)	0.4006 (4)	5.8 (2)
C(15)	−0.3123 (4)	0.1650 (3)	0.5269 (4)	5.8 (2)
C(16)	−0.2343 (4)	0.1373 (3)	0.6258 (4)	4.7 (2)
C(17)	−0.0425 (3)	0.1819 (2)	0.9133 (3)	3.1 (1)
C(18)	−0.0757 (3)	0.2588 (2)	0.9268 (3)	3.2 (1)
C(19)	−0.0842 (3)	0.2908 (2)	1.0578 (3)	3.7 (1)
C(20)	−0.1711 (3)	0.2363 (2)	1.0884 (4)	4.0 (1)
C(21)	−0.1460 (4)	0.1585 (2)	1.0686 (4)	4.3 (2)
C(22)	−0.1361 (4)	0.1266 (2)	0.9380 (4)	4.1 (1)
C(23)	0.2955 (3)	0.1075 (2)	1.0481 (3)	3.2 (1)
C(24)	0.2367 (3)	0.1469 (2)	1.1192 (4)	3.9 (1)
C(25)	0.2471 (4)	0.1450 (2)	1.2413 (4)	4.7 (2)
C(26)	0.3186 (4)	0.1051 (3)	1.2966 (4)	5.0 (2)
C(27)	0.3795 (5)	0.0664 (3)	1.2282 (4)	5.8 (2)
C(28)	0.3691 (4)	0.0674 (3)	1.1063 (4)	4.9 (2)
C(29)	0.4993 (3)	0.3275 (2)	0.9927 (3)	3.3 (1)
C(30)	0.5071 (3)	0.2938 (2)	1.1022 (3)	3.9 (1)
C(31)	0.5570 (4)	0.3556 (3)	1.2290 (4)	5.0 (2)
C(32)	0.6790 (4)	0.3992 (3)	1.2430 (4)	5.7 (2)
C(33)	0.6771 (4)	0.4312 (3)	1.1347 (5)	5.6 (2)
C(34)	0.6227 (3)	0.3709 (2)	1.0061 (4)	4.2 (1)
C(35)	0.4450 (5)	0.3064 (2)	0.7229 (5)	5.9 (2)
C(36A)	0.4255 (7)	0.2634 (4)	0.5959 (7)	3.6 (3)
C(36B)	0.520 (1)	0.2960 (6)	0.655 (1)	6.1 (5)
C(37)	0.4911 (5)	0.3165 (3)	0.5280 (5)	6.9 (2)
C(38)	0.4664 (7)	0.3945 (4)	0.5502 (6)	9.4 (3)
C(39A)	0.4831 (9)	0.4319 (5)	0.6763 (9)	4.3 (3)
C(39B)	0.398 (1)	0.4133 (5)	0.621 (1)	5.3 (4)
C(40)	0.4181 (4)	0.3848 (2)	0.7436 (4)	4.4 (2)
C(41)	0.2157 (3)	0.4023 (2)	1.1333 (3)	3.4 (1)
C(42)	0.1803 (4)	0.4504 (2)	1.0625 (4)	4.8 (2)
C(43)	0.1612 (4)	0.5198 (2)	1.1188 (5)	5.9 (2)
C(44)	0.1776 (5)	0.5433 (3)	1.2444 (6)	6.6 (2)
C(45)	0.2126 (5)	0.4982 (3)	1.3168 (5)	6.7 (2)
C(46)	0.2324 (4)	0.4282 (2)	1.2624 (4)	4.9 (2)
C(47)	0.1054 (3)	0.3224 (2)	0.6232 (3)	3.2 (1)
C(48)	0.0522 (4)	0.3829 (2)	0.6339 (4)	4.3 (1)
C(49)	0.0079 (4)	0.4065 (3)	0.5298 (4)	5.2 (2)
C(50)	0.0183 (4)	0.3708 (3)	0.4147 (4)	5.3 (2)
C(51)	0.0713 (4)	0.3112 (3)	0.4037 (4)	4.6 (2)
C(52)	0.1145 (3)	0.2856 (2)	0.5063 (3)	3.8 (1)
H(1)	0.265 (3)	0.304 (2)	1.141 (3)	4.3 (9)*

[a] $B(\mathrm{eq}) = {}^8/_3\pi^2\sum_i\sum_j u_{ij}a_i{}^*a_j{}^*a_i{\cdot}a_j$. Starred atoms were refined isotropically.

All computer programs and the sources of the scattering factors are contained in the SHELXTL (5.1) program library (G. Sheldrick, Nicolet XRD, Madison, WI).

Further crystallographic details are given in Table I. Final atomic coordinates are presented in Table VI and selected bond distances and angles in Table VII.

Table V. Selected Bond Lengths and Angles for 1B[a]

Bond Lengths (Å)

Ru–P(1)	2.441 (1)	Ru–P(2)	2.313 (1)	Ru–P(3)	2.411 (1)
Ru–Cl	2.515 (1)	Ru–C(1)	2.319 (4)	Ru–C(2)	2.169 (3)
Ru–C(3)	2.084 (3)	C(1)–C(2)	1.248 (5)	C(1)–C(47)	1.450 (5)
C(2)–C(3)	1.396 (5)	C(3)–C(4)	1.343 (5)	C(4)–H(1)	0.94 (4)
C(4)–C(41)	1.462 (5)				

Bond Angles (deg)

C(3)–Ru–C(2)	38.3 (1)	C(1)–Ru–Cl	97.42 (9)
C(3)–Ru–P(2)	109.5 (1)	P(3)–Ru–P(1)	178.02 (3)
C(3)–Ru–C(1)	70.3 (1)	P(3)–Ru–Cl	87.36 (3)
C(3)–Ru–P(3)	89.7 (1)	P(1)–Ru–Cl	91.48 (3)
C(3)–Ru–P(1)	91.1 (1)	C(2)–C(1)–C(47)	147.0 (4)
C(3)–Ru–Cl	167.3 (1)	C(2)–C(1)–Ru	67.3 (2)
C(2)–Ru–P(2)	147.7 (1)	C(47)–C(1)–Ru	145.7 (3)
C(2)–Ru–C(1)	32.1 (2)	C(1)–C(2)–C(3)	148.2 (3)
C(2)–Ru–P(3)	91.25 (9)	C(1)–C(2)–Ru	80.6 (2)
C(2)–Ru–P(1)	88.24 (9)	C(3)–C(2)–Ru	67.6 (2)
C(2)–Ru–Cl	129.4 (1)	C(4)–C(3)–C(2)	130.4 (3)
P(2)–Ru–C(1)	177.1 (1)	C(4)–C(3)–Ru	155.4 (3)
P(2)–Ru–P(3)	90.44 (3)	C(2)–C(3)–Ru	74.2 (2)
P(2)–Ru–P(1)	91.01 (3)	C(3)–C(4)–C(41)	127.6 (3)
P(2)–Ru–Cl	82.90 (3)	H(1)–C(4)–C(3)	118 (2)
C(1)–Ru–P(3)	92.47 (9)	H(1)–C(4)–C(41)	115 (2)
C(1)–Ru–P(1)	86.09 (9)		

[a] Estimated standard deviations in the least significant figure are given in parentheses.

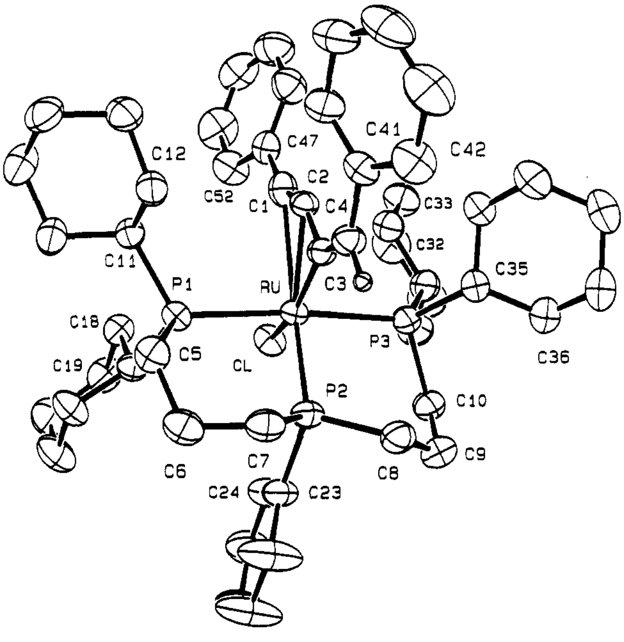

Figure 1. Molecular structure of *syn-mer*-RuCl(η^3-PhC$_3$CHPh)(Cyttp)·$^1/_2$C$_6$H$_6$. Hydrogen atoms and the solvent molecule are omitted for clarity, except for the hydrogen bonded to atom C(4). Thermal ellipsoids are drawn at the 50% probability level.

Results and Discussion

Description of the Structure of *syn-mer*-RuCl(η^3-PhC$_3$CHPh)(Cyttp)·$^1/_2$C$_6$H$_6$ (1A). The molecular structure of the compound is shown in Figure 1. The geometry of the coordination sphere about the ruthenium atom is roughly octahedral, and the compound contains an η^3-PhC$_3$CHPh ligand. The triphosphine is meridional around ruthenium. The phenyl group on the central phosphorus atom P(2) is on the same side of the Cyttp ligand as the chloride. The angle P(2)–Ru–Cl is 103.77 (3)°, which is significantly larger than those for P(1)–Ru–Cl (92.34 (3)°), P(3)–Ru–Cl (83.76 (3)°), and P(2)Ru–C(3) (96.78 (8)°). The relatively larger P(2)–Ru–Cl angle is caused by the steric interaction between the phenyl group on P(2) and the chloride. Such an angular pattern is similar to that in other six-coordinated complexes such as RuH$_2$(N$_2$)(Cyttp),[8] *anti-mer*-RuCl(η^3-PhC$_3$CHPh)(Cyttp)

Table VI. Positional Parameters (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) for 2

	x	*y*	*z*	*U*^{a}
Ru	3474.6 (2)	2867.2 (2)	2228.4 (1)	31.2 (1)
P(1)	3667.7 (8)	4696.5 (7)	2726.8 (4)	36.4 (3)
P(2)	4326.7 (8)	3662.2 (7)	1315.8 (4)	38.8 (3)
P(3)	3134.1 (8)	992.9 (7)	1725.2 (5)	37.2 (3)
C(1)	3537 (4)	5737 (3)	2076 (2)	47 (1)
C(2)	4335 (4)	5910 (3)	1531 (2)	48 (1)
C(3)	3951 (4)	4914 (3)	997 (2)	48 (1)
C(4)	3772 (4)	2845 (3)	439 (2)	52 (2)
C(5)	3846 (4)	1660 (3)	440 (2)	52 (2)
C(6)	2833 (3)	848 (3)	754 (2)	46 (1)
C(7)	1861 (3)	2883 (3)	1557 (2)	39 (1)
C(8)	906 (3)	2864 (3)	1149 (2)	44 (1)
C(9)	4931 (3)	2701 (3)	3123 (2)	37 (1)
C(10)	6099 (3)	2800 (3)	3469 (2)	40 (1)
C(11)	2558 (4)	4360 (3)	3924 (2)	55 (2)
C(12)	1370 (5)	4142 (4)	4205 (3)	84 (2)
C(13)	920 (5)	5137 (4)	4155 (3)	84 (2)
C(14)	724 (4)	5489 (4)	3398 (3)	77 (2)
C(15)	1895 (4)	5688 (4)	3111 (3)	72 (2)
C(16)	2343 (4)	4684 (3)	3152 (2)	53 (2)
C(17)	5224 (4)	6555 (3)	3752 (2)	60 (2)
C(18)	6438 (4)	7025 (4)	4326 (2)	77 (2)
C(19)	7579 (4)	7105 (4)	4042 (3)	76 (2)
C(20)	7487 (4)	5996 (4)	3691 (2)	66 (2)
C(21)	6301 (3)	5565 (3)	3109 (2)	52 (2)
C(22)	5137 (3)	5419 (3)	3407 (2)	45 (1)
C(23)	6669 (2)	4929 (2)	1042 (1)	53 (2)
C(24)	7948	5162	1104	62 (2)
C(25)	8586	4533	1527	64 (2)
C(26)	7944	3671	1889	57 (2)
C(27)	6665	3438	1827	47 (1)
C(28)	6027	4068	1404	41 (1)
C(29)	4738 (3)	−316 (3)	1494 (2)	51 (2)
C(30)	6000 (4)	−483 (3)	1773 (2)	57 (2)
C(31)	6075 (4)	−954 (3)	2488 (2)	56 (2)
C(32)	5779 (4)	−240 (3)	3020 (2)	52 (2)
C(33)	4526 (3)	−62 (3)	2742 (2)	44 (1)
C(34)	4496 (3)	460 (3)	2023 (2)	40 (1)
C(35)	1610 (3)	−1350 (3)	1614 (2)	59 (2)
C(36)	526 (4)	−2196 (3)	1847 (3)	78 (2)
C(37)	−691 (4)	−1956 (3)	1579 (3)	86 (2)
C(38)	−550 (4)	−752 (4)	1829 (3)	84 (2)
C(39)	541 (3)	94 (3)	1598 (3)	60 (2)
C(40)	1760 (3)	−149 (3)	1901 (2)	47 (1)
C(41)	−1352 (2)	1881 (2)	821 (1)	55 (2)
C(42)	−2545	1779	423	61 (2)
C(43)	−2702	2509	−104	66 (2)
C(44)	−1665	3342	−232	65 (2)
C(45)	−472	3444	167	53 (2)
C(46)	−315	2714	693	42 (1)
C(47)	7755 (2)	2456 (2)	4379 (2)	65 (2)
C(48)	8180	2056	5024	91 (3)
C(49)	7356	1600	5455	91 (3)
C(50)	6105	1543	5242	81 (2)
C(51)	5680	1943	4597	66 (2)
C(52)	6504	2399	4166	46 (1)
C(53)	3784 (3)	2248 (3)	3287 (2)	35 (1)
C(54)	2626 (3)	2025 (3)	3111 (2)	39 (1)
C(55)	1466 (2)	826 (2)	3891 (1)	56 (2)
C(56)	362	326	4111	71 (2)
C(57)	−743	506	3763	73 (2)
C(58)	−743	1187	3196	61 (2)
C(59)	361	1688	2977	50 (2)
C(60)	1465	1507	3324	40 (1)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VII. Selected Bond Lengths and Angles for 2

Bond Lengths (Å)

Ru–P(1)	2.405 (1)	Ru–P(2)	2.290 (1)	Ru–P(3)	2.417 (1)
Ru–C(7)	2.037 (3)	Ru–C(9)	2.200 (3)	Ru–C(53)	2.191 (3)
Ru–C(54)	2.258 (3)	C(7)–C(8)	1.205 (5)	C(9)–C(53)	1.379 (5)
C(53)–C(54)	1.249 (5)				

Bond Angles (deg)

P(1)–Ru–P(2)	90.61 (3)	P(1)–Ru–P(3)	176.18 (4)
P(2)–Ru–P(3)	91.50 (3)	P(1)–Ru–C(7)	88.0 (1)
P(2)–Ru–C(7)	82.4 (1)	P(3)–Ru–C(7)	89.2 (1)
Ru–C(7)–C(8)	178.1 (3)	C(9)–C(53)–C(54)	148.7 (3)

(see below), and *mer*-Ru(C≡CPh)(η^3-PhC$_3$CHPh)(Cyttp) (see below). The mutually trans Ru–P(1) and Ru–P(3) bonds are longer than the unique Ru–P(2) bond. The Ru–P bonding pattern is similar to that in other meridional ruthenium phosphine complexes such as RuH$_2$(N$_2$)(Cyttp),[8] *anti-mer*-RuCl(η^3-PhC$_3$CHPh)(Cyttp) (see below), and *mer*-Ru(C≡CPh)(η^3-PhC$_3$CHPh)(Cyttp) (see below), RuH(O$_2$CH)(PPh$_3$)$_3$,[9] RuH(O$_2$CMe)(PPh$_3$)$_3$,[10] RuHCl(PPh$_3$)$_3$,[11] and RuCl$_2$(PPh$_3$)$_3$.[12] The Ru–P and Ru–Cl bond distances are normal compared with those of other ruthenium complexes.[13]

The acetylenic group of the PhC$_3$CHPh fragment is weakly bound to ruthenium as indicated by the long Ru–C(1) and Ru–C(2) bonds and short C(1)≡C(2) bond distances. The bonding interaction between ruthenium and the acetylenic group is evidenced by the bent-back angle (C(2)–C(1)–C(47) of 156.7 (3)°. Such angles have been reported to range from 168° to 134° for the π-bonded acetylenes in several complexes.[14] For comparison, the bend-back angles are 168 (4)° in [Pt(Me)(PMe$_2$Ph)$_2$(MeC≡CMe)]PF$_6$[14a] and 151.5 (5)° and 145.0 (5)° in [Ru(NH$_3$)$_5$(DMAD)](PF$_6$)$_2$.[14b] The angle of noncoordinated C≡C—Ph was observed to be 175.6 (10)° in Ru(C(C≡CPh)=CHPh)(O$_2$CCF$_3$)(CO)(PPh$_3$)$_2$[15] and 177.5° in [CpMo(CO)$_2$]$_2$(μ-1,2-η-Ph≡CC≡CPh).[16] The C(1)–C(2) bond at 1.220 (4) Å is at the lower end of the carbon–carbon triple-bond lengths in some π-bonded acetylenes (range 1.22–1.32 Å),[14] for example 1.238 (7) Å in [Ru(NH$_3$)$_5$(DMAD)](PF$_6$)$_2$[14b] and 1.27 (1) Å in Mo(PhC≡CH)(CO)(PEt$_3$)$_2$Br$_2$.[14e] The bond length, however, is only slightly longer than that for noncoordinated carbon–carbon triple bonds of a similar fragment in Ru(C(C≡CPh)=CHPh)(O$_2$CCF$_3$)(CO)(PPh$_3$)$_2$ (1.208 (13) Å)[15] and in [CpMo(CO)$_2$](μ-1,2-η-PhC≡CC≡CPh) (1.208 (5) Å).[16] The bond Ru–C(2) (2.229 (3) Å) is slightly longer than the Ru–C bonds in the acetylene complex [Ru(NH$_3$)$_5$(DMAD)](PF$_6$)$_2$ (average *d*(Ru–C) = 2.131 Å).[14b] Thus, the acetylenic group in isomer **1A** is weakly bonded to ruthenium. The Ru–C(3) bond distance (2.040 (3) Å) is in the range for Ru–C(vinyl) bonds (range 2.003 (11)–2.16

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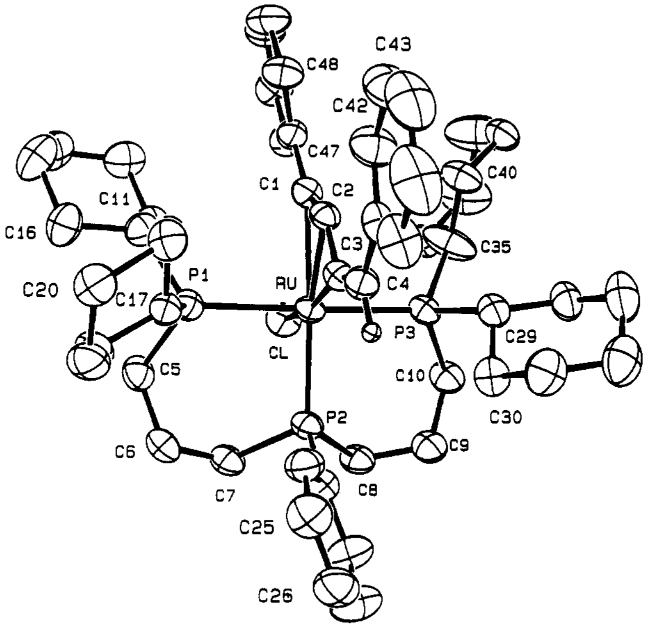

Figure 2. Molecular structure of *anti-mer*-RuCl(η^3-PhC$_3$CHPh)(Cyttp). Hydrogen atoms are omitted for clarity, except for the hydrogen bonded to atom C(4). Thermal ellipsoids are drawn at the 50% probability level. Only one orientation of the disordered cyclohexyl ring is shown.

(2) Å),[15,17] for example, 2.03 (1) Å in RuCl(PhC=CHPh)(CO)(PPh$_3$)$_2$[17e] and 2.076 (8) Å in Ru(C(C≡CPh)=CHPh)(O$_2$CCF$_3$)(CO)(PPh$_3$)$_2$.[15]

Description of the Structure of *anti-mer*-RuCl(η^3-PhC$_3$CHPh)(Cyttp) (1B). The molecular structure of the compound is shown in Figure 2. The geometry of the coordination sphere about the Ru atom is similar to that of **1A**, and the compound also contains an η^3-PhC$_3$CHPh ligand. There are several differences between the structures of **1A** and **1B**. The most apparent difference is that in **1B** the phenyl group on the central phosphorus atom is on the opposite sides of the Cyttp ligand as the chloride. As a consequence, the angle P(2)-Ru-C(3) (109.5 (1)°) is larger than the angle P(2)-Ru-Cl (82.90 (3)°), owing to the steric interaction between the phenyl group on P(2) and the vinyl group; the opposite trend is observed in **1A**. Interestingly, the angles P(1)-Ru-Cl (91.48 (3)°) and P(3)-Ru-Cl (87.36 (3)°) in isomer **1B** are similar to those observed in isomer **1A** (P(1)-Ru-Cl = 92.34 (3)°, P(3)-Ru-Cl = 83.76 (3)°).

The acetylenic group is more strongly bound to ruthenium in **1B** than in **1A**. The bond distance of C(1)-C(2) (1.248 (5) Å) is in the range for carbon-carbon triple-bond lengths in π-bonded acetylene complexes (generally ranging from 1.22 to 1.32 Å)[14] and is significantly longer than that in isomer **1A** (1.220 (4) Å). The bond Ru-C(1) is 2.319 (4) Å long, which is shorter than that in isomer **1A** (2.553 (3) Å) and longer than the Ru-C bonds in the acetylene complex [Ru(NH$_3$)$_5$(DMAD)](PF$_6$)$_2$ (average *d*(Ru-C) = 2.131 Å).[14b] The Ru-C(2) bond (2.169 (3) Å) is also shorter than that in isomer **1A** (2.229 (3) Å) and comparable with the Ru-C bonds in the acetylene complex [Ru(NH$_3$)$_5$(DMAD)](PB$_6$)$_2$ (2.144 (5), 2.117 (6) Å).[14b] The bend-back angle C(2)-C(1)-C(47) is 147.0 (4)°. Thus, the acetylenic group is bonded to ruthenium more strongly in isomer **1B** than in isomer **1A**, although the origin is not clear to our knowledge.

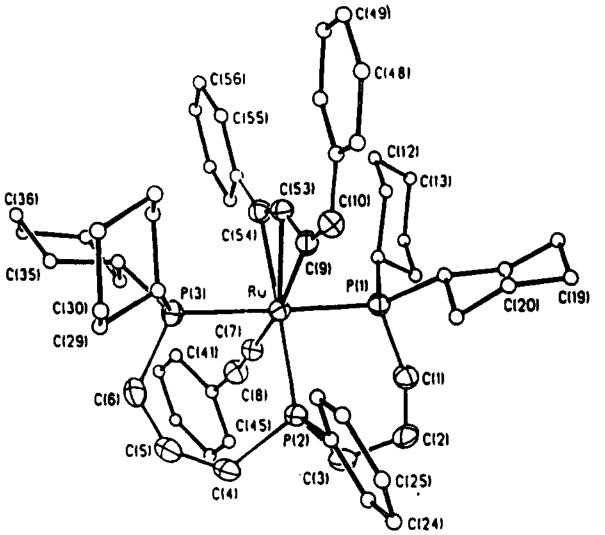

Figure 3. Molecular structure of *mer*-Ru(C≡CPh)(η^3-PhC$_3$CHPh)(Cyttp). Hydrogen atoms are omitted for clarity. The cyclohexyl and phenyl rings are drawn with arbitrary size spheres to enhance clarity.

The bond C(2)-C(3) is 1.396 (5) Å long, which is comparable to that in isomer **1A** (1.416 (4) Å) and shorter than the C—C≡ bond in Ru(C(C≡CPh)=CHPh)(O$_2$CCF$_3$)(CO)(PPh$_3$)$_2$ (1.437 (12) Å),[15] in which the acetylenic group is not bonded to the ruthenium. In fact, such a bond length is similar to the allylic carbon-carbon bond lengths in Ru(NO)(η^3-C$_3$H$_5$)(PPh$_3$)$_2$ (being 1.38 (1) and 1.41 (1) Å, respectively).[18b] The Ru-C(3) bond distance (2.084 (3) Å) is in the range for Ru-C(vinyl) bond lengths[15,17] (range 2.003 (1)-2.16 (2) Å).

The X-ray structures of **1A** and **1B** are consistent with their spectroscopic data in solution.[3]

Description of the Structure of *mer*-Ru(C≡CPh)(η^3-PhC$_3$CHPh)(Cyttp) (2). The molecular structure of *mer*-Ru(C≡CPh)(η^3-PhC$_3$CHPh)(Cyttp) is shown in Figure 3. The overall geometry around ruthenium is roughly octahedral. The three phosphorus atoms are bound to ruthenium in a meridional fashion as indicated by its ^{31}P and ^{13}C NMR spectra in solution.[3] The phenylacetylide group is nearly linear (Ru-C(7)-C(8) = 178.1 (3)°) and is cis to the three phosphorus atoms of the triphosphine. The distances between ruthenium and C(7) and between C(7) and C(8) are 2.037 (3) and 1.205 (5) Å, respectively, which are consistent with the distances observed for other ruthenium acetylide complexes.[19] The phenyl group on the central phosphorus atom is on the same side of the Cyttp ligand as the vinyl group. As a consequence, the angle P(2)-Ru-C(9) (110.9 (1)°) is significantly larger than the angle P(2)-Ru-C(7) (82.4 (1)°), presumably owing to the steric interaction between the phenyl group on P(2) and the vinyl group. These angles are remarkably consistent with the comparable angles in **1B**: P(2)-Ru-C(3) = 109.5 (1)° and P(2)-Ru-Cl = 82.90 (3)°.

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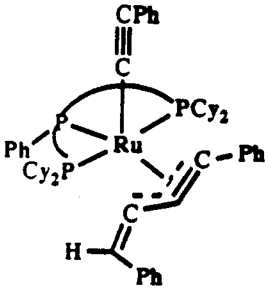
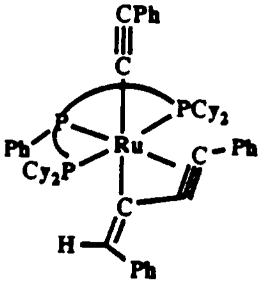
The most surprising feature of the compound is the presence of an η^3-PhC_3CHPh ligand that must have been formed by end-to-end coupling of two phenylacetylene fragments. The distances between ruthenium and C(9), C(53), and C(54) are comparable at 2.200 (3), 2.191 (3), and 2.258 (3) Å, respectively. The Ru–C bonding pattern in compound 2 for the η^3-PhC_3CHPh ligand is unusual compared with other known similar complexes, such as $RuCl(\eta^3$-$PhC_3CHPh)(Cyttp)$ (isomers **1A** and **1B** (see Tables II and IV)) and $[Os(\eta^3$-$PhC_3CHPh)(PMe_3)_4]PF_6$.[4] The Ru–C(54) bond (2.258 (3) Å) is significantly shorter than that observed in the similar complexes $RuCl(\eta^3$-$PhC_3CHPh)(Cyttp)$: **1A**, 2.558 (3) Å; **1B**, 2.319 (4) Å. This implies that the acetylenic group is more strongly bonded to ruthenium in $Ru(C{\equiv}CPh)(\eta^3$-$PhC_3CHPh)(Cyttp)$ than in **1A** or **1B**. The Ru–C(9) bond (2.200 (3) Å), on the other hand, is significantly longer than that observed in the similar complexes $RuCl(\eta^3$-$PhC_3CHPh)(Cyttp)$: 2.040 (3) Å, **1A**; 2.084 (3) Å, **1B**.

In fact, while the values 2.036 (3) and 2.084 (3) Å are in the range[15,17] for Ru–C(vinyl) bond lengths (2.003 (1)–2.16 (2) Å), the value 2.200 (3) Å is in the range for Ru–C (π-olefin) bond lengths (for example, it ranged from 2.14 to 2.38 Å in several ruthenium olefin complexes)[20,21] and Ru–C(allyl) bond lengths[19] (for example,[19b] d(Ru–C) = 2.130 (7), 2.214 (7), and 2.258 (8) Å in $Ru(NO)(C_3H_5)(PPh_3)_2$). The bond distance between C(53) and C(54) is 1.249 (5) Å, which is in the range for carbon–carbon triple-bond lengths in π-acetylene complexes (generally ranging from 1.22 to 1.32 Å).[14] The bond length between C(9) and C(53) is 1.379 (5) Å, which is similar to C–C bond distances in η^3-allyl complexes.[19] The angles C(10)–C(9)–C(53), C(9)–C(53)–C(54), and C(53)–C(54)–C(60) are 133.0 (3), 148.7 (3), and 144.6 (3)°, respectively. These values suggest hybridization intermediate between sp and sp^2 for the central carbon atoms C(9), C(53), and C(54) of the C_4 connection between the phenyl groups.

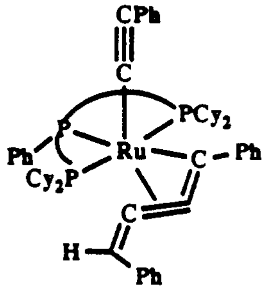
On the basis of the X-ray diffraction results, the structure of $Ru(C{\equiv}CPh)(\eta^3$-$PhC_3CHPh)(Cyttp)$ (2) can be best described as **A**, which is a combination of the canonical forms **B** and **C**. To our knowledge, this type of complex is still very rare in the literature,[4,22] although η^3-allyl complexes are abundant.[23] The true structures of **1A** and **1B** could also be regarded as a combination of two canonical forms similar to **B** and **C**, but with more contribution from form **B**.



A



B



C

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Supplementary Material Available: Tables of complete bond distances and angles, calculated positional parameters and B values for hydrogen atoms, and anisotropic thermal parameters for the non-hydrogen atoms for **1A**, **1B**, and **2** (32 pages); listings of observed and calculated structure factors for **1A**, **1B**, and **2** (64 pages). Ordering information is given on any current masthead page.

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