Journal of Organometallic Chemistry, 364 (1989) 391–397
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09591

Crystal structure of the maleic anhydride complex $Ru(\eta^2\text{-}C_4H_2O_3)(CO)(CN\text{-}p\text{-tolyl})(PPh_3)_2$

C.E.F. Rickard, W.R. Roper *, L.J. Wright and L. Young

Department of Chemistry, The University of Auckland, Auckland (New Zealand)

(Received September 30th, 1988)

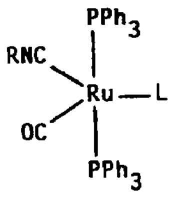
Abstract

The structure of the maleic anhydride complex $Ru(\eta^2\text{-}C_4H_2O_3)(CO)(CN\text{-}p\text{-tolyl})(PPh_3)_2$ (**1**) has been determined by X-ray crystallography. Crystals of **1** are monoclinic, space group $P2_1/c$, a 9.917(1), b 20.244(3), c 20.768(3) Å, β 99.80(1)°. $Z = 4$, D_c 1.406 g cm^{-3}. The structure was solved by conventional Patterson and Fourier techniques and refined by full matrix least squares. The refinement converged to $R = 0.061$, $R_w = 0.063$. The geometry about ruthenium is approximately trigonal bipyramidal with the maleic anhydride and the two triphenylphosphines equatorial. The maleic anhydride coordinates to ruthenium via the alkene (C(1)–C(4)) bond. The elongated C(1)–C(4) bond and the values of $\nu(C\equiv N)$ and $\nu(C\equiv O)$ in the infrared spectrum suggest a strong alkene π-acceptor component in the Ru-maleic anhydride interaction.

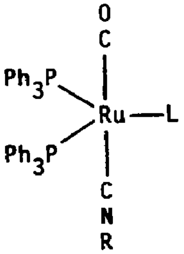
Introduction

The electron-rich d^8 ruthenium(0) complex $Ru(CO)(CNR)(PPh_3)_3$ (R = *p*-tolyl) readily undergoes both oxidative addition and ligand substitution reactions [1]. The ligand substitution reactions probably proceed via addition to the coordinatively unsaturated "$Ru(CO)(CNR)(PPh_3)_2$" which is formed transiently in solution on dissociation of a triphenylphosphine ligand. The stereochemistry of the resulting substitution products isolated from solution appears to depend on the nature of the coordinating ligand. Thus, a *trans*-arrangement of triphenylphosphine ligands is preferred for the products of carbon disulfide and dioxygen addition (structure **A** below) whereas a *cis*-arrangement appears to be favoured for maleic anhydride (ma), fumaronitrile (fn), maleonitrile (mn), and dimethylfumarate (df) (structure **B** below) [2].

0022-328X/89/$03.50



A (L = O_2, CS_2)



B (L = ma, fn, mn, df)

Only three other structurally-characterized mononuclear complexes in which maleic anhydride bonds in a dihapto fashion via the double bond between carbon atoms have been reported [3–5]. We therefore determined the structure of the maleic anhydride adduct $Ru(\eta^2\text{-}C_4H_2O_3)(CO)(CNR)(PPh_3)_2$ (**1**) by a single crystal X-ray crystallographic study, and report the results here.

Results and discussion

Pale yellow crystals of **1** can be isolated in good yield and in high purity after reaction of $Ru(CO)(CNR)(PPh_3)_3$ with free maleic anhydride in benzene followed by recrystallization of the product from dichloromethane/ethanol solution. The carbonyl stretching frequencies of the π-bound maleic anhydride ligand are observed in the IR spectrum at 1789 and 1729 cm^{-1}. These values are very close to those reported for other maleic anhydride complexes [4,6], but are distinctly lower than those for free maleic anhydride (1850 and 1780 cm^{-1}) [4]. The stretching frequencies of the metal bound carbonyl and isocyanide ligands are observed at 1955 and 2148 cm^{-1}, respectively. The corresponding bands in the precursor complex, $Ru(CO)(CNR)(PPh_3)_3$, appear at the much lower values of 1901 and 2090 cm^{-1}, respectively [1]. These changes indicate the maleic anhydride behaves as a very good π-acceptor ligand in complex **1**.

Crystals suitable for a single crystal X-ray crystallographic structure determination were grown from dichloromethane/ethanol solution. The structure was solved by conventional Patterson and Fourier techniques and the molecular geometry is shown in Figs. 1 and 2. The ruthenium atom is five coordinate, with the phosphine and maleic anhydride ligands occupying the equatorial plane and the carbonyl and isocyanide ligands the axial positions. The equatorial plane is not symmetric, the maleic anhydride ligand lying slightly closer to one triphenylphosphine than the other (C(4)–Ru–P(2) 98° and C(1)–Ru–P(1) 116.4°). Surprisingly the maleic anhydride ligand adopts a position adjacent to the more bulky *p*-tolylisocyanide ligand, but the rings are so orientated that all contacts are of Van der Waal's type. The carbon–carbon double bond is symmetrically bonded to the metal atom with Ru–C(1) 2.206(11) and Ru–C(4) 2.180(11) Å. These ruthenium carbon distances fall within the range of values reported for other ruthenium(0)-alkene complexes [7,8]. The length of the double bond C(1)–C(4) is 1.45 Å and this is significantly longer than the corresponding distance of 1.303 Å in free maleic anhydride [9]. A similar bond lengthening on coordination has been reported for the maleic anhydride ligand in other structurally characterised complexes [3–5]. This elongation of the double bond is consistent with there being a large alkene π-acceptor component to

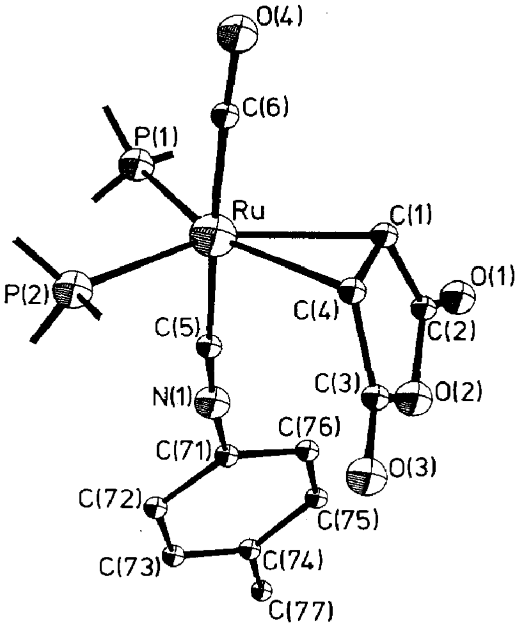


Fig. 1. Molecular geometry for Ru(η^2-$C_4H_2O_3$)(CO)(CN-*p*-tolyl)(PPh_3)$_2$ with the phenyl rings of the triphenylphosphine ligands omitted for clarity.

the Ru-alkene bond. Other bond lengths in the maleic anhydride moiety are within normally accepted values. The maleic anhydride ligand is not completely planar, the oxygen atom of the heterocycle being displaced by 0.07 Å from the plane of the carbon atoms towards the metal and the carbonyl oxygens by 0.05 Å away from the metal. The plane of the maleic anhydride ligand makes an angle of 107° with the

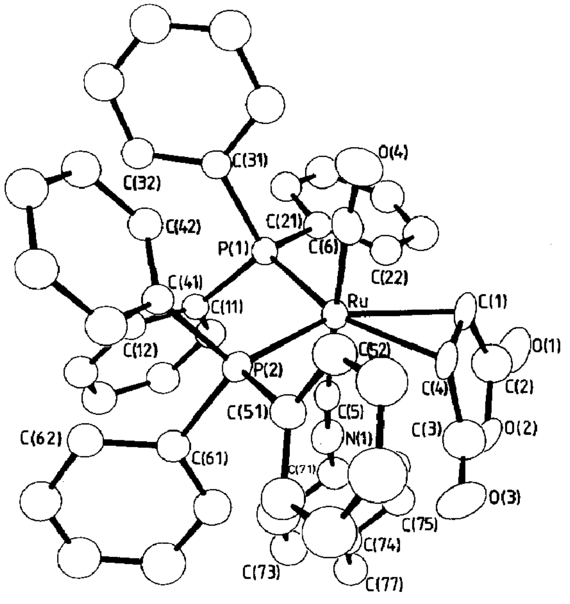


Fig. 2. Molecular geometry for Ru(η^2-$C_4H_2O_3$)(CO)(CN-*p*-tolyl)(PPh_3)$_2$.

Table 1

Atomic coordinates for Ru(η^2-$C_4H_2O_3$)(CO)(CN-*p*-tolyl)(PPh_3)$_2$

Atom	*x/a*	*y/b*	*z/c*
Ru	0.26736(9)	0.18138(5)	0.23931(5)
P(1)	0.4038(2)	0.1030(1)	0.3068(1)
P(2)	0.4046(2)	0.2256(1)	0.1678(1)
N(1)	0.1652(9)	0.0547(5)	0.1566(5)
O(1)	−0.0985(8)	0.1045(5)	0.2591(5)
O(2)	−0.0717(8)	0.1519(5)	0.1645(5)
O(3)	−0.0237(10)	0.2249(6)	0.0904(5)
O(4)	0.3447(9)	0.2921(4)	0.3353(4)
C(1)	0.0590(10)	0.1981(5)	0.2599(6)
C(2)	−0.0432(12)	0.1469(8)	0.2314(8)
C(3)	−0.0046(14)	0.2078(8)	0.1457(8)
C(4)	0.0811(10)	0.2369(6)	0.2039(6)
C(5)	0.2052(10)	0.1020(6)	0.1847(5)
C(6)	0.3179(11)	0.2493(6)	0.2981(5)
C(11)	0.4782(10)	0.0415(5)	0.2591(5)
C(12)	0.5796(10)	0.0617(5)	0.2247(5)
C(13)	0.6296(12)	0.0167(6)	0.1823(6)
C(14)	0.5764(12)	−0.0471(6)	0.1737(6)
C(15)	0.4729(12)	−0.0666(6)	0.2092(6)
C(16)	0.4232(11)	−0.0226(5)	0.2519(5)
C(21)	0.3152(10)	0.0504(5)	0.3590(5)
C(22)	0.1736(11)	0.0491(6)	0.3488(5)
C(23)	0.1033(13)	0.0069(7)	0.3866(6)
C(24)	0.1785(13)	−0.0342(6)	0.4324(6)
C(25)	0.3221(13)	−0.0336(6)	0.4431(6)
C(26)	0.3898(11)	0.0090(6)	0.4048(5)
C(31)	0.5463(10)	0.1321(5)	0.3694(5)
C(32)	0.6840(11)	0.1160(5)	0.3702(5)
C(33)	0.7864(13)	0.1442(6)	0.4188(6)
C(34)	0.7471(13)	0.1867(7)	0.4640(6)
C(35)	0.6141(13)	0.2029(6)	0.4673(6)
C(36)	0.5080(12)	0.1748(6)	0.4178(6)
C(41)	0.5689(10)	0.2652(5)	0.2006(5)
C(42)	0.6304(10)	0.2508(5)	0.2645(5)
C(43)	0.7560(11)	0.2805(5)	0.2892(5)
C(44)	0.8177(11)	0.3251(6)	0.2507(5)
C(45)	0.7576(12)	0.3373(5)	0.1881(6)
C(46)	0.6310(11)	0.3087(6)	0.1616(5)
C(51)	0.3219(11)	0.2987(5)	0.1234(5)
C(52)	0.2997(12)	0.3501(6)	0.1629(6)
C(53)	0.2424(14)	0.4121(7)	0.1348(7)
C(54)	0.2067(16)	0.4141(8)	0.0670(8)
C(55)	0.2230(15)	0.3621(8)	0.0278(8)
C(56)	0.2844(12)	0.3008(6)	0.0553(6)
C(61)	0.4487(10)	0.1734(5)	0.1028(5)
C(62)	0.5873(11)	0.1637(5)	0.0960(5)
C(63)	0.6155(13)	0.1214(6)	0.0451(6)
C(64)	0.5161(14)	0.0890(7)	0.0059(7)
C(65)	0.3779(14)	0.0986(7)	0.0117(7)
C(66)	0.3428(12)	0.1413(6)	0.0619(6)
C(71)	0.1067(12)	−0.0058(6)	0.1337(6)
C(72)	0.1691(16)	−0.0430(8)	0.0903(8)
C(73)	0.1068(14)	−0.1031(7)	0.0666(7)
C(74)	−0.0074(12)	−0.1260(6)	0.0870(6)
C(75)	−0.0667(12)	−0.0879(6)	0.1318(6)
C(76)	−0.0094(12)	−0.0276(6)	0.1548(6)
C(77)	−0.0673(12)	−0.1944(6)	0.0652(6)

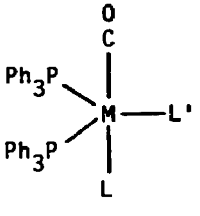
plane defined by the metal and the alkene carbon atoms. This angle is characteristically greater than 90° in coordinated alkenes. The bonds between Ru and the carbon atoms of the mutally *trans* CO and CNR ligands do not differ greatly in length from the corresponding distances reported for other ruthenium(0) and ruthenium(II) complexes [10–13]. It is noteworthy that the Ru–CO distance (1.850(13) Å) is significantly shorter than the Ru–CNR distance (2.004(13) Å), indicating that in this arrangement CO functions as the better π-acceptor ligand. Distances within the isocyanide ligand are within the normally accepted values, as are the distances within the phosphine ligands.

In conclusion the structural and spectroscopic data indicate that the maleic anhydride ligand acts as a very good π-acceptor in complex **1**. This is consistent with other studies which indicate that coordinated maleic anhydride often acts in this manner [3–6].

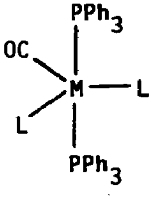
We also make the more general observation that on addition of neutral ligands L′ to the complexes $M(CO)(L)(PPh_3)_3$ (M = Ru, Os; L = CO, CN-*p*-tolyl, CS) (eq. 1) the arrangement of ligands in the product **3** isolated from solution appears to

$$\underset{(2)}{M(CO)L(PPh_3)_3} + L' \rightarrow \underset{(3)}{M(CO)(L)(L')(PPh_3)_2} + PPh_3 \qquad (1)$$

depend on the π-acceptor characteristics of L′. Thus, when L′ is a very good π-acceptor (e.g. C_2F_4, maleic anhydride, fumaronitrile, maleonitrile, dimethylfumarate) complex **3** has the arrangement shown in **C** below [2,14]. When L′ is a poorer π-acceptor (e.g. O_2, CS_2, C_2H_4, CH_2O) complex **3** has the structure shown in **D** with the two triphenylphosphine of the trigonal bipyramid [15,16].



C



D

Table 2

Important interatomic distances for $Ru(\eta^2\text{-}C_4H_2O_3)(CO)(CN\text{-}p\text{-tolyl})(PPh_3)_2$ (Å)

Ru–P(1)	2.381(3)	P(2)–C(61)	1.83(1)
Ru–P(2)	2.355(3)	C(1)–C(2)	1.50(2)
Ru–C(1)	2.206(11)	C(1)–C(4)	1.45(2)
Ru–C(4)	2.180(11)	C(2)–O(1)	1.22(2)
Ru–C(5)	2.004(13)	C(2)–O(2)	1.37(2)
Ru–C(6)	1.850(13)	O(2)–C(3)	1.40(2)
P(1)–C(11)	1.82(1)	C(3)–O(3)	1.19(2)
P(1)–C(21)	1.84(1)	C(3)–C(4)	1.48(2)
P(1)–C(31)	1.85(1)	C(5)–N(1)	1.16(1)
P(2)–C(41)	1.84(1)	N(1)–C(71)	1.40(2)
P(2)–C(51)	1.86(1)	C(6)–O(4)	1.16(1)

Table 3

Important bond angles for $Ru(\eta^2\text{-}C_4H_2O_3)(CO)(CN\text{-}p\text{-tolyl})(PPh_3)_2$ (°)

P(1)–Ru–P(2)	107.1(1)	Ru–P(2)–C(41)	120.2(4)
P(1)–Ru–C(1)	116.4(3)	Ru–P(2)–C(51)	111.2(4)
P(1)–Ru–C(4)	155.0(3)	Ru–P(2)–C(61)	118.9(4)
P(1)–Ru–C(5)	83.6(3)	Ru–C(1)–C(4)	69.7(6)
P(1)–Ru–C(6)	92.5(4)	Ru–C(1)–C(2)	114.2(8)
P(2)–Ru–C(1)	136.4(3)	C(2)–C(1)–C(4)	103.9(1.1)
P(2)–Ru–C(4)	98.0(3)	Ru–C(4)–C(1)	71.7(6)
P(2)–Ru–C(6)	90.7(3)	C(3)–C(4)–C(1)	107.3(1.2)
C(1)–Ru–C(4)	38.6(4)	C(1)–C(2)–O(2)	111.0(1.3)
C(1)–Ru–C(5)	91.4(4)	C(1)–C(2)–O(1)	129.0(1.5)
C(1)–Ru–C(6)	85.2(5)	C(2)–O(2)–C(3)	108.3(1.2)
C(4)–Ru–C(5)	93.5(5)	O(2)–C(3)–C(4)	109.2(1.4)
C(4)–Ru–C(6)	87.6(5)	C(4)–C(3)–O(3)	130.7(1.7)
C(5)–Ru–C(6)	173.0(5)	Ru–C(5)–N(1)	175.4(1.1)
Ru–P(1)–C(11)	112.1(4)	C(5)–N(1)–C(71)	168.7(1.3)
Ru–P(1)–C(21)	116.8(4)	Ru–C(6)–O(4)	177.5(1.0)
Ru–P(1)–C(31)	119.4(4)		

Experimental

The general experimental techniques and instruments used have been described elsewhere [17]. IR spectra were recorded on a Perkin–Elmer 597 spectrometer with Nujol mulls between KBr discs. $Ru(CO)(CNR)(PPh_3)_3$ was prepared by published methods [18].

$Ru(\eta^2\text{-}C_4H_2O_3)(CO)(CNR)(PPh_3)_2$

$Ru(CO)(CNR)(PPh_3)_3$ (200 mg) and maleic anhydride (22 mg) were added under a stream of nitrogen to deoxygenated benzene (20 ml). The solution was stirred for approximately 1 h at 25 °C, then most of the benzene was removed under vacuum and the product precipitated by the careful addition of hexane. Recrystallization from dichloromethane/ethanol solution yielded pale yellow crystals of **1** (145 mg, 86%). M.p. 178–180 °C. Anal. Found, C, 68.00; H, 4.58. $C_{49}H_{39}O_4NP_2Ru$ calcd.: C, 67.73; H, 4.52%.

X-ray crystallography

Crystals of $Ru(\eta^2\text{-}C_4H_2O_3)(CO)(CNR)(PPh_3)_2$ obtained from dichloromethane/ethanol were monoclinic, a 9.917(1), b 20.244(3), c 20.768(3) Å, β 99.80(1)°, space group $P2_1/c$, $M_r = 868.9$, $Z = 4$, D_c 1.406 g cm^{-3}, λ(Mo-K_α) 0.71069 Å, μ(Mo-K_α) 5.01 cm^{-1}. Intensities of 3025 reflections with $I > 3\sigma(I)$ were measured on a CAD-4 diffractometer using the $\omega/2\theta$ scan technique and Zr filtered Mo-K_α radiation. The intensity of three reflections were monitored through the data collection as a check for misalignment or decomposition, no evidence for either being found. Data were corrected for Lorentz and polarisation effects and empirical absorption corrections applied. The structure was solved by conventional Patterson and Fourier techniques and refined by full matrix least squares (weight = $1.63/(\sigma(F) + 0.001\ F^2)$, refinement converged to $R = 0.061$, $R_w = 0.063$. Atomic coordinates are listed in Table 1 and important bond distances and angles in Tables 2 and 3, respectively.

References

1 D.F. Christian and W.R. Roper, J. Chem. Soc., Chem. Commun., (1971) 1271.
D.F. Christian, Ph.D. Thesis, The University of Auckland, 1973.

2 R. Kuwae, K. Kawakami and T. Tanaka, Inorg. Chim. Acta, 22 (1977) 39.

3 Yu. T. Struchkov, V.G. Andrianov, V.N. Setkina, N.K. Baranetskaya, V.I. Losilkina and D.N. Kursanov, J. Organomet. Chem., 182 (1979) 213.

4 K.A. Woode, J.C.J. Bart, M. Calcaterra and G. Agnès, Organometallics, 2 (1983) 627.

5 G. Hunter, T.J.R. Weakley, K. Mislow, and M.G. Wong, J. Chem. Soc. Dalton, (1986) 577.

6 M. Herberhold and C.R. Jablonski, Inorg. Chim. Acta, 7 (1973) 241.

7 W.-W. Wong, K.W. Chiu, J.A. Statler, G. Wilkinson, M. Motevalli and M.B. Hursthouse, Polyhedron, 3 (1984), 1255.

8 P. Pertici, G. Vitulli, W. Porzio, M. Zocchi, P.L. Barili and G. Deganello, J. Chem. Soc. Dalton Trans., (1983) 1553.

9 R.E. Marsh, E. Ubell and H.E. Wilcox, Acta Cryst., 15 (1962) 35.

10 G.R. Clark, T.J. Collins, S.M. James and W.R. Roper, J. Organomet. Chem., 125 (1977) C23.

11 D.F. Christian, G.R. Clark and W.R. Roper, J. Organomet. Chem., 81 (1974) C7.

12 G.R. Clark, K.R. Grundy, R.O. Harris, S.M. James and W.R. Roper, J. Organomet. Chem., 90 (1975), C37.

13 W.R. Roper, J. Organomet. Chem., 300 (1986) 167.

14 A.K. Burrell and W.R. Roper, manuscript in preparation.

15 T.J. Collins, K.R. Grundy and W.R. Roper, J. Organomet. Chem., 231 (1982) 161.

16 G.R. Clark, C.E.L. Headford, K. Marsden and W.R. Roper, J. Organomet. Chem., 213 (1982) 335.

17 G.R. Clark, C.M. Cochrane, K. Marsden, W.R. Roper and L.J. Wright, J. Organomet. Chem., 315 (1986) 211.

18 K.R. Grundy, Inorg. Chim. Acta, 53 (1981) L225.