Inorganica Chimica Acta, 100 (1985) 115–123

The Structures of Cyclopentadienyl(phenylacetylido)bis(triphenylphosphine)-ruthenium(II) and Cyclopentadienyl(carbonyl)bis(triphenylphosphine)ruthenium(II) Tetraphenylborate: Comparison of Metal–Ligand π-Interactions

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Received November 30, 1984

Abstract

The structures of $Ru(C_5H_5)(C_2C_6H_5)[P(C_6H_5)_3]_2$, **I**, and $[Ru(C_5H_5)(CO)[P(C_6H_5)_3]_2][B(C_6H_5)_4]$, **II**, have been determined by X-ray diffraction methods at –162 °C. Complex **I** crystallizes with four molecules in space group C_{2h}^5-$P2_1/c$ of the monoclinic system in a cell of dimensions: a = 11.256(2) Å, b = 17.139(3) Å, c = 22.084(4) Å, and β = 118.52(1)°. The structure has been refined to an R index on F^2 of 0.046 for 6214 observations and 441 variables. The carbonyl cation, complex **II**, crystallizes in the monoclinic space group C_{2h}^5-$P2_1/a$, with four formula units in a cell of dimensions a = 26.413(6), b = 14.953(7), c = 12.747(3) Å, β = 96.40(1)°. The structure of **II** has been refined to an R index on F^2 of 0.069 for 10,072 observations and 641 variables. In complexes **I** and **II** the central Ru atom is in a distorted octahedral environment, with the cyclopentadienyl ring assuming three coordination sites *trans* to the two phosphines and either the acetylide or the carbonyl ligand. The Ru–C(acetylido) distance in complex **I** is 2.016(3) Å while in complex **II** the Ru–C(carbonyl) distance is 1.869(2) Å.

Examination of the structural data and comparison with other Ru(II) complexes suggest little if any metal–ligand d_π–p_π interaction in the metal alkynyl complex, whereas the carbonyl complex displays extensive π-bonding.

Introduction

That d_π–p_π backbonding interactions influence the metal–carbon bond of alkynyl–transition metal complexes remains uncertain [1]. The readily synthesized alkynyl complexes are generally robust, and exhibit a metal–carbon bond that is more stable kinetically than the corresponding metal–alkyl bond [2]. Strong metal–ligand interactions may be responsible for the strength of the metal–alkynyl bond since the acetylide π* orbitals have the same symmetry and similar orbital energy as the metal d orbitals [3].

We have undertaken an X-ray crystallographic study of the complexes $Ru(Cp)(\text{-}C\equiv CPh)(PPh_3)_2$ and $[Ru(Cp)(CO)(PPh_3)_2][BPh_4]$ in an attempt to ascertain the amount of backbonding in a typical metal alkynyl complex. To date, no structural comparison of congruent metal acetylide and metal carbonyl complexes has appeared in the literature. We have chosen the metal system $Ru(Cp)(PPh_3)_2$ for it readily stabilizes metal–carbon bonds to produce a variety of hydrocarbyl complexes that are generally air stable and thermally robust.

Experimental*

The ruthenium compounds **I** and **II** were prepared as described previously [4, 5]. Crystals of the acetylide complex, **I**, were grown by slow diffusion of ethanol into a saturated chloroform solution of the compound. Complex **II** readily crystallized from a methylene chloride/petroleum ether mixture. Both crystallizations were performed with the use of normal Schlenk techniques.

Preliminary Weissenberg and precession photographs were recorded with the use of CuKα X-radiation. A Picker FACS-1 diffractometer was used to obtain lattice parameters and collect intensities in a manner standard in this laboratory [6a]. Table I summarizes the crystal details and intensity data for the data collections, both at –162 °C. For each data collection the intensities of six strong reflections, remeasured every 100 reflections during the data collection, revealed no significant loss of intensity.

For each structure the position of the Ru atoms was found in a Patterson synthesis. The positions of

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*Tables IV–IX, XI and XII have been deposited with the Editor-in-Chief in Padua.

0020-1693/85/$3.30

TABLE I. Crystallographic Details for Cyclopentadienyl(phenylacetylido)bis(triphenylphospine)ruthenium(II) (Complex I) and Cyclopentadienyl(carbonyl)bis(triphenylphosphine)ruthenium(II) Tetraphenylborate (Complex II).

	Complex I	Complex II
Formula	$C_{49}H_{40}P_2Ru$	$C_{66}H_{55}BOP_2Ru$
Formula mass	791.9	1036.9
Space group	C_{2h}^5-$P2_1/c$	C_{2h}^5-$P2_1/a$
a (Å)	11.256(2)	26.413(6)
b (Å)	17.139(3)	14.953(7)
c (Å)	22.084(4)	12.747(3)
β (°)	118.52(1)	96.40(1)
Volume (Å^3)	3743	5003
Z	4	4
ρ_c (g cm^{-3}) (−162 °C)	1.405	1.378
ρ_m (g cm^{-3}) (20 °C)	1.37(5) (by flotation in CCl_4/C_6H_5Cl)	1.32(5) by flotation in CCl_4/C_6H_5Cl mixture)
Crystal dimensions (mm)	Crystal # 1:[a] 0.17 × 0.28 × 0.82	0.286 × 0.464 × 0.540
	Crystal # 2: 0.16 × 0.17 × 0.88	–
Crystal volume (mm^3)	Crystal # 1: 0.043	0.054
	Crystal # 2: 0.026	–
μ (MoKα) (cm^{-1})	5.3	4.1
Temperature (°C)	−162[b]	−162
Transmission factors	0.890–0.934	0.849–0.900
Scan mode	$\theta-2\theta$	$\theta-2\theta$
Scan speed	2° in 2θ min^{-1}	2° in 2θ min^{-1}
Scan range (°)	0.9 below Kα_1 to 1.00 above Kα_2	0.9 below Kα_1 to 1.00 above Kα_2
Background counts (s)	10 at each end of scan with rescan option[c]	
Data collected	$\pm h, +k, +l$	$\pm h, +k, +l$
2θ limits (°)	3.0–50.0	3.0–53.0
Unique data	6214	10,072
Unique data with $F_o^2 > 3\sigma(F_o^2)$	5296	7501
Final number of variables	441	641
$R(F)$ $(F_o^2 > 3\sigma(F_o^2))$	0.038	0.057
$R_w(F)$	0.042	0.060
$R(F^2)$	0.046	0.069
$R_w(F^2)$	0.082	0.076
Error in observation of unit weight, e^2	1.64	1.08

[a] Two crystals were used to collect data for complex I, as the crystal used initially cracked and was lost. The data for each crystal were corrected for absorption and placed on a common scale. [b] The low temperature system is based on a design by J. C. Huffman, ref. [6b]. [c] Ref. [6c].

the 2 P and 46 C atoms for complex I and 2 P, O, B, and 58 C atoms for complex II were found with the use of DIRDIF [7]. The positions of the remaining non-hydrogen atoms were obtained from a series of difference electron density syntheses after absorption corrections had been applied to the data.

The positions of the hydrogen atoms were idealized (C–H = 0.95 Å, B(H) = B(C) + 1.0 Å^2). These hydrogen-atom positions were not varied in the refinement. Phenyl ring C(3)–C(8) of complex I is disordered and alternative positions of atoms C(4)–C(8) were found in a difference Fourier synthesis. The two rings C(3), C(4), C(5), C(6), C(7), C(8) and C(3) [common atom], C(4*), C(5*), C(6*), C(7*) and C(8*) were refined as rigid groups with carbon atoms treated isotropically and the occupancy of the C(3)–C(8*) ring allowed to vary. This parameter refined to a value of 0.48(3).

For both structures the final least-squares refinements were carried out on F_o^2 with the use of all unique data, including those with $F_o^2 < 0$. Agreement indices as well as crystallographic details are found in Table I. The following data are tabulated: final positional parameters (Table II, Complex I;

TABLE II. Positional Parameters for the Non-Hydrogen Atoms of $Ru(Cp)(C_2Ph)(PPh_3)_2$, I.

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	0.242058(22)	0.431587(12)	0.175314(11)	C(33)	0.10909(30)	0.30781(17)	0.28717(15)
P(1)	0.424709(70)	0.352216(39)	0.234750(35)	C(34)	0.09521(31)	0.26414(18)	0.33615(15)
P(2)	0.068680(72)	0.347421(40)	0.157170(36)	C(35)	0.04381(34)	0.19022(18)	0.32119(16)
C(1)	0.25280(26)	0.46288(15)	0.26581(14)	C(36)	0.00562(46)	0.15946(19)	0.25700(19)
C(2)	0.25959(27)	0.48414(16)	0.31987(14)	C(37)	0.01818(40)	0.20349(17)	0.20714(17)
C(9)	0.33382(30)	0.53703(17)	0.15516(15)	C(38)	0.01625(27)	0.28789(15)	0.07932(14)
C(10)	0.19684(31)	0.55342(15)	0.13551(15)	C(39)	−0.08967(31)	0.31008(17)	0.01566(15)
C(11)	0.11451(28)	0.50309(17)	0.08162(14)	C(40)	−0.12254(34)	0.26621(19)	−0.04328(15)
C(12)	0.19980(30)	0.45448(17)	0.06623(14)	C(41)	−0.05107(36)	0.19999(19)	−0.03965(16)
C(13)	0.33421(29)	0.47543(17)	0.11223(14)	C(42)	0.05624(32)	0.17718(18)	0.02291(16)
C(14)	0.44297(26)	0.29226(16)	0.30741(14)	C(43)	0.08883(28)	0.22069(16)	0.08160(15)
C(15)	0.50481(28)	0.31940(17)	0.37477(14)	C(44)	−0.09348(27)	0.39571(16)	0.13623(13)
C(16)	0.51484(31)	0.27165(21)	0.42824(15)	C(45)	−0.10244(28)	0.47635(16)	0.13833(14)
C(17)	0.46444(31)	0.19704(19)	0.41442(16)	C(46)	−0.22707(29)	0.51257(16)	0.11523(15)
C(18)	0.40249(31)	0.16932(17)	0.34763(16)	C(47)	−0.34328(29)	0.46907(18)	0.09201(15)
C(19)	0.39139(29)	0.21626(16)	0.29478(15)	C(48)	−0.33484(29)	0.38843(18)	0.09343(15)
C(20)	0.57952(28)	0.41293(15)	0.27152(13)	C(49)	−0.21111(29)	0.35209(16)	0.11524(15)
C(21)	0.58114(29)	0.48187(16)	0.30663(14)	C(3)	0.2579(2)	0.4994(1)	0.3843(1)
C(22)	0.68808(34)	0.53262(18)	0.32980(15)	C(4)	0.1348(2)	0.5098(2)	0.3830(1)
C(23)	0.79698(37)	0.51673(20)	0.31887(18)	C(5)	0.1301(3)	0.5209(2)	0.4440(2)
C(24)	0.79741(36)	0.44946(21)	0.28450(19)	C(6)	0.2486(4)	0.5217(3)	0.5062(1)
C(25)	0.68995(30)	0.39754(17)	0.26122(15)	C(7)	0.3718(3)	0.5114(2)	0.5075(1)
C(26)	0.46218(26)	0.27903(15)	0.18529(14)	C(8)	0.3764(2)	0.5002(2)	0.4465(1)
C(27)	0.38711(27)	0.27733(16)	0.11394(14)	C(4*)	0.2117(4)	0.5803(2)	0.3909(2)
C(28)	0.41604(28)	0.22323(17)	0.07579(15)	C(5*)	0.2025(3)	0.5975(1)	0.4498(2)
C(29)	0.51942(30)	0.17036(17)	0.10846(17)	C(6*)	0.2259(4)	0.5399(2)	0.4981(1)
C(30)	0.59458(29)	0.17047(17)	0.17942(16)	C(7*)	0.2586(4)	0.4650(2)	0.4876(2)
C(31)	0.56648(28)	0.22445(16)	0.21806(15)	C(8*)	0.2678(4)	0.4478(2)	0.4287(2)
C(32)	0.06981(28)	0.27897(16)	0.22165(14)				

Table III, Complex II), thermal parameters (Table IV, Complex I; Table V, Complex II), positions of hydrogen atoms (Table VI, Complex I; Table VII, Complex II), $10|F_o|$ *vs.* $10|F_c|$ (Table VIII, Complex I; Table IX, Complex II), principal bond lengths and angles (Table X), and bond lengths and angles within phenyl groups (Table XI, Complex I; Table XII, Complex II).

Discussion

The coordination geometry about the central Ru atom in both complexes is distorted tetrahedral if the cyclopentadienyl ring is considered to occupy one coordination site. Alternatively, this geometry may be viewed as distorted octahedral if the cyclopentadienyl ring is allotted three facial coordination sites. The latter viewpoint will be utilized in this work. The dihedral angle between the Cp ring and the plane containing atoms Ru, P(1), and P(2) is 59.39° in the acetylide complex **I** and 55.08° for the carbonyl complex **II**.

Tables XI and XII display average C–C distances of phenyl groups with standard deviations calculated on the assumption that the values averaged are from the same population. From these standard deviations it appears that standard deviations estimated from the inverse matrix may be optimistic by a factor of 2. This we keep in mind in the following discussion.

The five C atoms of the Cp ring in the acetylide complex (**I**) are approximately equidistant from the Ru atom, with values ranging from 2.227(3) to 2.256(3) Å. Similarly, the Ru–C distances in the carbonyl complex **II** range from 2.235(2) to 2.271(2) Å. These Ru–Cp distances may be compared with those in $RuCl(Cp)(PR_3)_2$, R = Ph, Me [8] (2.192(3)–2.220(3) Å), in $Ru(Cp)_2$ [9] (2.193(16) to 2.223(19) Å), and in $[Ru(Cp)(1,3\text{-butadiene})(PMe_3)_2][PF_6]$ (2.196(5) to 2.258(4) Å) [10]. The section of the Cp ring in complex **I** that is furthest from the Ru atom (C(12)) is nearly *trans* to the acetylide ligand. Similarly, in complex **II** atoms C(4) and C(5) are furthest from the Ru atom and are approximately *trans* to the CO ligand. Thus it is tempting to ascribe the observed variations in Ru–C(Cp) distances to such *trans* effects. A similar observation has been made previously [10] for that portion of a Cp ring *trans* to a phosphine ligand. Both Cp rings are planar within the limits of error; the maximum deviations being that of atom C(12) in complex **I** at −0.0053(32) Å and atom

TABLE III. Positional Parameters for the Non-Hydrogen Atoms of $[Ru(Cp)(CO)(PPh_3)_2][BPh_4]$, **II**.

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	0.188763(6)	0.11286(1)	0.30045(1)	C(32)	0.0816(1)	0.2470(2)	0.1799(2)
P(1)	0.20159(2)	0.07864(4)	0.12624(4)	C(33)	0.0513(1)	0.3112(2)	0.1239(2)
P(2)	0.10139(2)	0.08825(3)	0.29112(4)	C(34)	−0.0006(1)	0.2965(2)	0.1033(2)
C	0.21148(7)	−0.0735(1)	0.3815(1)	C(35)	−0.0221(1)	0.2194(2)	0.1378(2)
B	0.37827(9)	0.0678(1)	0.5984(2)	C(36)	0.00789(9)	0.1551(2)	0.1933(2)
C(1)	0.20149(8)	−0.0046(2)	0.3461(2)	C(37)	0.07706(7)	−0.0186(1)	0.2385(2)
C(2)	0.2522(1)	0.1660(2)	0.4140(2)	C(38)	0.08338(8)	−0.0952(1)	0.3014(2)
C(3)	0.2054(1)	0.1875(2)	0.4526(2)	C(39)	0.06613(9)	−0.1779(2)	0.2629(2)
C(4)	0.17834(9)	0.2470(2)	0.3788(2)	C(40)	0.04157(9)	−0.1845(2)	0.1607(2)
C(5)	0.20790(9)	0.2603(2)	0.2945(2)	C(41)	0.0354(1)	−0.1090(2)	0.0978(2)
C(6)	0.25401(8)	0.2099(2)	0.3165(2)	C(42)	0.05372(8)	−0.0266(2)	0.1359(2)
C(7)	0.18129(8)	−0.0251(1)	0.0574(2)	C(43)	0.42604(9)	0.0762(1)	0.6917(2)
C(8)	0.17022(8)	−0.1022(2)	0.1105(2)	C(44)	0.42219(8)	0.0459(1)	0.7942(2)
C(9)	0.15985(9)	−0.1825(1)	0.0566(2)	C(45)	0.46302(9)	0.0482(1)	0.8731(2)
C(10)	0.16072(8)	−0.1864(2)	−0.0516(2)	C(46)	0.5100(1)	0.0805(2)	0.8521(2)
C(11)	0.1725(1)	−0.1098(2)	−0.1056(2)	C(47)	0.51554(8)	0.1096(2)	0.7505(2)
C(12)	0.1829(1)	−0.0298(2)	−0.0520(2)	C(48)	0.47408(8)	0.1077(2)	0.6726(2)
C(13)	0.17762(8)	0.1650(1)	0.0327(2)	C(49)	0.32404(8)	0.0785(2)	0.6495(2)
C(14)	0.20514(8)	0.2436(2)	0.0243(2)	C(50)	0.31415(8)	0.1558(2)	0.7070(2)
C(15)	0.1862(1)	0.3116(2)	−0.0439(2)	C(51)	0.2674(1)	0.1725(2)	0.7445(2)
C(16)	0.1397(1)	0.3008(2)	−0.1046(2)	C(52)	0.22853(8)	0.1092(2)	0.7286(2)
C(17)	0.11164(9)	0.2231(2)	−0.0955(2)	C(53)	0.2379(1)	0.0300(2)	0.6778(2)
C(18)	0.13042(9)	0.1556(2)	−0.0272(2)	C(54)	0.28454(9)	0.0150(2)	0.6393(2)
C(19)	0.26966(8)	0.0721(1)	0.1110(2)	C(55)	0.38476(8)	0.1462(2)	0.5089(2)
C(20)	0.30364(8)	0.0431(2)	0.1959(2)	C(56)	0.36207(8)	0.2309(2)	0.5063(2)
C(21)	0.3552(1)	0.0343(2)	0.1859(2)	C(57)	0.37123(9)	0.2959(2)	0.4327(2)
C(22)	0.37313(8)	0.0542(2)	0.0902(2)	C(58)	0.4042(1)	0.2789(2)	0.3579(2)
C(23)	0.3397(1)	0.0806(2)	0.0051(2)	C(59)	0.4274(1)	0.1953(2)	0.3574(2)
C(24)	0.28802(9)	0.0900(1)	0.0148(2)	C(60)	0.41749(9)	0.1305(2)	0.4308(2)
C(25)	0.07948(8)	0.0878(1)	0.4227(2)	C(61)	0.11738(8)	0.4707(2)	0.4601(2)
C(26)	0.10967(8)	0.0484(1)	0.5075(2)	C(62)	0.15345(9)	0.4433(2)	0.5434(2)
C(27)	0.0923(1)	0.0430(2)	0.6064(2)	C(63)	0.1490(1)	0.3649(2)	0.6000(2)
C(28)	0.0450(1)	0.0780(2)	0.6227(2)	C(64)	0.1071(1)	0.3100(2)	0.5765(2)
C(29)	0.01523(8)	0.1180(2)	0.5397(2)	C(65)	0.0701(1)	0.3348(2)	0.4957(2)
C(30)	0.03208(8)	0.1222(2)	0.4406(2)	C(66)	0.07590(8)	0.4130(2)	0.4380(2)
C(31)	0.06068(8)	0.1694(1)	0.2158(2)				

C(3) in complex **II** at 0.0069(24) Å from the respective best-weighted least-squares planes. Distances within the ring for complex **I** range from 1.402(4) to 1.429(4) Å, while those in complex **II** range from 1.410(4) to 1.434(3) Å. In each complex the Cp ring has two short and three long C–C bonds (**I**, C(12)–C(13) 1.408(4) Å, C(10)–C(11) 1.402(4) Å, *vs.* 1.420(4), 1.429(4), and 1.416(4) Å; **II**, C(2)–C(6) 1.410(4) Å, C(4)–C(5) 1.412(3) *vs.* 1.434(4), 1.427(3), 1.419(4) Å). Such a 'diene' arrangement has been documented for $C_5(CH_3)_5$ complexes [11, 12] where the range of C–Me distances provides a calibration of the estimated standard deviations. This diene arrangement is believed to be a manifestation of the asymmetrical field about the Cp rings.

Cis phosphines coordinated to Ru(II) centers generally have Ru–P bond lengths in the range 2.20–2.39 Å whereas *trans* phosphines have Ru–P distances in the range 2.33–2.48 Å [13]. The values found in this work (2.29–2.34 Å) are normal. The two Ru–P bond distances in the carbonyl complex **II** are ~0.04 Å longer than the corresponding bond lengths of the acetylide complex **I**.

The C–C triple bond of the acetylide complex **I** has a length of 1.215(4) Å. This value agrees well with literature values for the C–C bond lengths of terminal alkynyl ligands, which range from 1.18 to 1.24 Å [14]. As expected, the M–C ≡ C linkage in complex **I** is essentially linear (178.0(2)°). The C–O bond length of the carbonyl complex **II** is normal at 1.144(3) Å. The C–O bond lengths of ruthenium η^1-carbonyls have been reported from 1.10 to 1.20 Å [15, 16]. The length of the present C–O bond may be interpreted in favor of the Ru = C = O resonance form and extensive π-backbonding. However, the C–O bond is short and polar and it will be most sensitive to the temperature at which the data set was collected and the extent of that data set. In the

TABLE X. Bond Distances (Å) and Bond Angles (°) in $Ru(Cp)(C_2Ph)(PPh_3)_2$ (I) and $[Ru(Cp)(CO)(PPh_3)_2][BPh_4]$ (II).

Complex I		Complex II	
Ru–P(1)	2.285(1)	Ru–P(1)	2.340(1)
Ru–P(2)	2.303(1)	Ru–P(2)	2.327(1)
Ru–C(1)	2.016(3)	Ru–C(1)	1.869(2)
Ru–C(9)	2.229(3)	Ru–C(2)	2.235(2)
Ru–C(10)	2.228(3)	Ru–C(3)	2.239(2)
Ru–C(11)	2.238(3)	Ru–C(4)	2.271(2)
Ru–C(12)	2.256(3)	Ru–C(5)	2.265(2)
Ru–C(13)	2.227(3)	Ru–C(6)	2.244(2)
P(1)–C(14)	1.833(3)	P(1)–C(7)	1.833(2)
P(1)–C(20)	1.851(3)	P(1)–C(13)	1.822(2)
P(1)–C(26)	1.840(3)	P(1)–C(19)	1.832(2)
P(2)–C(32)	1.840(3)	P(2)–C(25)	1.834(2)
P(2)–C(38)	1.837(3)	P(2)–C(31)	1.822(2)
P(2)–C(44)	1.851(3)	P(2)–C(37)	1.822(2)
C(1)–C(2)	1.215(4)	C(1)–O	1.144(3)
C(2)–C(3)	1.456(4)	C(2)–C(3)	1.419(4)
C(9)–C(10)	1.416(4)	C(3)–C(4)	1.427(3)
C(10)–C(11)	1.402(4)	C(4)–C(5)	1.412(3)
C(11)–C(12)	1.429(4)	C(5)–C(6)	1.434(3)
C(12)–C(13)	1.408(4)	C(6)–C(2)	1.410(4)
C(13)–C(9)	1.420(4)	B–C(43)	1.639(3)
		B–C(49)	1.646(3)
		B–C(55)	1.658(3)
		B–C(61)	1.642(3)
P(1)–Ru–P(2)	100.50(3)	P(1)–Ru–P(2)	99.47(2)
C(1)–Ru–C(9)	99.6(1)	C(1)–Ru–C(2)	92.11(9)
C(1)–Ru–C(10)	92.1(1)	C(1)–Ru–C(3)	100.83(9)
C(1)–Ru–C(11)	118.6(1)	C(1)–Ru–C(4)	136.02(9)
C(1)–Ru–C(12)	153.4(1)	C(1)–Ru–C(5)	153.16(8)
C(1)–Ru–C(13)	134.8(1)	C(1)–Ru–C(6)	118.00(9)
Ru–P(1)–C(14)	122.05(8)	Ru–P(1)–C(7)	125.01(7)
Ru–P(1)–C(20)	108.51(9)	Ru–P(1)–C(13)	112.91(7)
Ru–P(1)–C(26)	117.60(9)	Ru–P(1)–C(19)	111.09(7)
C(14)–P(1)–C(20)	104.0(1)	C(7)–P(1)–C(13)	103.0(1)
C(14)–P(1)–C(26)	100.1(1)	C(7)–P(1)–C(19)	98.2(1)
C(20)–P(1)–C(26)	102.1(1)	C(13)–P(1)–C(19)	104.0(1)
Ru–P(2)–C(32)	124.9(1)	Ru–P(2)–C(25)	111.47(7)
Ru–P(2)–C(38)	112.18(8)	Ru–P(2)–C(31)	116.45(7)
Ru–P(2)–C(44)	114.59(9)	Ru–P(2)–C(37)	117.69(7)
C(32)–P(2)–C(38)	89.7(1)	C(31)–P(2)–C(25)	104.6(1)
C(32)–P(2)–C(44)	96.9(1)	C(31)–P(2)–C(37)	103.10(9)
C(38)–P(2)–C(44)	100.2(1)	C(25)–P(2)–C(37)	101.49(9)
Ru–C(1)–C(2)	178.0(2)	Ru–C(1)–O	174.2(2)
C(9)–C(10)–C(11)	108.6(2)	C(2)–C(3)–C(4)	107.7(2)
C(10)–C(11)–C(12)	108.3(3)	C(3)–C(4)–C(5)	108.2(2)
C(11)–C(12)–C(13)	107.0(2)	C(4)–C(5)–C(6)	107.8(2)
C(12)–C(13)–C(9)	109.0(2)	C(5)–C(6)–C(2)	107.8(2)
C(13)–C(9)–C(10)	107.0(3)	C(6)–C(2)–C(3)	108.5(2)
C(1)–C(2)–C(3)	171.9(3)	C(43)–B–C(49)	109.8(2)
		C(43)–B–C(55)	108.3(2)
		C(43)–B–C(61)	108.1(2)
		C(49)–B–C(55)	111.4(2)
		C(49)–B–C(61)	112.0(2)
		C(55)–B–C(61)	107.2(2)

present instance of an extensive data set collected at −162 °C one would anticipate little foreshortening of the apparent bond length.

The difference between the Ru–C_2Ph and Ru–CO bond lengths (2.016(3) *vs.* 1.869(2) Å) is the most obvious distinction between complexes **I** and **II**. The

TABLE XIII. Selected Ru–C Bond Distances.

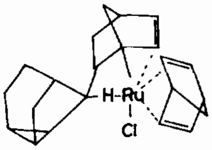
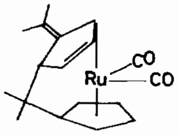
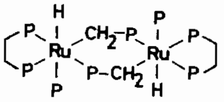
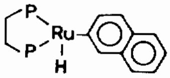
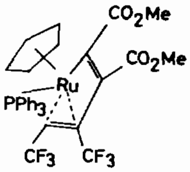
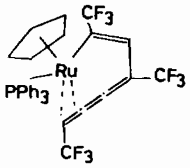
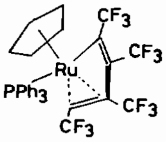
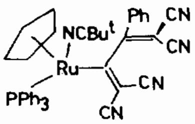
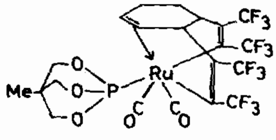
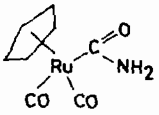
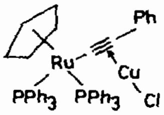
Complex	Ru–C Bond Length	α-C Hybridization	Ref.
 **A**	2.099(2)	sp^3	19
 **B**	2.180(2)	sp^3	20
 **C**	2.203(6) 2.219(6)	sp^3	21
 **D**	2.160(10)	sp^2	22
 **E**	2.082(5)	sp^2	23
 **F**	2.11(1)	sp^2	24
 **G**	2.05	sp^2	25
 **H**	2.074(3)	sp^2	26

TABLE XIII. *(Continued)*

 **J**	1.912(9) 2.184(15) (*trans* to P)	sp^2	27
 **K**	2.084(7) 2.080(6) 2 independent molecules/unit cell	sp^2	28
$Ru(C_2Ph)(PMe_2Ph)_4$ **L**	2.051	*sp*	29
 **M**	2.017(9)	*sp*	30

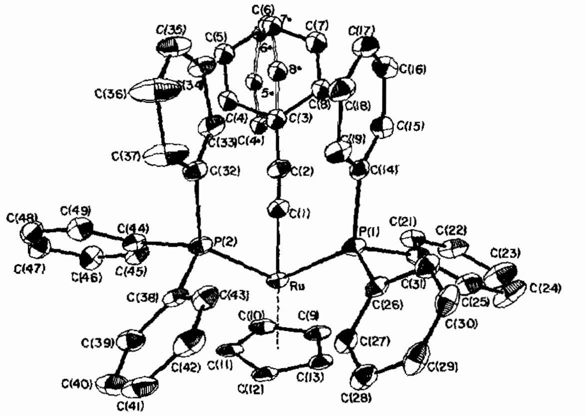


Fig. 1. Thermal ellipsoid plot (50% probability) of **I** showing the atom numbering scheme. The hydrogen atoms have been omitted for clarity. The disorder in phenyl ring C(3)–C(8) has been represented by drawing two alternative positions for atoms C(4)–C(8).

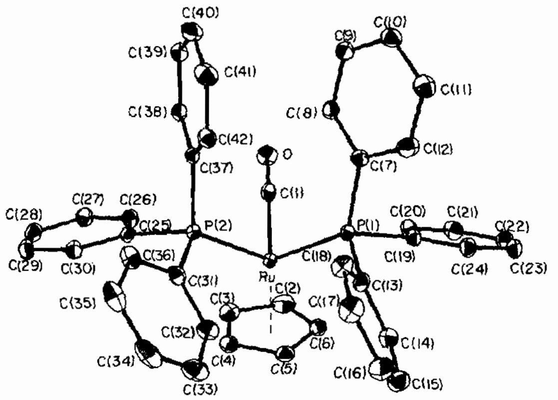


Fig. 2. Thermal ellipsoid plot (50% probability) of **II**, featuring only the $[RuCp(CO)(PPh_3)_2]^+$ cation. Hydrogen atoms have been omitted for clarity.

covalent radius of a Ru(II) atom has been estimated to be 1.33 Å [17] and those of sp^3, sp^2, and sp C atoms are 0.77, 0.73, 0.60 Å [18], respectively. Therefore one would expect Ru–sp^3C, Ru–sp^2C, and Ru–spC bond lengths to be about 2.10, 2.06, and 1.93 Å, respectively. Table XIII presents some recent results on Ru–C bond lengths [19–30]. Complexes **B** and **C** [20, 21] have Ru–C distances that are ~0.1 Å greater than the calculated sum of covalent radii. The Ru–C bond in complex **C** may be lengthened significantly by the phosphine ligand *trans* to it. The only Ru–sp^2C bond distance less than the sum of the covalent radii is that of **J** (1.912(9) Å) which also has an Ru–sp^2C bond with a length of 2.184(15) Å [25]. The latter Ru–C bond is *trans* to a phosphite ligand.

The Ru–spC bond length of the acetylide in the present work is nearly identical with that in the related complex $[Ru(C_5H_5)(C_2Ph)(PPh_3)_2CuCl]$ (2.017(9) Å) [30]. Both of these values as well as that in $Ru(C_2Ph)(PMe_2Ph)_4$ (2.051 Å) [29] are significantly greater than 1.93 Å, as estimated from radii values. A number of tri- and tetraruthenium clusters have been found to contain μ-η^3-acetylides, -C_2R groups σ-bound to one Ru atom and π-bound to the remaining Ru atoms. In these instances the Ru–σ(C) bond is generally short; *e.g.*, 1.947(3) Å in $Ru_3(H)(CO)_9(C_2Bu^t)$ [31], 1.96(2) Å in $[Ru_3(CO)_9(C_6H_9)HgBr]_2$ [32], 1.946(4) Å in $Ru_3(H)(CO)_8(C_2Bu^t)(PPh_2OEt)$ [33], 1.904(14) Å in $Ru_3(H)(CO)_9C_2CCH_2Ph$ [34], 1.95(2) Å in $[Ru_3(CO)_9C_2Bu^t][AsPh_4]$ [35], and 1.944(21) Å in $Ru_3(H)(CO)_7((C_6H_9)(C_6H_{10}))$ [36]. Catti, Gervasio, and Mason [31] have ascribed partial double-bond character to this Ru–σC bond as well as reduction of the bond order of the C ≡ C bond. Carty [37] has suggested that coordination of the acetylide moiety to an increasing number of metal atoms strengthens and hence shortens the M–C bond. Perhaps π-coordination of the acetylide group lowers the energy of the π^* orbital of the metal–acetylide interaction, enabling backbonding to occur. This pathway is not available to a monomeric acetylide.

The Ru–C bond distance (1.869(2) Å) in the carbonyl complex is normal for a monomeric ruthenium carbonyl complex. Ru–CO bond distances generally range from 1.74 to 1.98 Å [38]. The larger values are usually found in bonds involving axial CO groups in triruthenium clusters, such as $Ru_3(CO)_{12}$ [39] and $Ru_3(CO)_{11}$(t-BuCN) [40]. In these instances the Ru atoms are effectively surrounded by carbonyl groups competing for π backbonding from the metal center. The length of the Ru–C bond in the present carbonyl complex is similar to that in $[Ru(C_5H_5)(=C=C=CPh_2)(PMe_3)_2]^+$ [41]. In this allenylidene complex the Ru–C bond is 1.884(5) Å in length and is described as a Ru = C bond. On this basis one would expect that resonance form (A) is a major contributor to the present carbonyl complex:

$$\text{(A) Ru}=\text{C}=\text{O} \longleftrightarrow \text{(B) Ru–C}\equiv\text{O}$$

In this way we may also rationalize the variation in Ru–P bond lengths in complexes **I** and **II**. In complex **I**, owing to the lack of backbonding capacity of the acetylide, the two phosphine ligands may exhibit some π-character with the result of a shortened Ru–P distance. In complex **II** the backbonding from the CO group compensates for any excess charge on the metal and the Ru–P bond lengths are not shortened.

We have examined the structures of two similar Ru(II) complexes, $Ru(Cp)(C_2Ph)(PPh_3)_2$ and $[Ru(Cp)(CO)(PPh_3)_2][BPh_4]$. As expected, the Ru–C(O) bond (1.869(2) Å) is much shorter than the Ru–C(acetylido) bond (2.016(3) Å). These results suggest that the CO ligand is involved in extensive π-backbonding while the acetylide ligand shows little, if any, metal–ligand p_π–d_π interaction. This finding supports the categorization of acetylide ligands as σ-bonding groups.

Acknowledgments

This research was supported by the National Science Foundation (Grant CHE-83-08076). We thank Johnson-Matthey, Inc., Malvern, Pa., for the generous loan of ruthenium used in this study.

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