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Reactions of transition metal σ-acetylide complexes

XV *. Preparation and X-ray structure of $RuCl(PPh_3)_2$-(η-$C_5H_4C_2CO_2Me$)

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Abstract

One of the products from reactions between $Ru(C_2Ph)(PPh_3)_2(\eta$-$C_5H_5)$ and $C_2(CO_2Me)_2$ is the complex $RuCl(PPh_3)_2(\eta$-$C_5H_4C_2CO_2Me)$, whose spectroscopic properties and X-ray structure are described. Crystals are monoclinic, space group $P2_1/n$ with unit cell dimensions a 14.138(11), b 16.751(6), c 16.420(6) Å, β 103.38(4)° and $Z = 4$. The structure was refined by a full-matrix least-squares procedure to final R 0.047 and R_w 0.050 for 2826 reflections with $I \geqslant 2.5\sigma(I)$.

Introduction

Several groups have described reactions between transition metal complexes containing σ-bonded C(*sp*) ligands and olefins or alkynes [1–5]. Initial cycloaddition reactions between the unsaturated moieties may be followed by ring-opening reactions to give a variety of new systems. Recent examples include the cycloaddition of olefins to σ-acetylide complexes, which afford σ-cyclobutenyl, σ-butadienyl and η^3-allylic ligands (Scheme 1) [1], and the addition of alkynes to vinylidenes to give vinylvinylidenes, possibly via an initial cycloadduct (Scheme 2) [6]. We describe below an interesting consequence of the reaction between a σ-acetylide and an alkyne.

Results and discussion

The reaction between $Ru(C_2Ph)(PPh_3)_2(\eta$-$C_5H_5)$ and $C_2(CO_2Me)_2$ was carried out in dichloromethane; the initially yellow solution rapidly changed to dark red,

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* For Part 14, see Ref. 12.

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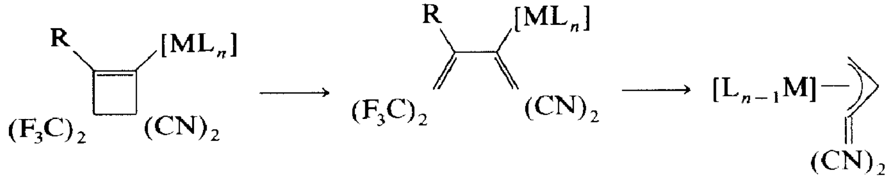
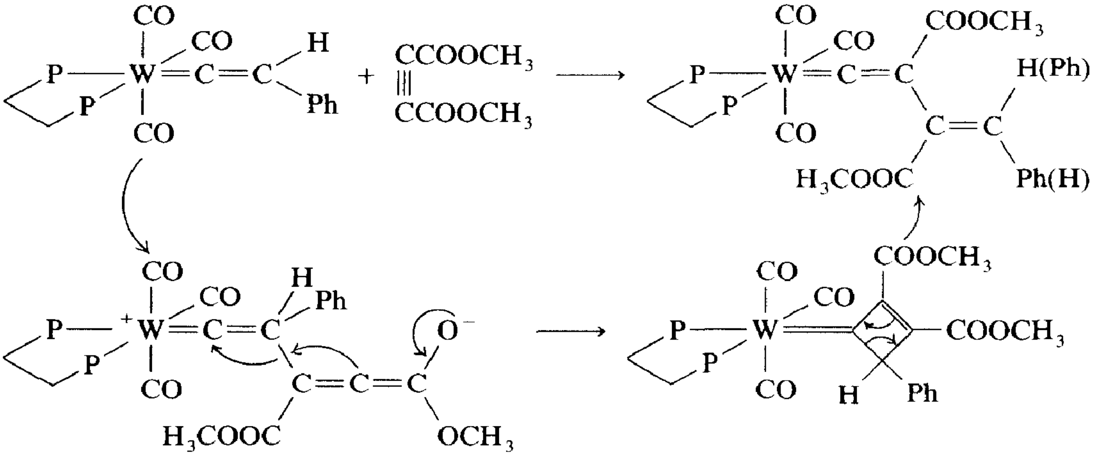


Scheme 1

and extensive purification gave a small amount of an orange crystalline solid (**1**). A doublet ν(CC) absorption at 2217 and 2204 cm^{-1} was present in the IR spectrum, together with broad ν(CO) bands at 1707 and 1290 cm^{-1}. The ^1H NMR spectrum did not contain a C_5H_5 singlet, although two multiplets at δ 4.57 and 3.79 were present; a singlet at δ 3.71 was assigned to the CO_2Me protons, and resonances between δ 7.01 and 7.27 to the PPh_3 ligand. The latter signals had relative intensities ca. 1/10. In the FAB mass spectrum, a molecular ion at m/z 808 fragmented by loss of Cl, Ph and PPh_3 fragments. The CO_2Me group resisted fragmentation until loss of the Cl and PPh_3 ligands had occurred, after which it appears to be eliminated as a whole to give ions such as $[Ru(PPh_n)(C_5H_4C_2)]^+$ ($n = 2, 3$). These data and the elemental analysis suggested a formulation in which the phenylacetylide ligand had been replaced by $(Cl + C_2CO_2Me)$, and a single-crystal X-ray study was carried out to determine the molecualr structure.

A computer-generated representation of the molecular structure of **1** is shown in Fig. 1, and the structural parameters are listed in Table 1. These data show that complex **1** is $RuCl(PPh_3)_2(\eta\text{-}C_5H_4C_2CO_2Me)$. The ruthenium atom is attached to a chlorine atom [Ru-Cl 2.419(2) Å; cf. 2.453(2) Å in $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ [7]] and two PPh_3 ligands [Ru–P(1) 2.326(2), Ru–P(2) 2.329(2) Å; cf 2.336(1) Å in $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ [7]] at three facial sites of a distorted octahedron [angles P(1)–Ru–P(2) 99.9(1), P(1)–Ru–Cl 89.3(1), P(2)–Ru–Cl 93.4(1)°]. The substituted cyclopentadienyl group occupies the other three positions [Ru–C 2.191–2.225(8), av.



Scheme 2

Table 1

Bond distances (Å) and angles (°) for $\mathrm{RuCl(PPh_3)_2(\eta\text{-}C_5H_4C_2CO_2Me)}$ (**1**)

P(1)–Ru	2.326(2)	P(2)–Ru	2.329(2)
Cl–Ru	2.419(2)	C(1)–Ru	2.224(7)
C(2)–Ru	2.206(7)	C(3)–Ru	2.191(8)
C(4)–Ru	2.195(8)	C(5)–Ru	2.225(8)
C(10)–P(1)	1.855(6)	C(16)–P(1)	1.851(6)
C(22)–P(1)	1.830(6)	C(28)–P(2)	1.839(6)
C(34)–P(2)	1.847(6)	C(40)–P(2)	1.836(7)
C(2)–C(1)	1.422(11)	C(5)–C(1)	1.421(10)
C(3)–C(2)	1.453(11)	C(4)–C(3)	1.401(11)
C(5)–C(4)	1.453(11)	C(6)–C(5)	1.440(12)
C(7)–C(6)	1.171(12)	C(8)–C(7)	1.461(15)
O(1)–C(8)	1.217(14)	O(2)–C(8)	1.291(14)
C(9)–O(2)	1.490(12)		
P(2)–Ru–P(1)	99.9(1)	Cl–Ru–P(1)	89.3(1)
Cl–Ru–P(2)	93.4(1)	C(1)–Ru–P(1)	149.8(2)
C(1)–Ru–P(2)	90.7(2)	C(1)–Ru–Cl	118.4(2)
C(2)–Ru–P(1)	112.6(2)	C(2)–Ru–P(2)	97.8(2)
C(2)–Ru–Cl	153.0(2)	C(2)–Ru–C(1)	37.4(3)
C(3)–Ru–P(1)	89.8(2)	C(3)–Ru–P(2)	134.0(2)
C(3)–Ru–Cl	131.9(2)	C(3)–Ru–C(1)	63.3(3)
C(3)–Ru–C(2)	38.6(3)	C(4)–Ru–P(1)	103.8(2)
C(4)–Ru–P(2)	154.2(2)	C(4)–Ru–Cl	97.0(2)
C(4)–Ru–C(1)	63.5(3)	C(4)–Ru–C(2)	63.6(3)
C(4)–Ru–C(3)	37.2(3)	C(5)–Ru–P(1)	141.7(2)
C(5)–Ru–P(2)	118.3(2)	C(5)–Ru–Cl	90.5(2)
C(5)–Ru–C(1)	37.3(3)	C(5)–Ru–C(2)	62.6(3)
C(5)–Ru–C(3)	62.8(3)	C(5)–Ru–C(4)	38.4(3)
C(10)–P(1)–Ru	107.7(2)	C(16)–P(1)–Ru	120.7(2)
C(16)–P(1)–C(10)	103.7(3)	C(22)–P(1)–Ru	118.9(2)
C(22)–P(1)–C(10)	100.9(3)	C(22)–P(1)–C(16)	102.4(2)
C(28)–P(2)–Ru	125.0(2)	C(34)–P(2)–Ru	114.6(2)
C(34)–P(2)–C(28)	97.4(3)	C(40)–P(2)–Ru	110.0(2)
C(40)–P(2)–C(28)	104.2(3)	C(40)–P(2)–C(34)	103.1(3)
C(2)–C(1)–Ru	70.6(4)	C(5)–C(1)–Ru	71.4(4)
C(5)–C(1)–C(2)	108.2(7)	C(1)–C(2)–Ru	72.0(4)
C(3)–C(2)–Ru	70.1(4)	C(3)–C(2)–C(1)	107.4(7)
C(2)–C(3)–Ru	71.3(4)	C(4)–C(3)–Ru	71.6(5)
C(4)–C(3)–C(2)	108.7(8)	C(3)–C(4)–Ru	71.2(5)
C(5)–C(4)–Ru	71.9(5)	C(5)–C(4)–C(3)	107.5(7)
C(1)–C(5)–Ru	71.3(4)	C(4)–C(5)–Ru	69.7(4)
C(4)–C(5)–C(1)	108.2(7)	C(6)–C(5)–Ru	120.7(6)
C(6)–C(5)–C(1)	125.8(8)	C(6)–C(5)–C(4)	125.8(8)
C(7)–C(6)–C(5)	174.1(9)	C(8)–C(7)–C(6)	171.4(11)
O(1)–C(8)–C(7)	122.1(14)	O(2)–C(8)–C(7)	113.1(12)
O(2)–C(8)–O(1)	124.4(13)	C(9)–O(2)–C(8)	112.0(11)
C(15)–C(10)–P(1)	121.4(2)	C(11)–C(10)–P(1)	118.6(2)
C(21)–C(16)–P(1)	118.5(1)	C(17)–C(16)–P(1)	121.4(1)
C(27)–C(22)–P(1)	121.4(1)	C(23)–C(22)–P(1)	118.5(1)
C(33)–C(28)–P(2)	122.5(2)	C(29)–C(28)–P(2)	117.3(2)
C(39)–C(34)–P(2)	120.9(2)	C(35)–C(34)–P(2)	119.1(2)
C(45)–C(40)–P(2)	121.9(2)	C(41)–C(40)–P(2)	117.6(2)

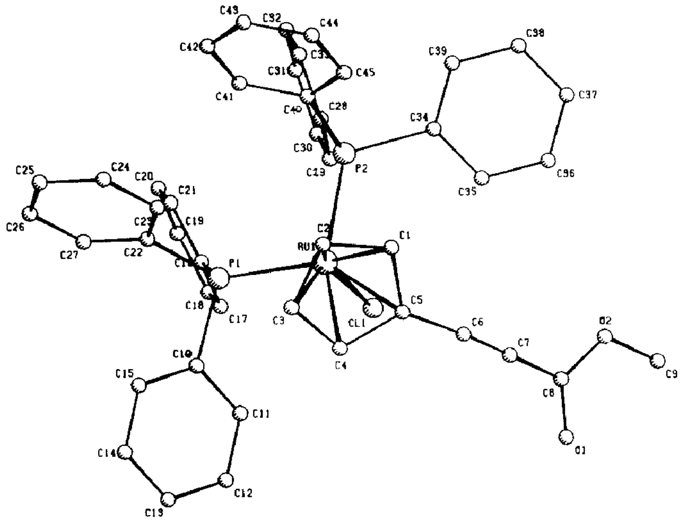
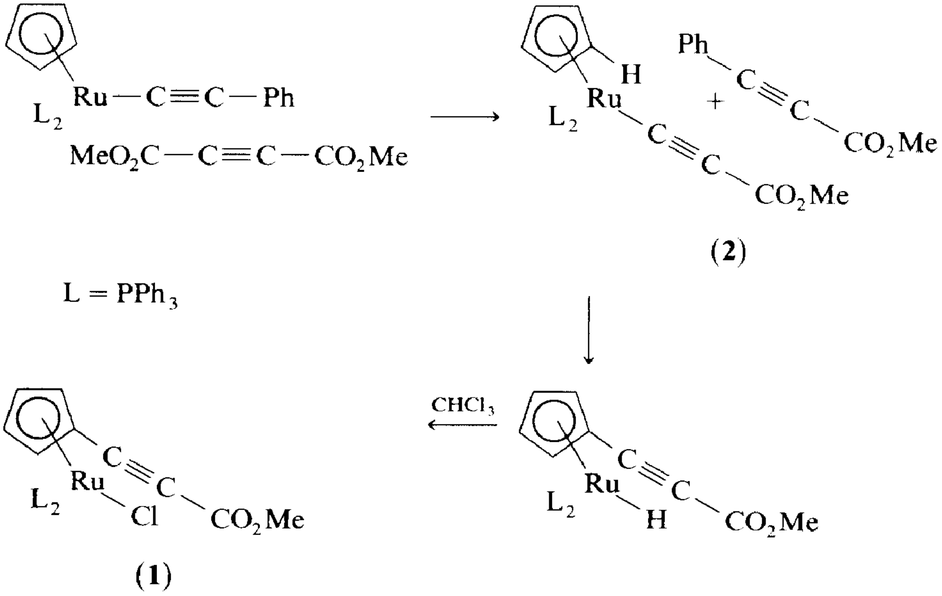


Fig. 1. Molecular structure of $RuCl(PPh_3)_2(\eta\text{-}C_5H_4C_2CO_2Me)$ (1), showing atom numbering scheme.

2.208 Å], there being some asymmetry in the attachment of the C_5 ring such that C(1) and C(5) are furthest from the metal. The C_2CO_2Me substituent at C(5) does not interact with the ruthenium; the C≡C triple bond [C(6)–C(7) 1.17(1) Å] is normal, and the alkyne is essentially linear [C(5)–C(6)–C(7) 174.1(9), C(6)–C(7)–C(8) 171.4(11)°].

Speculation on the mechanism of formation of **1** is rendered difficult by the low yield and the formation of several other as yet uncharacterised materials in the original reaction. One possibility involves initial "dismutation" of the metal acetylide



Scheme 3

and reactant alkyne to give known (methoxycarbonyl)ethynyl derivative **2** [8], followed by exchange of C_2CO_2Me and ring H and chlorination of the resulting Ru–H bond during work-up (Scheme 3). However, we have been unable to demonstrate the occurrence of the group transfer reaction for **2** under similar reaction conditions. Many examples of intramolecular migration of alkyl groups from a metal to a coordinated polyene ligand have been described [9], but similar chemistry of unsaturated *C*-bonded ligands is rare. Further studies of this and related reactions are under way, and we shall report on them as more information becomes available.

Experimental

Preparation of $RuCl(PPh_3)_2(\eta\text{-}C_5H_4C_2CO_2Me)$

The reaction between $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (300 mg, 0.38 mmol) and $C_2(CO)_2Me)_2$ (162 mg, 1.14 mmol) in CH_2Cl_2 (30 ml) was carried out at ambient temperature. After 4 h, TLC indicated that several products were present. Purification by column chromatography (alumina, 5/45/50 acetone/petroleum spirit/dichloromethane), followed TLC of the second, orange, fraction (silica gel, 5/45/50 acetone/petroleum spirit/dichloromethane) afforded an orange band, which was extracted (MeOH) and crystallised (MeOH) to give orange-red needles of $RuCl(PPh_3)_2(\eta\text{-}C_5H_4C_2CO_2Me)$ (**1**). Anal. Found: C, 65.83; H, 4.58; *M* (mass spectrometry), 808; $C_{45}H_{37}ClO_2P_2Ru$ calc.: C, 66.87; H, 4.61%; *M*, 808. Infrared (film): $\nu(C{\equiv}C)$ 2217sh, 2204m cm^{-1}; $\nu(CO)$ 1707s, 1290s cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 3.71 (s, 3H, CO_2Me), 3.79 (2, 2H, C_5H_4), 4.57 (s, 2H, C_5H_4), 7.01–7.27 (m, 30H, Ph). FAB MS: 808, $[M]^+$, 46; 773, $[M-Cl]^+$, 66; 696*, $[M-Cl-Ph]^+$, 7; 625*, $[M-PPh_2]^+$, 6; 546, $[M-PPh_3]^+$, 52; 511, $[M-Cl-PPh_3]^+$, 100; 469*, $[RuCl(PPh_2)(C_5H_4C_2CO_2Me)]^+$, 7; 451*, $[Ru(PPh_3)(C_5H_4C_2)]^+$, 15; 373*, $[Ru(PPh_2)(C_5H_4C_2)]^+$, 9; 362*, $[Ru(PPh_3)]^+$, 10; 285*, $[Ru(PPh_2)]^+$, 14. Peaks marked with * are centres of multiplets related by addition or loss of H.

Crystallography

Intensity data were measured at room-temperature on an Enraf–Nonius CAD4F diffractometer fitted with Mo-K_α (graphite-monochromatised) radiation, $\lambda = 0.71073$ Å, with the use of the $\omega : 2\theta$ scan technique. No significant decomposition of the crystal occurred during the data collection. Routine corrections were made for Lorentz and polarization effects [10] but no absorption correction was applied.

Crystal data

(1) $RuCl(PPh_3)_2(\eta\text{-}C_5H_4CO_2Me) \equiv C_{45}H_{37}ClO_2P_2Ru$, MW = 808.2, Monoclinic, space group $P2_1/n$ (C_{2h}^5, No. 14), *a* 14.138(11), *b* 16.751(6), *c* 16.420(6) Å, β 103.38(4)°, *U* 3783.1 Å^3, d_c 1.419, d_x 1.44 g cm^{-3}, $Z = 4$, $F(000) = 1656$, $\mu = 5.59$ cm^{-1}, $\theta = 1$–$22.5°$. 6186 data collected, of which 4956 were unique, and 2826 with $I \geqslant 2.5\sigma(I)$ were refined to $R = 0.047$, $R_w = 0.050$.

The structure was solved by normal heavy-atom methods and refined by a full-matrix least-squares procedure based on *F* [10]. Phenyl atoms were refined as hexagonal rigid groups and the remaining non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at their calculated positions (C–H 0.97 Å). A weighting scheme, $w = 3.53/[\sigma^2(F) + 0.0002F^2]$, was included

Table 2

Fractional atomic coordinates (Ru $\times 10^5$, others $\times 10^4$) of non-hydrogen atoms in $RuCl(PPh_3)_2(\eta\text{-}C_5H_4C_2CO_2Me)$

Atom	*x*	*y*	*z*
Ru	34953(4)	14829(4)	11791(4)
Cl	1947(1)	1195(1)	236(1)
P(1)	2697(2)	2278(1)	1970(1)
P(2)	3905(2)	2448(1)	298(1)
O(1)	1765(8)	−1505(7)	−763(7)
O(2)	2553(6)	−874(5)	−1595(6)
C(1)	4778(5)	753(5)	1081(5)
C(2)	4983(6)	1166(5)	1859(5)
C(3)	4288(6)	894(5)	2326(5)
C(4)	3668(6)	334(5)	1840(5)
C(5)	3980(6)	233(5)	1063(5)
C(6)	3509(6)	−258(6)	367(7)
C(7)	3051(7)	−642(6)	−181(7)
C(8)	2370(9)	−1027(8)	−876(9)
C(9)	1834(11)	−1255(9)	−2294(8)
C(10)	2141(4)	1606(4)	2628(3)
C(11)	1519(4)	1002(4)	2238(3)
C(12)	1096(4)	483(4)	2716(3)
C(13)	1296(4)	568(4)	3584(3)
C(14)	1918(4)	1172(4)	3974(3)
C(15)	2340(4)	1691(4)	3496(3)
C(16)	1679(4)	2932(3)	1454(4)
C(17)	750(4)	2628(3)	1129(4)
C(18)	5(4)	3135(3)	728(4)
C(19)	188(4)	3947(3)	651(4)
C(20)	1117(4)	4251(3)	976(4)
C(21)	1863(4)	3744(3)	1378(4)
C(22)	3415(3)	2936(3)	2768(3)
C(23)	4425(3)	2864(3)	2957(3)
C(24)	4993(3)	3332(3)	3588(3)
C(25)	4549(3)	3871(3)	4031(3)
C(26)	3539(3)	3942(3)	3842(3)
C(27)	2972(3)	3475(3)	3210(3)
C(28)	3114(4)	3275(3)	−179(4)
C(29)	2128(4)	3108(3)	−479(4)
C(30)	1503(4)	3697(3)	−899(4)
C(31)	1863(4)	4452(3)	−1019(4)
C(32)	2849(4)	4619(3)	−720(4)
C(33)	3475(4)	4030(3)	−300(4)
C(34)	4171(4)	2049(3)	−673(3)
C(35)	3822(4)	1296(3)	−955(3)
C(36)	4022(4)	981(3)	−1683(3)
C(37)	4572(4)	1419(3)	−2130(3)
C(38)	4922(4)	2173(3)	−1848(3)
C(39)	4721(4)	2488(3)	−1120(3)
C(40)	5049(4)	2937(4)	814(4)
C(41)	5003(4)	3549(4)	1380(4)
C(42)	5858(4)	3875(4)	1864(4)
C(43)	6758(4)	3589(4)	1783(4)
C(44)	6804(4)	2977(4)	1218(4)
C(45)	5950(4)	2650(4)	733(4)

and the refinement continued until convergence. No special features were noted from the analysis of variance which indicated an appropriate weighting scheme had been applied.

Scattering factors for neutral Ru (corrected for f' and f'') were from Ref. 11 and values for the remaining atoms were those incorporated in SHELX [10]. Data solution and refinement were performed with the SHELX program system on the University of Adelaide's VAX11/785 computer system.

Fractional atomic coordinates are listed in Table 2. Listing of thermal parameters, complete bond distances and angles, hydrogen atom parameters, and of the observed and calculated structure factors are available from the authors.

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