

CYCLOPENTADIENYL-RUTHENIUM AND -OSMIUM CHEMISTRY

XXVII *. X-RAY STRUCTURES OF $\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppe})(\eta\text{-C}_5\text{H}_5)$ AND OF $[\text{Ru}(\text{L})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]\text{X}$ ($\text{L} = \text{C}(\text{OMe})\text{Et}$, $\text{X} = \text{PF}_6$; $\text{L} = \text{C}=\text{CMePh}$, $\text{X} = \text{I}$)

MICHAEL I. BRUCE*, MARK G. HUMPHREY, MICHAEL R. SNOW* and
 EDWARD R.T. TIEKINK

Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001 (Australia)

(Received April 4th, 1986)

Summary

Determinations of the crystal structures of the acetylide $\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppe})(\eta\text{-C}_5\text{H}_5)$, the vinylidene $[\text{Ru}(\text{C}=\text{CMePh})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]\text{I}$ and the carbene $[\text{Ru}\{\text{C}(\text{OMe})\text{Et}\}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$, have enabled comparison of the Ru–C(α) bonds in these and a number of related complexes. Cationic complexes have Ru–C bonds shorter (by 0.05–0.1 Å) than values expected on the basis of normal covalent radii, but in the case of vinyl and acetylide complexes there does not appear to be any significant shortening of the Ru–C bond which can be ascribed to back-bonding from the metal to the unsaturated carbon-bonded ligand. $\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppe})(\eta\text{-C}_5\text{H}_5)$ crystallises in the monoclinic space group $P2_1/n$, with a 14.642(4), b 14.018(3), c 16.490(4) Å, β 105.08(2)°, Z 4; $[\text{Ru}(\text{C}=\text{CMePh})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]\text{I}$ crystallises in the orthorhombic space group $P2_12_12_1$, a 12.612(4), b 15.607(3), c 22.357(6) Å, Z 4; $[\text{Ru}\{\text{C}(\text{OMe})\text{Et}\}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$ crystallises in the orthorhombic space group $P2_12_12_1$, a 11.999(3), b 14.948(1), c 22.342(3) Å, Z 4. For 4841, 2614 and 3299 data ($I > 2.5\sigma(I)$), respectively, refinements converged with R , R_w values of 0.038 and 0.048, 0.047 and 0.053, and 0.040 and 0.044 for the three complexes.

Introduction

There has been considerable experimental and theoretical interest in the interconversion of alkynyl, vinylidene, carbene, and vinyl complexes, and we have reported extensive studies carried out with complexes containing the $\text{Ru}(\text{L})_2(\eta\text{-C}_5\text{H}_5)$ ($\text{L} =$

* For Part XXVI, see ref. 18.

PPh_3 , $\text{L}_2 = \text{dppe}$) moiety [1]. Much of the unusual reactivity of metal-alkynyl and metal-vinylidene complexes can be traced to a frontier orbital of which a significant part is localised on the β -carbon of the organic fragment [2]. In this connection it is of interest to determine the amount of back-bonding between the metal and the C_2 units in representative complexes. Thus we have determined the molecular structures of the complexes $\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppe})(\eta\text{-C}_5\text{H}_5)$ (**1a**), $[\text{Ru}(\text{C}=\text{CMePh})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]\text{I}$ (**2**) and $[\text{Ru}\{\text{C}(\text{OMe})\text{Et}\}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]\text{[PF}_6\text{]}$ (**3**); the resulting structural information has been combined with that already available for $\text{Ru}\{\text{C}(\text{OPr}^i)=\text{CHPh}\}(\text{CO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ (**4**) [3], $\text{Ru}\{\text{C}(\text{CO}_2\text{Me})=\text{CH}(\text{CO}_2\text{Me})\}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ (**5**) [4], and a range of similar complexes containing ruthenium bonded to variously hybridised carbons to provide information on the changes which result from conversion of one group to another. We had also completed the structure of $\text{Ru}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ (**1b**) in the course of these studies, but an account of a structural comparison of **1b** with $[\text{Ru}(\text{CO})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]\text{[BPh}_4\text{]}$ (**6**) has been given by others [5]; however, these data have also been included in our comparison.

Experimental

Synthesis of complexes

The compounds $\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppe})(\eta\text{-C}_5\text{H}_5)$ (**1a**) [6], $\text{Ru}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ (**1b**) [6] and $[\text{Ru}\{\text{C}(\text{OMe})\text{Et}\}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]\text{[PF}_6\text{]}$ (**3**) [7] were prepared by literature methods. Suitable crystals of **1a** and **1b** were grown from dichloromethane/pentane (at -30°C), while the cationic complex **3** was obtained from a dichloromethane/methanol mixture.

Preparation of $[\text{Ru}(\text{C}=\text{CMePh})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]\text{I}$ (**2**)

A mixture of $\text{Ru}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ (250 mg, 0.316 mmol) and iodomethane (336 mg, 2.37 mmol) was heated in refluxing dichloromethane (12 ml) for 16 h. The reaction mixture was cooled to room temperature and then filtered into diethyl ether (100 ml), precipitating $[\text{Ru}(\text{C}=\text{CMePh})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]\cdot\text{CH}_2\text{Cl}_2$ as a red powder (200 mg, 62%), m.p. $135\text{--}138^\circ\text{C}$ (dec). (Found: C, 60.47; H, 4.52. $\text{C}_{50}\text{H}_{43}\text{IP}_2\text{Ru}\cdot\text{CH}_2\text{Cl}_2$ calcd.: C, 60.13; H, 4.45%). Infrared (Nujol): $\nu(\text{C}=\text{C})$ 1690m, 1666s cm^{-1} ; other bands at 1593m, 1438s, 1432(sh), 1270m, 1093s, 1028m, 842m, 823m, 760m, 755(sh), 745m, 730m, 702(sh), 699s, 688m cm^{-1} . ^1H NMR: δ (CDCl_3) 1.94 (s, 3H, Me), 5.21 (s, 5H, C_5H_5), 5.30 (s, 2H, CH_2Cl_2), 6.9–7.6 (m, 35H, Ph). X-ray quality crystals were obtained by slow vapour diffusion of methanol into a dichloromethane solution.

Crystallography

Intensity data sets for each of the compounds **1a**, **1b**, **2**, and **3** were collected at room-temperature on an Enraf–Nonius CAD4F diffractometer with the use of $\text{Mo-K}\alpha$ (graphite monochromator) radiation, λ 0.71073 Å. High angle Friedel pairs were also included in the data sets for compounds **2** and **3** which crystallized in the non-centrosymmetric space group $P2_12_12_1$. These measurements subsequently enabled the assignment of the absolute structures of **2** and **3** to a confidence level of 99.95% using the Hamilton significance test [8]. For each sample no significant decomposition of the crystal occurred during their respective data collections. Corrections were applied for Lorentz and polarization effects using the program

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TABLE 1
CRYSTAL DATA FOR COMPLEXES 1a, 1b, 2 AND 3

	1a	1b	2	3
Formula	$C_{39}H_{34}P_2Ru$	$C_{49}H_{40}P_2Ru$	$C_{50}H_{43}IP_2Ru, CH_3OH$	$C_{45}H_{43}F_6OP_3Ru$
Formula weight	665.7	791.9	965.9	907.9
Crystal syst.	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1/n$ variant, C_{2h}^5 , No. 14	$P2_1/n$ variant, C_{2h}^5 , No. 14	$P2_12_12_1$ D_2^2 , No. 19	$P2_12_12_1$ D_2^2 , No. 19
<i>a</i> (Å)	14.642(4)	11.315(1)	12.612(4)	11.999(3)
<i>b</i> (Å)	14.018(3)	17.376(4)	15.607(3)	14.948(1)
<i>c</i> (Å)	16.490(4)	19.582(6)	22.357(6)	22.342(3)
β (°)	105.08(2)	92.36(1)		
<i>U</i> (Å ³)	3268	3845	4401	4007
<i>Z</i>	4	4	4	4
D_{calc} (g cm ⁻³)	1.353	1.368	1.458	1.505
μ (Mo-K α) (cm ⁻¹)	5.61	4.81	11.19	5.24
<i>F</i> (000), electrons	1368	1632	1916	1856
Scan mode	$\omega: \theta$	$\omega: \theta$	$\omega: 2\theta$	$\omega: 2\theta$
θ -range, (°)	1.4–30	1.3–21	1–25	1–25
Refl. meas.	6921	4505	4114	3503
Unique refls.	5747	3674	4114	3503
Criterion of observability	$I \geq 2.5\sigma(I)$	$I \geq 2.5\sigma(I)$	$I \geq 2.5\sigma(I)$	$I \geq 2.5\sigma(I)$
Refls. used	4841	3020	2614	3299
Final <i>R</i>	0.038	0.030	0.047	0.040
Weighting scheme, <i>k</i>	1.0	2.2	0.6	4.0
Final <i>R_w</i>	0.0016	0.0001	0.0046	0.0002
Residual ρ (e Å ⁻³)	0.048	0.033	0.053	0.044
	0.80	0.40	0.61	0.66

TABLE 2

FRACTIONAL ATOMIC COORDINATES ($\times 10^5$ Ru, $\times 10^4$ for remaining atoms) FOR
 Ru(C \equiv CPh)(dppe)(η -C₅H₅) (1a)

Atom	x	y	z
Ru(1)	49300(2)	26057(2)	29396(1)
P(1)	5165(1)	4134(1)	2643(1)
P(2)	5925(1)	2970(1)	4190(1)
C(1)	3950(2)	3098(2)	3492(2)
C(2)	3374(2)	3375(2)	3843(2)
C(3)	2760(1)	3290(2)	5087(1)
C(4)	2068(1)	3501(2)	5504(1)
C(5)	1291(1)	4066(2)	5113(1)
C(6)	1208(1)	4420(2)	4306(1)
C(7)	1900(1)	4209(2)	3889(1)
C(8)	2676(1)	3644(2)	4280(1)
C(9)	5800(2)	4249(2)	4396(2)
C(10)	5702(3)	4845(3)	3603(2)
C(11)	6353(2)	2651(2)	5928(2)
C(12)	6226(2)	2221(2)	6654(2)
C(13)	5519(2)	1536(2)	6597(2)
C(14)	4937(2)	1282(2)	5812(2)
C(15)	5064(2)	1713(2)	5086(2)
C(16)	5771(2)	2397(2)	5144(2)
C(17)	7518(2)	1876(2)	4211(2)
C(18)	8466(2)	1727(2)	4226(2)
C(19)	9093(2)	2497(2)	4344(2)
C(20)	8772(2)	3416(2)	4448(2)
C(21)	7824(2)	3565(2)	4433(2)
C(22)	7198(2)	2795(2)	4315(2)
C(23)	3267(2)	4484(1)	1779(2)
C(24)	2513(2)	5054(1)	1348(2)
C(25)	2662(2)	6018(1)	1210(2)
C(26)	3565(2)	6413(1)	1503(2)
C(27)	4318(2)	5843(1)	1934(2)
C(28)	4169(2)	4878(1)	2072(2)
C(29)	5612(1)	4227(2)	1104(1)
C(30)	6219(1)	4178(2)	578(1)
C(31)	7198(1)	4169(2)	921(1)
C(32)	7570(1)	4208(2)	1791(1)
C(33)	6963(1)	4256(2)	2317(1)
C(34)	5984(1)	4265(2)	1973(1)
C(35)	4183(3)	1937(3)	1695(3)
C(36)	5170(3)	1953(3)	1758(3)
C(37)	5631(3)	1378(3)	2455(3)
C(38)	4928(3)	1007(3)	2822(3)
C(39)	4033(3)	1352(3)	2352(3)
C(35')	4378(6)	1083(5)	2699(5)
C(36')	5371(6)	1064(5)	2795(5)
C(37')	5569(6)	1624(5)	2142(5)
C(38')	4697(6)	1989(5)	1643(5)
C(39')	3961(6)	1655(5)	1987(5)

TABLE 3

FRACTIONAL ATOMIC COORDINATES ($\times 10^5$ Ru, $\times 10^4$ for remaining atoms) FOR
 $[\text{Ru}(\text{C}=\text{CMePh})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]\text{I}$ (2)

Atom	x	y	z
Ru(1)	19433(6)	48137(6)	19933(4)
P(1)	1650(2)	4909(2)	961(1)
P(2)	3706(2)	4300(2)	1990(2)
I	1282(1)	93(1)	1062(1)
C(1)	2097(12)	6227(8)	2205(7)
C(2)	1009(10)	6024(8)	2076(6)
C(3)	652(11)	5460(8)	2526(6)
C(4)	1510(11)	5286(9)	2910(6)
C(5)	2385(11)	5765(8)	2701(7)
C(6)	1347(9)	3723(6)	2038(5)
C(7)	874(9)	3000(7)	2129(6)
C(8)	212(12)	2518(8)	1666(7)
C(12)	-527(5)	4578(5)	1182(2)
C(13)	-1573(5)	4446(5)	1001(2)
C(14)	-1821(5)	4414(5)	394(2)
C(15)	-1023(5)	4513(5)	-33(2)
C(16)	23(5)	4644(5)	148(2)
C(11)	271(5)	4677(5)	756(2)
C(22)	1017(5)	6526(5)	522(4)
C(23)	1192(5)	7387(5)	385(4)
C(24)	2215(5)	7725(5)	414(4)
C(25)	3062(5)	7202(5)	581(4)
C(26)	2887(5)	6342(5)	718(4)
C(21)	1864(5)	6004(5)	689(4)
C(32)	3027(8)	4509(5)	-16(4)
C(33)	3512(8)	3914(5)	-392(4)
C(34)	3354(8)	3039(5)	-301(4)
C(35)	2710(8)	2760(5)	168(4)
C(36)	2225(8)	3354(5)	544(4)
C(31)	2383(8)	4229(5)	453(4)
C(42)	5261(5)	4385(5)	2903(3)
C(43)	5627(5)	4243(5)	3484(3)
C(44)	4940(5)	3923(5)	3919(3)
C(45)	3887(5)	3745(5)	3773(3)
C(46)	3521(5)	3887(5)	3193(3)
C(41)	4208(5)	4207(5)	2758(3)
C(52)	5282(6)	3138(5)	1602(4)
C(53)	5663(6)	2327(5)	1450(4)
C(54)	4967(6)	1634(5)	1416(4)
C(55)	3891(6)	1751(5)	1534(4)
C(56)	3510(6)	2562(5)	1685(4)
C(51)	4206(6)	3255(5)	1719(4)
C(62)	4806(7)	5855(5)	1906(3)
C(63)	5376(7)	6492(5)	1610(3)
C(64)	5729(7)	6355(5)	1026(3)
C(65)	5512(7)	5581(5)	739(3)
C(66)	4941(7)	4944(5)	1035(3)
C(61)	4589(7)	5081(5)	1619(3)
C(72)	1592(8)	1742(5)	2693(4)
C(73)	1863(8)	1350(5)	3232(4)
C(74)	1659(8)	1765(5)	3773(4)
C(75)	1184(8)	2572(5)	3774(4)
C(76)	913(8)	2964(5)	3235(4)
C(71)	1118(8)	2550(5)	2694(4)
O(sol)	2025(12)	-636(10)	2465(6)
O(sol)	2029(21)	-1539(14)	2374(12)

TABLE 4

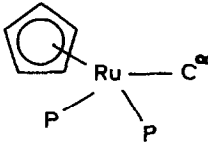
FRACTIONAL ATOMIC COORDINATES ($\times 10^5$ Ru, $\times 10^4$ for remaining atoms) FOR
 $[\text{Ru}\{\text{C}(\text{OMe})\text{Et}\}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$ (3)

Atom	x	y	z
Ru(1)	-19486(4)	732(3)	-18025(2)
P(1)	-3116(1)	-697(1)	-1136(1)
P(2)	-659(1)	-1050(1)	-2049(1)
C(1)	-2859(6)	230(5)	-2697(3)
C(2)	-1756(7)	603(4)	-2744(3)
C(3)	-1674(6)	1321(4)	-2343(3)
C(4)	-2680(7)	1425(5)	-2039(3)
C(5)	-3399(6)	738(5)	-2253(3)
C(6)	-987(5)	397(4)	-1128(3)
O(1)	-453(4)	-221(3)	-837(2)
C(7)	333(7)	-53(7)	-350(3)
C(8)	-793(7)	1357(5)	-925(3)
C(9)	-1514(7)	1621(5)	-374(3)
P(3)	3919(3)	-1228(2)	-3868(1)
F(1)	5071(7)	-864(8)	-4047(3)
F(2)	-4002(15)	-5683(6)	-1701(4)
F(3)	-3370(8)	-5443(4)	-748(4)
F(4)	-2778(7)	-6595(7)	-1306(5)
F(5)	-3882(9)	-6765(5)	-543(8)
F(6)	-4443(9)	-7051(5)	-1459(4)
C(12)	-5336(3)	-647(2)	-717(2)
C(13)	-6277(3)	-231(2)	-478(2)
C(14)	-6333(3)	700(2)	-453(2)
C(15)	-5448(3)	1215(2)	-666(2)
C(16)	-4507(3)	799(2)	-905(2)
C(11)	-4451(3)	-133(2)	-930(2)
C(22)	-1907(4)	-1647(2)	-261(2)
C(23)	-1495(4)	-1793(2)	315(2)
C(24)	-1784(4)	-1213(2)	779(2)
C(25)	-2486(4)	-488(2)	667(2)
C(26)	-2898(4)	-343(2)	92(2)
C(21)	-2609(4)	-922(2)	-372(2)
C(32)	-4045(4)	-1828(2)	-1987(2)
C(33)	-4419(4)	-2639(2)	-2222(2)
C(34)	-4421(4)	-3406(2)	-1866(2)
C(35)	-4048(4)	-3362(2)	-1276(2)
C(36)	-3674(4)	-2551(2)	-1041(2)
C(31)	-3672(4)	-1784(2)	-1396(2)
C(42)	-1813(3)	-1731(3)	-3048(2)
C(43)	-1969(3)	-1921(3)	-3653(2)
C(44)	-1106(3)	-1772(3)	-4060(2)
C(45)	89(3)	-1433(3)	-3861(2)
C(46)	67(3)	-1243(3)	-3256(2)
C(41)	-795(3)	-1392(3)	-2849(2)
C(52)	1058(3)	232(2)	-1980(2)
C(53)	2165(3)	518(2)	-1973(2)
C(54)	3027(3)	-105(2)	-2014(2)
C(55)	2782(3)	-1015(2)	-2063(2)
C(56)	1675(3)	-1301(2)	-2071(2)
C(51)	813(3)	-677(2)	-2029(2)
C(62)	-1227(3)	-2865(3)	-1817(2)
C(63)	-1156(3)	-3672(3)	-1505(2)
C(64)	-419(3)	-3756(3)	-1026(2)
C(65)	247(3)	-3034(3)	-858(2)
C(66)	176(3)	-2227(3)	-1169(2)
C(61)	-561(3)	-2143(3)	-1649(2)

SUSCAD [9]. Crystal data and relevant data collection parameters are collected in Table 1.

The structures were solved by normal Patterson methods and refined, in each case, by a block-matrix least-squares method using the program SHELX [9]. For **1a** all non-hydrogen atoms were refined with anisotropic thermal parameters except the carbon atoms of the cyclopentadienyl (cp) group which was found to be disordered. The cp ring was modelled in two orientations which, at the convergence of the refinement, had site occupancy factors of 0.65 and 0.35 respectively. Hydrogen atoms were included in the model at their calculated positions and a weighting scheme, $w = k/[\sigma^2(F) + g|F|^2]$, included. A similar disorder was found for the phenyl group of the acetylide ligand of **1b** and refinement in two orientations yielded site occupancy factors 0.54 and 0.46. The refinement for **1b** was similar to that for **1a** in all other respects. It is noteworthy that, even at -162°C , Ibers et al. [5] found a similar disorder in the phenyl group. For **2** and **3**, the phenyl rings were refined as hexagonal rigid groups with individual thermal parameters and the remaining non-hydrogen atoms refined anisotropically. Hydrogen atoms were included as for **1a**. The procedure UNDO in SHELX [9] was employed in order to determine the absolute configuration of each of the structures **2** and **3** as described above.

TABLE 5

SELECTED BOND LENGTHS (Å) AND ANGLES ($^\circ$) FOR **1a**, **1b**, **2** AND **3**


	(C≡CPh)(dppe)	(C≡CPh)(PPh ₃) ₂ ^a	(C=CMePh)(PPh ₃) ₂	(C(OMe)Et)(PPh ₃) ₂
Ru-cp	1 2.261(4), 2.276(8)	2.229(3) [2.229(3)]	2.264(12)	2.290(6)
	2 2.260(5), 2.282(8)	2.228(3) [2.228(3)]	2.234(11)	2.260(6)
	3 2.251(5), 2.265(9)	2.242(4) [2.238(3)]	2.256(12)	2.247(7)
	4 2.245(5), 2.248(8)	2.251(4) [2.256(3)]	2.245(12)	2.266(8)
	5 2.252(4), 2.255(9)	2.243(4) [2.227(3)]	2.239(13)	2.243(7)
Ru-P(1)	2.240(1)	2.307(1) [2.303(1)]	2.341(3)	2.347(2)
Ru-P(2)	2.250(1)	2.294(1) [2.285(1)]	2.363(3)	2.349(2)
Ru-C ^α	2.009(3)	2.017(5) [2.016(3)]	1.863(10)	1.959(6)
C ^α -C ^β	1.204(5)	1.214(7) [1.215(4)]	1.293(15)	1.523(9)
C ^β -Ph	1.444(5)	1.462(8) [1.456(4)]	1.477(16)	-
		1.418(8)		
C ^β -Me	-	-	1.529(17)	1.556(11)
C ^α -O	-	-	-	1.462(9)
P ¹ -Ru-P ²	83.3(0)	100.9(1) [100.50(3)]	99.6(1)	101.0(1)
P ¹ -Ru-C ^α	86.5(1)	89.2(1)	92.7(4)	89.1(2)
P ² -Ru-C ^α	82.7(1)	88.6(1)	94.0(4)	88.2(2)
Ru-C ^α -C ^β	178.1(3)	177.7(4) [178.0(2)]	172.8(11)	123.5(5)
C ^α -C ^β -Ph	176.3(4)	170.6(5) [171.9(3)]	117.0(11)	-
		170.6(5)		
C ^α -C ^β -Me	-	-	125.1(12)	112.9(6)
Ru-C ^α -O	-	-	-	120.0(4)
C ^α -O-Me	-	-	-	124.6(6)

^a Values in square brackets from ref. 5.

Neutral atom scattering factors for C, H, F, O, and P were those listed in SHELX [9] and those for Ru and I⁻ were obtained from the International Tables [10], the values being corrected for anomalous dispersion. Final non-hydrogen atomic coordinates for **1a**, **2** and **3** are listed in Tables 2, 3 and 4 respectively and selected interatomic parameters are summarized in Table 5. Tables of thermal parameters, hydrogen-atoms coordinates, and the structure factor tables have been deposited as supplementary material.

Results

Plots of a molecule of **1a**, and of the cations in **2** and **3**, are given in Figs. 1–3, respectively. In all three complexes, the coordination about the ruthenium atoms can be considered to be distorted octahedral, with the C₅H₅ group occupying three facial sites and the other three positions being taken up by two P atoms of the tertiary phosphine(s) and the C atom of the unsaturated fragment.

The separations of the five carbon atoms of the C₅ ring from the metal atom range from 2.245(5)–2.261(4) Å (difference 3σ) in **1a**, 2.234(11)–2.264(12) Å (2.5σ) in **2**, and 2.243(7)–2.290(6) Å (6.5σ) in **3** (Table 5). These values fall within the overall ranges found for several other related complexes, and although the differences are barely significant, the values for **1a** may be compared with distances of 2.227(3)–2.256(3) Å (9.5σ) found for **1b** [5]. The asymmetry results in that part of the C₅ ring which is furthest from the metal being approximately *trans* to the carbon ligand, as found previously in [Ru(η²-C₄H₆)(PMe₃)₂(η-C₅H₅)] [11] and in [Ru(CO)(PPh₃)₂(η-C₅H₅)] [5]. As mentioned earlier [11] and by others [12], a possible explanation is that the longer distances result from a *trans* effect of the carbon-donor ligand.

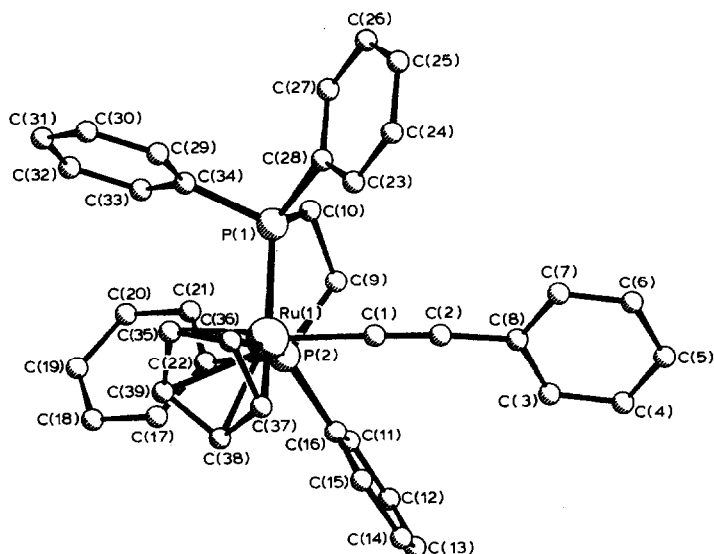


Fig. 1. Molecular structure and numbering scheme for Ru(C≡CPh)(dppe)(η-C₅H₅) (**1a**).

The Ru–P distances fall within the range of values (2.20–2.39 Å) reported for *cis*-coordinated tertiary phosphines. As expected, the distances in the chelate complex **1a** are shorter by ca. 0.055 Å than those found in the (PPh₃)₂ analogue **1b**, while in the cationic complexes **2** and **3**, the Ru–P separations are longer by about the same amount. This is probably the result of more efficient back donation from the metal into the organic fragment, and a similar phenomenon was found in [Ru(CO)(PPh₃)₂(η-C₅H₅)] [BPh₄] [5]. Theoretical calculations [13] and experimental results [14] suggest that any back donation into tertiary phosphines, PR₃, puts electron density into P–R σ* orbitals. Competition for electron density between PR₃ ligands and good π-acceptors, such as CO, CR₂ or C=CR₂, would lengthen the M–P bond and at the same time result in a decrease in the P–C bond. However, the e.s.d.'s in the P–C bond lengths preclude any meaningful discussion on this point.

The C≡C triple bonds in **1a** and **1b** have lengths of 1.204(15) and 1.215(4) Å, respectively, and are comparable to the value of 1.20(1) Å found in *trans*-Pd(C≡CC₆H₄C≡CH-2)(NCS)(PEt₃)₂ [14], for example. In **2**, the C=C bond of the vinylidene ligand is 1.293(15) Å, similar to the value of 1.313(10) Å found for the related complex [Ru(C=CHMe)(PMe₃)₂(η-C₅H₅)] [PF₆] [15]. In the acetylides, the Ru–C≡C moiety is essentially linear (178.1(3)° in **1a**, 178.0(2)° in **1b**), while in **2**, a slight bending at the α-carbon occurs to give a value of 172.8(11)°; in the Ru–C=CHMe complex mentioned above, the value is 180(2)° [15]. In the carbene complex **3**, the α-carbon is *sp*²-hybridised, with angles at this atom of 120.0(4) and 123.5(5)° for Ru–C(α)–O and Ru–C(α)–C(β), respectively; bonds from the α-carbon to the methyl and methoxy groups are normal at 1.523(9) and 1.462(9) Å, respectively.

The chief interest in these structure determinations lies in the magnitude of the Ru–C(α) separations, and we have been able to extend the earlier survey of Ru–C distances [5] into the shorter bonds found for the multiply-bonded ligands considered herein. For **1a** and **1b**, values of 2.009(3) and 2.017(5) Å are consistent with single bonds from Ru^{II} to a C(*sp*) atom, and indicate a very low degree of metal-to-ligand back-bonding. In the palladium complex mentioned above, the Pd–C bond is 1.952(7) Å [14], while in Rh(C≡CPh)(tnc)(NCMe)(PPh₃)₂, the Rh–C separation is 1.94(2) Å [16]. In contrast, the values found for the Ru–C=CR₂ bond in **2** and the Ru–CO bond in **4** are considerably shorter, and suggest that similar degrees of back-bonding from Ru to the α-carbon occur in these two complexes. The Ru–C bond in carbene complex **3** is intermediate between those in complexes **2** and **4** and in the σ-acetylides, at 1.959(6) Å.

Early studies of a series of manganese complexes included IR spectral data which suggested that vinylidenes are stronger π-accepting ligands than CO or CPh₂ [17]. The present studies bear out this conclusion, reinforcing theoretical arguments that extensive transfer of charge onto the vinylidene ligand occurs via its *p* and π* orbitals [2]. These results suggest that the vinylidene ligand should be more reactive towards nucleophilic ligands than CO. However, as we have pointed out on numerous occasions, the ruthenium complexes are kinetically stable, the bulky tertiary phosphine ligands hindering attack at the α-carbon. This is found to be especially true for **2**, which does not react with methanol or sodium methoxide, contrasting with the monosubstituted vinylidene [Ru(C=CHPh)(PPh₃)₂(η-C₅H₅)] [PF₆], which reacts to give [Ru{C(OMe)CH₂Ph}(PPh₃)₂(η-C₅H₅)] [PF₆] (by nucleophilic addition of MeOH) or Ru(C≡CPh)(PPh₃)₂(η-C₅H₅) (by deprotonation

TABLE 6

Ru-C DISTANCES IN SOME RuR(L)₂(η-C₅H₅) COMPLEXES

R	(L ₂)	Ru-C (Å)	Δ ^a	Reference
C=CPh(N=NC ₆ H ₃ Me _{2-3,4})	(PPh ₃) ₂	1.823(9)	-0.11	19
C=CPh(I)	(PPh ₃) ₂	1.839(7)	-0.09	20
C=CHMe	(PMe ₃) ₂	1.845(7)	-0.08	15
C=CPh(C ₇ H ₇)	(dppe)	1.848(9)	-0.08	19
C=CBr(C ₆ H ₄ Br-4)	(PPh ₃) ₂	1.85(1)	-0.08	21
C=CMePh	(PPh ₃) ₂	1.863(10)	-0.07	This work
CO	(PPh ₃) ₂	1.869(2)	-0.06	5
C(OMe)Et	(PPh ₃) ₂	1.959(6)	-0.10	This work
C≡CPh	(dppe)	2.009(3)	+0.08	This work
C ₆ F ₄ N=NC ₆ F ₅	(C ₆ F ₅ N=NC ₆ F ₄)(PPh ₂ (C ₆ H ₄ -η-C ₅ H ₅))	2.013(6)	-0.04	22
C≡CPh	(PPh ₃) ₂	2.016(3)	+0.09	5
C≡CPh		2.017(5)		This work
C≡CPh ↓ CuCl	(PPh ₃) ₂	2.017(9)	+0.09	23
C(CO ₂ Me)=CHC(OMe)	{-C(OMe)-}(PPh ₃)	2.04	-0.02	24
C(CF ₃)=C(CF ₃)-	{-C(CF ₃)=CH(CF ₃)}(PPh ₃)	2.05	-0.01	25
C=CPhC(CF ₃) ₂ C(CN) ₂	(CO)(PPh ₃)	2.054(8)	-0.01	26
C=C(CN) ₂ CPh=CH- (C ₆ H ₄ NO ₂ -4)	(dppe)	2.063(8)	0.0	27
C=C(CN) ₂ CPh=C(CN) ₂	(dppe)	2.068(4)	+0.01	28
C(CO ₂ Me)=CH(CO ₂ Me)- <i>cis</i>	(dppe)	2.071(12)	+0.01	4
C=C(CN) ₂ CPh=C(CN) ₂	(CNBu ^t)(PPh ₃)	2.074(3)	+0.01	29
C(CO ₂ Me)=CH- (CO ₂ Me)- <i>trans</i>	(CO)(PPh ₃)	2.080(8)	+0.02	4
C(O)NH ₂	(CO) ₂	2.080(6)	+0.02	30
		2.084(7) ^b		
C(CO ₂ Me)=C(CO ₂ Me)-	{-C(CF ₃)=CH(CF ₃)}(PPh ₃)	2.082(5)	+0.02	31
C(OPr ⁱ)=CHPh	(CO)(PPh ₃)	2.103(6)	+0.04	32
C=C(CN) ₂ CMe=C(CF ₃) ₂	(CO)(PPh ₃)	2.106(5)	+0.05	33
C(CF ₃)=CH-	{-C(CF ₃)=C=C=CH(CF ₃)}(PPh ₃)	2.11(1)	+0.05	34
CH ₂ {Ru(CO) ₂ (η-C ₅ H ₅)}	(CO) ₂	2.18	+0.08	35

^a Δ = Ru-C(found) - Ru-C(calcd.). Calculated values from covalent radii sums: C(sp) 0.66, C(sp²) 0.70, C(sp³) 0.77, Ru^{II} 1.33 Å. ^b Two independent molecules.

with NaOMe), respectively [7]. In contrast, the analogous iron complexes containing Fe(CO)(L)(η-C₅H₅) (L = CO or PPh₃) groups are exceedingly sensitive to traces of moisture or alcohols [1].

Structural results for a range of complexes containing Ru-C bonds in the Ru(L)₂(η-C₅H₅) series are now available, and just one aspect of these, the Ru-C bond length, is summarised in Table 6. Whilst a similar compilation has been presented before [5], it is useful to extend the available data by inclusion of a number of examples which were either not available to or not used by the previous authors. The most obvious conclusion that can be drawn is that the experimentally determined bond lengths in the neutral complexes are, in general, somewhat longer than those calculated on the basis of covalent radii of 0.60, 0.73, 0.77 and 1.33 Å for C(sp), C(sp²), C(sp³) and Ru^{II}, respectively [5], whereas in the cationic complexes, they are shorter by some 0.06–0.1 Å.

It is difficult, if not impossible, to establish an internally consistent set of values for Ru-C(*sp*), Ru-C(*sp*²) and Ru-C(*sp*³) bond lengths in the absence of any back-bonding. Nevertheless the results summarised in Table 2 strongly suggest that a considerable degree of back-bonding is occurring from the metal to the organic fragment in the case of CO and C=CR₂, where the metal-bonded carbon is part of an unsaturated organic ligand. The Ru-C bonds (1.82–1.87 Å) are shorter than those in the substituted vinyl complexes (2.04–2.11 Å) by between 0.07–0.29 Å. There appears to be no significant difference between the Ru-CO bond in [Ru(CO)(PPh₃)₂(η-C₅H₅)]⁺ and those in the neutral complexes of type RuR(CO)(L)(η-C₅H₅). Finally, the Ru-C bonds in the four *o*-phenylacetylide complexes are nearly 0.1 Å longer than calculated, suggesting that rather than there being any multiple bonding between the metal and the α -carbon, there may be a relative deficiency of electron density in this region.

Acknowledgements

Grateful acknowledgement is made to the Australian Research Grants Scheme for support of this work. MGH holds a Commonwealth Post-Graduate Research Award. We thank Dr. E. Horn for collecting data for compounds **1a** and **1b**.

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