Journal of Organometallic Chemistry, 280 (1985) 253–259
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE PREPARATION AND CRYSTAL STRUCTURE OF $(\eta^5\text{-}C_5H_5)Ru[(C_6H_5)_3P]_2(CO)_5Co \cdot THF$

G. DOYLE

Corporate Research Science Laboratories, Exxon Research & Engineering Co., Route 22 East, Annandale, New Jersey 08801 (U.S.A.)

and D. VAN ENGEN

Analytical Division, Exxon Research & Engineering Co., Route 22 East, Annandale, New Jersey 08801 (U.S.A.)

(Received July 11th, 1984)

Summary

The reaction of $(\eta^5\text{-}C_5H_5)Ru[(C_6H_5)_3P]_2Cl$ with $Co(CO)_4^-$ leads to a mixture of metal containing products. One of these products $(\eta^5\text{-}C_5H_5)Ru[(C_6H_5)_3P]_2(CO)_5Co \cdot THF$ was isolated in pure form and its structure determined. The complex crystallizes in space group $P2_1/n$ with a 15.015(1), b 18.543(3), c 16.984(2) Å, β 110.75(1)°, $V = 4422$ Å^3 and $Z = 4$. The structure has been refined to $R = 0.072$, R_w 0.073 for 3643 observed reflections. The molecule consists of a $(\eta^5\text{-}C_5H_5)Ru[(C_6H_5)_3P]_2(CO)^+$ cation a $Co(CO)_4^-$ anion and a THF molecule of crystallization. The cation has a typical "piano-stool" structure and the $Co(CO)_4^-$ anion has a nearly ideal tetrahedral configuration.

Introduction

Since the discovery of the methanol homologation reaction over three decades ago [1] there has been a number of advances in the catalysts employed which has resulted in both higher methanol conversions and higher selectivities to ethanol. The earliest catalysts, which were simple cobalt compounds, have been largely superseded by more complex systems. Among the best catalysts available are mixtures of a cobalt compound, a ruthenium compound and a phosphine along with an iodide promoter [2–5]. It seemed reasonable to us that a complex containing the Co, Ru, and phosphine in close proximity might show enhanced activity over simple mixtures of compounds. We have subsequently shown that the metallic components probably function independently and that mixtures of Co and Ru complexes perform virtually identically as compounds containing Co and Ru in the same molecule [6]. Although

0022-328X/85/$03.30

this approach did not lead to a more active catalyst system, some interesting new complexes were prepared, one of which is described here.

Results and discussion

The reaction of $TlCo(CO)_4$ with $(\eta^5\text{-}C_5H_5)Ru[P(C_6H_5)_3]_2Cl$ in THF which we have previously described [6] yields a product which gives an elemental analysis in excellent agreement with the composition $C_5H_5Ru[P(C_6H_5)_3]_2Co(CO)_4$. This material, which is obtained as a purple microcrystalline solid in relatively poor yields, displays a fairly complex infrared spectrum in the CO stretching region. Bands were observed at 2020, 1967, 1908 and 1744 cm^{-1} indicating a relatively unsymmetrical geometry probably containing a bridging carbonyl for the $Co(CO)_4$ moiety in the complex. It is possible that this material contained a mixture of products although only a single cyclopentadienyl resonance was observed in the NMR spectrum. Another likely possibility is that a ligand exchange reaction could have taken place, resulting in the transfer of a phosphine to the cobalt and a CO ligand to ruthenium, a known reaction of $(\eta^5\text{-}C_5H_6)Ru[P(C_6H_5)_3]_2Cl$ [7]. An attempt to resolve this issue by an X-ray diffraction study was not successful since crystals suitable for study could not be obtained.

Numerous minor modifications of the synthetic procedure were tried in order to increase the yields of the Ru–Co complex but these were generally not successful. In many cases the product contained considerable amounts of an orange solid which could be obtained in a pure form by fractional crystallization. This material gave an elemental analysis very similar to the purple solid but only two infrared bands at 1978 and 1872 cm^{-1} were observed in the CO stretching region.

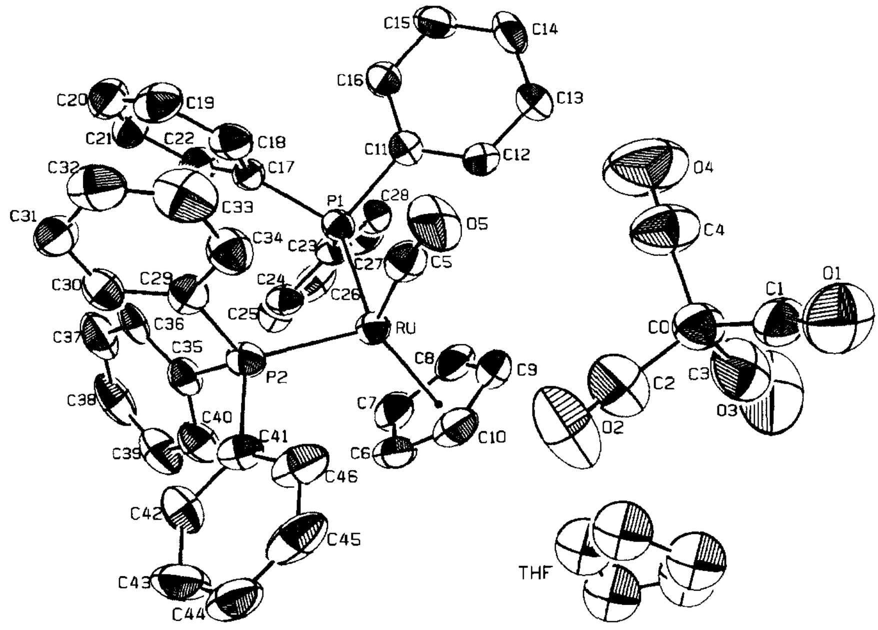

Fig. 1. A computer-generated perspective drawing of $(\eta^5\text{-}C_5H_5)Ru[(C_6H_5)_3P]_2(CO)_5Co$ THF.

A single crystal X-ray diffraction structure determination was carried out on this orange material which proved to be an ionic complex consisting of a $(\eta^5\text{-}C_5H_5)Ru[P(C_6H_5)_3]_2(CO)^+$ cation and a $Co(CO)_4^-$ anion (see Fig. 1). There is no close interaction between the ions or with the solvent (THF) of crystallization. The two triphenylphosphine, carbonyl and cyclopentadienyl ligands are coordinated to the ruthenium in a typical "piano-stool" fashion. The coordination about the cobalt atom deviates only slightly from an ideal tetrahedral geometry. There does not

(Continued on p. 258)

TABLE 1

TABLE OF SELECTED BOND DISTANCES (Å)

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Ru	CX [a]	1.892(10)	P(1)	C(11)	1.836(12)
Ru	C(5)	1.890(2)	P(1)	C(17)	1.830(9)
Ru	P(1)	2.347(13)	P(1)	C(23)	1.848(17)
Ru	P(2)	2.361(7)	P(2)	C(29)	1 833(12)
Co	C(1)	1.727(19)	P(2)	C(35)	1.828(17)
Co	C(2)	1.734(12)	P(2)	C(41)	1.814(16)
Co	C(3)	1.740(19)	C(6)	C(7)	1.429(16)
Co	C(4)	1.724(18)	C(6)	C(10)	1.370(13)
C(1)	O(1)	1.139(31)	C(7)	C(8)	1.410(11)
C(2)	O(2)	1.160(15)	C(8)	C(9)	1.367(15)
C(3)	O(3)	1.186(10)	C(9)	C(10)	1.415(13)
C(4)	O(4)	1.130(25)			
C(5)	O(5)	1.135(3)			

[a] CX is centroid of the cyclopentadienyl ring.

TABLE 2

TABLE OF SELECTED BOND ANGLES (°)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
CX	Ru	C(5)	121.0(4)	C(11)	P(1)	C(17)	101.4(6)
CX	Ru	P(1)	121.6(4)	C(11)	P(1)	C(23)	103.2(7)
CX	Ru	P(2)	120.7(5)	C(17)	P(1)	C(2)	102.6(6)
C(5)	Ru	P(1)	91.5(3)	Ru	P(2)	C(29)	121.4(5)
C(5)	Ru	P(2)	97.8(3)	Ru	P(2)	C(35)	109.9(7)
P(1)	Ru	P(2)	97.8(4)	Ru	P(2)	C(41)	113.5(4)
C(1)	Co	C(2)	107.1(9)	C(29)	P(2)	C(35)	108.0(5)
C(1)	Co	C(3)	106.3(5)	C(29)	P(2)	C(41)	98.3(7)
C(1)	Co	C(4)	109.1(7)	C(35)	P(2)	C(41)	104.0(6)
C(2)	Co	C(3)	112.4(6)	C(35)	P(2)	C(41)	104.0(6)
C(2)	Co	C(4)	111.3(6)	C(7)	C(6)	C(10)	108.8(8)
C(3)	Co	C(4)	110.4(7)	C(6)	C(7)	C(8)	105.2(9)
Co	C(1)	O(1)	177.9(9)	C(7)	C(8)	C(9)	110.3(9)
Co	C(2)	O(2)	175.3(19)	C(8)	C(9)	C(10)	107.2(7)
Co	C(3)	O(3)	174.5(7)	C(6)	C(10)	C(9)	108.5(9)
Co	C(4)	O(4)	177.2(12)				
Ru	C(5)	O(5)	172.8(1)				
Ru	P(1)	C(11)	113.7(6)				
Ru	P(1)	C(17)	120.8(6)				
Ru	P(1)	C(23)	113.0(6)				

TABLE 3

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS [a]

Atom	x	y	z	$B(\text{Å}^2)$	Atom	x	y	z	$B(\text{Å}^2)$
Ru	0.89032(5)	0.18050(4)	0.23295(5)	2.92(1)	C(40)	1.0600(7)	0.3345(6)	0.2104(6)	4.2(3)
Co	0.5597(1)	0.09637(9)	0.3174(1)	5.59(4)	C(41)	1.0392(7)	0.2959(5)	0.3871(5)	3.3(2)
P(1)	0.9380(2)	0.1032(1)	0.1458(2)	2.83(6)	C(42)	1.0917(7)	0.3584(6)	0.3997(7)	4.7(3)
P(2)	1.0424(2)	0.2249(1)	0.3147(2)	3.32(6)	C(43)	1.0871(9)	0.4079(6)	0.4620(8)	6.7(4)
C(1)	0.5045(8)	0.0677(6)	0.3854(8)	5.9(3)	C(44)	1.0345(8)	0.3974(7)	0.5107(7)	5.8(3)
O(1)	0.4654(7)	0.0490(6)	0.4283(6)	9.5(3)	C(45)	0.9809(8)	0.3335(7)	0.4986(6)	6.2(3)
C(2)	0.648(1)	0.1567(8)	0.3726(8)	7.6(4)	C(46)	0.9811(8)	0.2837(6)	0.4370(7)	5.5(3)
O(2)	0.7051(8)	0.1964(6)	0.4142(7)	11.7(4)	C(47)	0.541	0.320	0.186	9.0*
C(3)	0.472(1)	0.1367(8)	0.2328(8)	8.3(4)	C(48)	0.437	0.338	0.152	9.0*
O(3)	0.4093(8)	0.1586(7)	0.1727(7)	12.6(4)	C(49)	0.416	0.371	0.084	9.0*
C(4)	0.607(1)	0.0228(8)	0.2839(8)	8.3(5)	C(50)	0.500	0.406	0.084	9.0*
O(4)	0.6344(9)	-0.0258(6)	0.2594(8)	13.8(4)	C(51)	0.562	0.355	0.135	9.0*
C(5)	0.8857(7)	0.1031(6)	0.3038(6)	4.1(3)	H(6)	0.875	0.320	0.270	5.1*
O(5)	0.8731(5)	0.0580(4)	0.3437(5)	6.4(2)	H(7)	0.854	0.287	0.102	5.9*
C(6)	0.8326(7)	0.2931(5)	0.2257(6)	4.1(3)	H(8)	0.750	0.186	0.066	5.6*
C(7)	0.8245(7)	0.2696(6)	0.1433(7)	4.8(3)	H(9)	0.687	0.157	0.199	5.3*
C(8)	0.7612(7)	0.2106(6)	0.1258(7)	4.7(3)	H(10)	0.791	0.254	0.320	5.7*
C(9)	0.7328(7)	0.1975(5)	0.1926(7)	4.2(3)	H(12)	0.753	0.056	0.150	4.9*
C(10)	0.7708(7)	0.2493(6)	0.2552(7)	4.8(3)	H(13)	0.832	0.439	0.371	5.2*
C(11)	0.8722(6)	0.0176(5)	0.1226(6)	3.1(2)	H(14)	0.770	0.338	0.422	5.6*
C(12)	0.7832(7)	0.0107(5)	0.1298(6)	3.9(3)	H(15)	0.625	0.355	0.457	5.4*
C(13)	0.7317(7)	−0.0526(6)	0.1109(7)	4.2(3)	H(16)	0.520	0.457	0.406	4.9*
C(14)	0.7702(7)	-0.1109(6)	0.0824(7)	4.6(3)	H(18)	1.058	0.028	0.294	4.9*

C(15)	0.8600(7)	−0.1057(6)	0.0775(6)	4.4(3)	H(19)	1.226	−0.013	0.340	5.8*
C(16)	0.9109(7)	−0.0410(5)	0.0967(6)	3.9(3)	H(20)	1.325	0.012	0.258	5.9*
C(17)	1.0612(6)	0.0716(5)	0.1776(5)	2.7(2)	H(21)	1.252	0.065	0.115	5.5*
C(18)	1.1005(7)	0.0374(5)	0.2543(6)	3.7(3)	H(22)	0.082	0.102	0.066	5.1*
C(19)	1.1959(8)	0.0148(6)	0.2814(7)	4.8(3)	H(24)	0.000	0.219	0.102	4.2*
C(20)	1.2506(7)	0.0264(6)	0.2330(7)	5.0(3)	H(25)	0.520	0.238	0.457	4.9*
C(21)	1.2110(7)	0.0574(6)	0.1556(7)	4.5(3)	H(26)	0.416	0.287	0.338	5.9*
C(22)	1.1162(7)	0.0796(6)	0.1270(6)	4.1(3)	H(27)	0.354	0.389	0.338	6.2*
C(23)	0.9168(6)	0.1414(5)	0.0402(5)	2.9(2)	H(28)	0.825	0.058	−0.030	4.4*
C(24)	0.9632(7)	0.2043(5)	0.0357(6)	3.3(2)	H(30)	0.270	0.219	0.406	5.6*
C(25)	0.9576(7)	0.2325(6)	−0.0410(6)	3.8(3)	H(31)	1.368	0.133	0.477	5.7*
C(26)	0.9025(7)	0.1998(6)	−0.1128(6)	4.9(3)	H(32)	1.316	0.042	0.545	6.8*
C(27)	0.8524(8)	0.1366(6)	−0.1080(7)	5.2(3)	H(33)	0.666	0.473	0.033	7.3*
C(28)	0.8605(6)	0.1070(5)	−0.0332(5)	3.4(2)	H(34)	0.0296	0.1074	0.4210	5.6*
C(29)	1.1317(6)	0.1670(5)	0.3896(5)	3.4(2)	H(36)	0.207	0.186	0.254	4.6*
C(30)	1.2291(7)	0.1785(6)	0.4083(6)	4.6(3)	H(37)	0.270	0.254	0.152	6.6*
C(31)	1.2958(7)	0.1321(6)	0.4643(7)	4.7(3)	H(38)	1.186	0.356	0.081	6.3*
C(32)	1.2652(8)	0.0779(6)	0.5036(7)	5.7(3)	H(39)	0.041	0.406	0.117	6.7*
C(33)	1.1696(9)	0.0686(7)	0.4887(7)	6.3(4)	H(40)	0.020	0.371	0.219	5.4*
C(34)	1.1025(7)	0.1139(6)	0.4316(6)	4.6(3)	H(42)	1.137	0.371	0.363	5.7*
C(35)	1.0976(6)	0.2677(5)	0.2465(5)	3.3(2)	H(43)	0.125	0.457	0.457	7.6*
C(36)	1.1671(7)	0.2334(5)	0.2238(6)	3.6(2)	H(44)	1.033	0.435	0.556	6.9*
C(37)	1.997(7)	0.2650(6)	0.1636(7)	5.6(3)	H(45)	0.939	0.322	0.538	7.1*
C(38)	1.1610(8)	0.3310(6)	0.1263(7)	5.9(3)	H(46)	0.020	0.236	0.473	6.5*
C(39)	1.10944(8)	0.3665(6)	0.1486(7)	5.7(3)					

---

[a] Starred atoms were not refined. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as, $\frac{4}{3}[a^2 B_{1,1} + b^2 B_{2,2} + c^2 B_{3,3} + ab \cos \gamma\, B_{1,2} + ac \cos \beta\, B_{1,3} + bc \cos \alpha\, B_{2,3}]$.

appear to be any unusual bond lengths or bond angles in the complex (See Table 1 and 2).

A likely route to the formation of the $(\eta^5\text{-}C_5H_5)Ru[P(C_6H_5)_3]_2(CO)^+$ cation is the reaction of a solvated $(\eta^5\text{-}C_5H_5)Ru[P(C_6H_5)_3]_2^+$ cation with CO; the $(\eta^5\text{-}C_5H_5)Ru[P(C_6H_5)_3]_2^+$ species being formed by the abstraction of a chloride ion from $(\eta^5\text{-}C_5H_5)Ru[P(C_6H_5)_3]_2Cl$ and the CO ultimately being derived from the $Co(CO)_4^-$ anion. It is not certain to what extent this reaction occurs, but it is clear that to the extent that it does take place there will be an accompanying amount of other products derived from the loss of CO from the $Co(CO)_4^-$ anion. Low yields and mixtures of products are therefore not unexpected, but the nature of the other products was not determined.

Experimental

Preparation of $(\eta^5\text{-}C_5H_5)Ru[P(C_6H_5)_3]_2(CO)Co(CO)_4 \cdot THF$

Solid $(\eta^5\text{-}C_5H_5)Ru[P(C_6H_5)_3]_2Cl$ [8] (2.0 g, 2.75 mmol) was added incrementally to a solution of 0.74 g, (2.78 mmol) $NaCo(CO)_4$ in 75 ml dry THF under a nitrogen atmosphere. The mixture was stirred at room temperature for 40 h and then filtered. The filtrate was evaporated under vacuum to near dryness giving a maroon solid. This solid was collected on a filter and washed several times with pentane. This material was dissolved in a boiling 1/1 mixture of THF and hexane then stored at $-20°C$ for 3 days. A small amount of bright orange crystals were obtained upon filtration. Anal. Found: C, 62.31; H, 4.53; P, 7.05; Co, 6.53; Ru, 10.91. $C_{50}H_{43}P_2RuCoO_6$ calcd.: C, 62.44; H, 4.51; P 6.44; Co, 6.12; Ru, 10.51%.

Crystal structure determination

The material crystallizes in the monoclinic crystal class. A least-squares fit of 25 accurately measured 2θ values gave the following unit cell constants: a 15.015(1) Å, b 18.543(3) Å, c 16.984(2) Å, and β 110.75(1)°. The space group was uniquely determined to be $P2_1/n$ (standard: $P2_1/c$, no. 14) by observation of the following systematic absences: $0k0$: $k = 2n+1$, $h0l$: $h+l = 2n+1$. The density was calculated to be 1.44 g/cm^3 using mol.wt. 957.8, $V = 4422$ Å^3 and $Z = 4$.

One-quarter sphere of data with $2\theta \leq 50°$ was collected using Mo-K_α radiation and a variable speed ω–2θ scan technique. Of the 7403 unique intensities which were measured, 3643 fit the criteria $[|F_o|^2 \geq 2\sigma(F_0^2)]$ and were used in structure refinement.

The structure was solved by conventional heavy-atom techniques. The Ru and Co positions were determined from a three-dimensional Patterson synthesis. Following refinement of the heavy atom positions, the other nonhydrogen atoms were located in subsequent difference Fourier maps. A difference map calculated after isotropic refinement of $RuCoP_2C_{46}O_5$ revealed the presence of a solvent molecule of crystallization. The O atom of the THF group is probably disordered throughout all five positions since it could not be identified on the basis of temperature factors or bonding geometry. Thus, all five atoms of THF were entered and refined as carbons. Most of the hydrogen atoms were located on difference Fourier maps; the remainder were entered at their theoretically calculated positions. The hydrogen atoms of the THF molecule were not included in the final model. Full-matrix least-squares refinement with anisotropic temperature factors for $RuCoP_2C_{46}O_5$, fixed isotropic temperature factors for THF and hydrogen, and anomalous dispersion corrections for Ru and Co have converged to a current $R = 0.072$, $R_w = 0.073$. Positional parameters and their estimated standard deviations are given in Table 3.

References

1 I. Wender, R.A. Friedel and M. Orchin, Science, 113 (1951) 206.
2 U.S. Patents 4133966 (1979) and 4239924 (1980) to W.R. Pretzer, T.P. Kobylinski and J.E. Bozik (Gulf Research and Development Company).
3 U S. Patent 4253987, 1980, to R. Fiato (Union Carbide Corporation)
4 British Patent 2036739, 1980, to British Petroleum, Ltd.
5 U.S. Patent 4348541, 1982, to G. Doyle (Exxon Research & Engineering Company).
6 G. Doyle, J. Mol. Catal, 18 (1983) 251.
7 T Blackmore, M.I. Bruce and F.G.A. Stone, J. Chem. Soc. A, (1971) 2376.
8 M.I. Bruce and N.J. Widson, Austr. J. Chem., 30 (1977) 1601.