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Inorganica Chimica Acta 285 (1999) 318–321

Inorganica Chimica Acta

Note

New synthesis of $[RuH(CO)(PPh_3)_2L_2][BF_4]$ $[L_2 = 2py, 2(4\text{-}Mepy)\ or\ bpy]$ and X-ray crystal structure of $[RuH(CO)(PPh_3)_2(4\text{-}Mepy)_2][BF_4]$

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Received 27 May 1998; accepted 28 July 1998

Abstract

The title compounds were prepared by reaction of $RuH_2(CO)(PPh_3)_3$ with $[C_7H_7][BF_4]$ in the presence of excess pyridine, 4-picoline or 2,2′-bipyridine. The compounds were characterized by IR, ^1H and ^{31}P NMR, and X-ray crystallography (for the 4-Mepy complex). The spectroscopic data as well as the results of the X-ray crystal structure show that the complexes contain *trans*-oriented phosphines and *cis*-pyridines. Details of the structural content and selected bond distances and angles are internally consistent. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Ruthenium complexes; Hydride complexes; Carbonyl complexes; Pyridine complexes

1. Introduction

We recently reported the conversion of $OsH_2(CO)(PPh_3)_3$ to $[OsH(CO)(PPh_3)_2L_2]^+$ (L = pyridine or 4-tert-butylpyridine) by means of oxidation, hydride abstraction, and protonation [1]. The hydride abstraction route proved to be particularly convenient and we wondered if it might be applicable to the analogous ruthenium complexes as well. Complexes of the type $[RuH(CO)(PR_3)_2L_2]^+$ (R = Ph, 4-MeC_6H_4; $R_3 = MePh_2$; L_2 = 2py, 2DMAP, bpy, phen, Cy-DAB) have been previously prepared by the reaction of $RuHCl(CO)(PR_3)_3$ with the N-donor ligands [2,3]. We anticipated that our hydride abstraction route might provide a more convenient synthesis of these hydride complexes which may find use in catalytic hydrogenation reactions [2–4].

2. Experimental

2.1. Materials and general methods

All syntheses were carried out under argon using Schlenk techniques. All solvents were distilled from appropriate drying agents and stored under nitrogen. The complex $RuH_2(CO)(PPh_3)_3$ was prepared according to the literature procedure [5]. IR spectra were obtained using a Mattson Instruments Cygnus 100 FTIR and ^1H and ^{31}P NMR spectra were obtained on a Bruker AMX 360 NMR spectrometer. NMR chemical shifts are referenced to residual protons in the solvent (for ^1H) or 85% H_3PO_4 external standard (for ^{31}P).

2.2. Preparation of $[RuH(CO)(PPh_3)_2L_2][BF_4]$

A solution of $RuH_2(CO)(PPh_3)_3$ (0.15 g, 0.16 mmol) and pyridine (52 μl, 0.64 mmol) for **1**, 4-picoline (62 μl, 0.64 mmol) for **2**, or 2,2′-bipyridine (0.050 g, 0.32 mmol) for **3** in 10 ml of freshly distilled THF was prepared under argon. To this solution $[C_7H_7][BF_4]$ (0.043 g, 0.24 mmol) was added. The solution was then stirred at room temperature for a minimum of 6 h, during which time a precipitate was formed (**1, 2** = white; **3** = yellow). The precipitate was separated by filtration and washed with ether. Crude yield: 0.11 g **1**; 0.12 g **2**; 0.13 g **3**. The crude products were dissolved in CH_2Cl_2 and filtered into a flask containing THF. CH_2Cl_2 was removed under reduced pressure to yield recrystallized products. Yield after recrystallization: 0.093 g **1** (65%); 0.092 g **2** (62%); 0.12 g **3** (81%). *Anal.* Calc. for

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PII: S0020-1693(98)00355-7

Table 1
Experimental and statistical summary of compound **2**

Molecular formula	$C_{49}H_{45}BF_4N_2OP_2Ru$
Formula weight	927.7
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14, C_{2h}^5)
a (Å)	15.395(3)
b (Å)	18.156(4)
c (Å)	17.352(3)
β (°)	110.53(3)
V (Å^3)	4542.0(15)
Z	4
$D_{calc.}$ (Mg m^{-3})	1.357
$D_{meas.}$ (Mg m^{-3})	1.351(3)
μ (Mo Kα) (mm^{-1})	0.459
F(000) (e$^-$)	1904
2θ Range (°)	3.0–40.0
$\Delta\omega$ (°) (ω–2θ)	$1.15 + 0.34 \tan \theta$
R_{int}	0.052
R (R_w, R_{all})	0.070 (0.091, 0.094)
Unique reflections	3131
Extinction correction (e^{-2})(× 10^{-4})	1.3(9)
No. variable parameters	560
Goodness-of-fit	1.24

$C_{49}H_{45}BF_4N_2OP_2Ru \cdot C_4H_8O$ (**2**·THF): C, 63.67; H, 5.34; N, 2.80. Found: C, 63.88; H, 5.61; N, 2.78%. IR (mineral oil): ν_{max} (cm^{-1}) (CO) **1** = 1938 (1934 [2]); **2** = 1933; **3** = 1954 (1950 [2]). NMR (CD_2Cl_2): **1** = δ_H 6.6–7.8 [40H, m, py/PPh$_3$] and −13.0 [1H, t, J_{PH} 19.8, RuH] (−12.1, J_{PH} 19.5 [2]); δ_P 49.8 [s, PPh$_3$]; **2** = δ_H 6.4–7.6 [38H, m, 4-Mepy/PPh$_3$], 2.2 [3H, s, Me], 2.1 [3H, s, Me] and −13.0 [1H, t, J_{PH} 20.0, RuH]; δ_P 49.5 [s, PPh$_3$]; **3** = δ_H 6.4–8.6 [38H, m, bpy/PPh$_3$] and −11.3 [1H, t, J_{PH} 19.6, RuH] (−11.4, J_{PH} 19.2 [2]); δ_P 48.5 [s, PPh$_3$]. Single crystals for X-ray analysis were prepared by layering diethyl ether over a solution of **2** in CH_2Cl_2.

2.3. Crystallographic study of 2

Conoscopic examination of **2** using crystal rotation between two crossed polarizers on a Zeiss Photomicroscope (II) provided evidence that the system was biaxial (anisotropic in nature, birefringent) and optically homogeneous. Data were collected from a clear colorless parallelepiped-shaped crystal (0.36 mm × 0.08 mm × 0.49 mm). An Enraf-Nonius CAD4-F automated diffractometer equipped with graphite-monochromated Mo Kα radiation was employed, see Table 1 for crystal data and solution details. A least-squares refinement of 25 well centered high angle ($30.0 \leq 2\theta \leq 50.0°$) reflections yielded final lattice parameters. Crystal stability and hardware reliability were verified by monitoring three standard reflections as a function of time (every h). An intensity loss of 0.04% h^{-1} (1.8%, total decay) was observed which required a linear decay correction to the data set (maximum correction of 1.00933, average 1.00451) using the program DECAY [6]. A total of 4410 intensity measurements were collected of which 4222 were independent and 3131 fitted $F > 6.0\sigma(F)$. After the removal of the check reflections, the averaging of duplicate and equivalent data was carried out ($R_{int} = 0.052$). The remaining intensity data were corrected for Lorentz, polarization and X-ray absorption effects [6] (max., min., transmission factors = 0.9908, and 0.5461). Systematic absences of $0k0$ where $k = 2n + 1$ and $h0l$ where $l = 2n + 1$ were consistent with space group $P2_1/c$. A zero moment test (NZ-test) [7] on the observed data set indicated that it was centrosymmetric in nature.

The phase problem was resolved by using the Siemens SHELXTL PLUS (PC version) [8] which located the heavy atom (Ru). A series of difference Fourier maps located the atomic positions of the phosphorous, nitrogen, carbon, and oxygen atoms. These positions were refined isotropically for several full-matrix least-squares cycles before attempting to locate the BF_4^- anion, which was subsequently located by electron density mapping. Hydrogen atoms at calculated positions (C–H, 0.96 Å) on the phenyl rings and the 4-picoline groups were allowed to ride on their respective bonding atoms with fixed isotropic thermal parameters, $U_{iso} = 80 \times 10^{-3}$ Å^2. The hydride was also positioned at a distance of 1.78 Å (Ru–H, $U_{iso} = 80 \times 10^{-3}$ Å^2). Several cycles varying the anisotropic thermal parameters of all non-hydrogen atoms and applying a secondary correction to the data yielded final residual index values, $R = \Sigma\Delta F/\Sigma F_o$ and $R_w = \Sigma w\Delta F/\Sigma w\Delta F_o$ where $\Delta F = ||F_o - F_c||$ and $w = \sigma^{-2}$ (F_o), see Table 1. A final difference Fourier map revealed a maximum peak of 1.07 e$^-$ Å^{-3} in the vicinity of the Ru atom which is quite normal in compounds containing heavy metals. Elsewhere, the map was virtually featureless displaying only a random fluctuating background. Atomic scattering factors and associated anomalous dispersion corrections were obtained from the usual source [9].

3. Results and discussion

3.1. Synthesis and spectroscopy of [RuH(CO)(PPh$_3$)$_2$L$_2$][BF$_4$]

It has been shown previously that $OsH_2(CO)(PPh_3)_3$ can be converted to $[OsH(CO)(PPh_3)_2py_2]^+$ and related complexes by oxidation, hydride abstraction, and protonation, all performed in CH_2Cl_2 in the presence of an excess of a pyridine type ligand [1]. The second pyridine apparently substitutes for one PPh$_3$ after the first pyridine replaces a hydride in the oxidation, hydride abstraction, or protonation step. It was subsequently found that the ruthenium analog, $RuH_2(CO)(PPh_3)_3$, reacts similarly with hydride abstractors in CH_2Cl_2 in the presence of pyridine type ligands. Upon further investigation THF proved to be a more convenient solvent for the reaction since the product, $[RuH(CO)(PPh_3)_2L_2][BF_4]$, spontaneously precipitates from this solvent. Tropylium tetrafluoroborate, $[C_7H_7][BF_4]$, was more reactive than triphenylcarbenium and so was used as the hydride abstractor in the present study. As formed, the Ru–pyridine complexes contain a small amount of an insoluble brown impurity which is easily separated by recrystallization from CH_2Cl_2 and THF. When large excesses of $[C_7H_7][BF_4]$ are used the product also contains significant amounts of species derived from the reaction of the tropylium with PPh_3 and/or the excess pyridine ligand. These products are more difficult to separate from the organometallic product and so large excesses of hydride abstractor should be avoided. The complexes **1** (L = py), **2** (L = 4-Mepy) and **3** (L_2 = bpy) are stable in the air for extended times, but decompose rapidly in solution in the presence of air.

The infrared spectra of complexes **1**, **2** and **3** in mineral oil mulls display single strong carbonyl stretches at frequencies close to those previously reported in KBr disks (for complexes **1** and **3** [2]). The ^1H NMR spectra of **1** and **3** are also in agreement with literature reports [2]. All three compounds display singlets in their $^{31}P\{^1H\}$ NMR spectra, agreeing with the triplets observed for the Ru–H resonance in the ^1H NMR and confirming the chemical equivalency (*trans*-orientation) of the PPh_3 ligands. The *trans*-orientation of the PPh_3 ligands and the *cis*-orientation of the pyridines are also demonstrated in the X-ray crystal structure of **2**. This is the same geometry proposed for the osmium complexes through spectroscopic studies alone. Also in agreement with the osmium study, the ^1H NMR spectrum of the residue remaining after the synthesis of $[RuH(CO)(PPh_3)_2py_2][BF_4]$ displayed resonances attributable to cycloheptatriene but not bitropyl, confirming that the reaction involves hydride abstraction rather than oxidation followed by deprotonation.

3.2. *Crystal structure of $[RuH(CO)(PPh_3)_2(4\text{-}Mepy)_2]$-$[BF_4]$*

The resultant data of compound **2** best fit the centrosymmetric monoclinic space group $P2_1/c$ (No. 14). Crystallization occurs with four formula units per unit cell ($Z = 4$). The lack of any additional symmetry was verified by the program MISSYM [10]. The measured density of 1.351(3) Mg m^{-3} compares quite well with the calculated value (D_c = 1.357 Mg m^{-3}). A perspective view of compound **2** (see Fig. 1) shows the crystallographic numbering scheme. The arrangement of the functional groups about the Ru atom can be seen as a slightly distorted octahedron which is evidenced by the involved bond angles found in Table 2. The *cis* orientation of the 4-picoline groups and the *trans* orientation of the phosphines are in agreement with the data obtained from solution NMR spectroscopy. An important aspect of the structural analysis is that the hydride and carbonyl ligands are disordered, 50% of the time as seen in Fig. 1 and 50% in an exchanged orientation. Note, the occupancies of C(1), O(1) and C(1A), O(1A) were refined to 0.52(4), 0.54(4), 0.49(4), and 0.45(4), respectively. All bond distances and angles are internally consistent and are in good agreement with the values found in the Cambridge Structure Database [11]. Mean Ru–N, Ru–P, P–C, Ru–C and

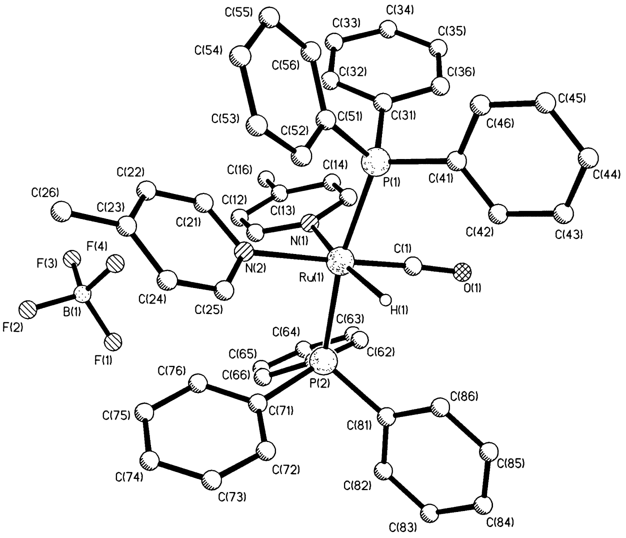

Fig. 1. The $[RuH(CO)(PPh_3)_2(4\text{-}Mepy)_2][BF_4]$ molecule with the atom numbering scheme shown.

Table 2
Selected interatomic bond lengths (Å) and angles (°) for compound **2**

Ru–N(1)	2.195(9)	N(1)–C(11)	1.34(2)
Ru–N(2)	2.217(7)	N(1)–C(15)	1.35(2)
Ru–C(1)	1.87(2)	C(11)–C(12)	1.40(2)
Ru–C(1A)	1.83(2)	C(12)–C(13)	1.35(2)
Ru–H(1)	1.78	C(13)–C(14)	1.35(2)
Ru–H(1A)	1.79	C(14)–C(15)	1.38(2)
Ru–P(1)	2.368(3)	C(13)–C(16)	1.54(3)
Ru–P(2)	2.355(3)	N(2)–C(21)	1.35(1)
P(1)–C(31)	1.831(10)	N(2)–C(25)	1.33(1)
P(1)–C(41)	1.815(11)	C(21)–C(22)	1.36(1)
P(1)–C(51)	1.830(8)	C(22)–C(23)	1.35(2)
P(2)–C(61)	1.843(12)	C(23)–C(24)	1.37(2)
P(2)–C(71)	1.818(10)	C(24)–C(25)	1.36(2)
P(2)–C(81)	1.822(9)	C(23)–C(26)	1.49(2)
C(1)–O(1)	1.17(2)	C(1A)– O(1A)	1.18(2)
N(1)–Ru–N(2)	93.2(3)	Ru–P(1)–C(31)	113.5(4)
N(1)–Ru–H(1)	85.8(7)	Ru–P(1)–C(41)	115.9(3)
N(1)–Ru–C(1)	176.5(6)	Ru–P(1)–C(51)	117.7(3)
N(2)–Ru–C(1)	84.2(5)	Ru–P(2)–C(61)	115.1(3)
C(1)–Ru–H(1)	97.2(8)	Ru–P(2)–C(71)	113.4(3)
P(1)–Ru–N(1)	95.5(2)	Ru–P(2)–C(81)	116.4(4)
P(1)–Ru–N(2)	92.1(2)	Ru–N(1)–C(11)	121.4(8)
P(2)–Ru–N(1)	90.1(2)	Ru–N(2)–C(25)	120.4(7)
P(2)–Ru–N(2)	95.5(2)	C(16)–C(13)–C(14)	119.9(13)
P(1)–Ru–P(2)	170.3(1)	C(26)–C(23)–C(24)	121.3(13)

Ring	Distance (Ph)		Angle (Ph)	
	Mean	Range	Mean	Range
C(31)–C(36)	1.37(5)	1.30–1.45	120(3)	115.7–125.1
C(41)–C(46)	1.37(2)	1.35–1.39	120(1)	117.3–121.3
C(51)–C(56)	1.38(2)	1.34–1.41	120(2)	117.6–122.0
C(61)–C(66)	1.38(4)	1.30–1.43	120(2)	117.4–123.2
C(71)–C(76)	1.38(1)	1.37–1.39	120(1)	119.0–121.6
C(81)–C(86)	1.38(1)	1.36–1.40	120(1)	117.3–121.1

C–O bond lengths are presented in Table 2, 2.20(1), 2.362(7), 1.827(9), 1.85(2) and 1.17(2) Å, respectively. Specifically, it is found that the average P–C bond length is in direct agreement with observed results found in other structures containing triphenylphosphine groups [12,13] and in BIDICS [14]. When considering the 4-picoline groups the mean N–C(sp^2), C(sp^3)–C(sp^2) and C(sp^2)–C(sp^2) bond distances are 1.34(1), 1.52(3) and 1.37(2) Å, respectively. The angles of Ru–P(1, 2) – C(31, 41, 51, 61, 71, 81) are greater than the ideal tetrahedral geometry (109.5°) and the angles between C(31), C(41), C(51) and C(61), C(71), C(81) are much less than ideality. However, the mean bond angles about P(1) and P(2) are 109.5°. Further, the Ru–C≡O bond angle associated with the disordered carbonyl group is 177.7(14)°. This near linear angular arrangement is an indication of strong directional bonding related to the interaction of the ruthenium 4d orbitals and the CO orbitals. The mean C–C bond lengths and C–C–C bond angles in each phenyl ring can be considered ideal [15], see Table 2. Planarity of all rings has been verified by employing a least-squares planes program MPLN [8]. The mean deviation from planarity for the six phenyl rings was 0.009 Å while the mean deviation from planarity for the two pyridine ligands was 0.012 Å. The plane associated with the Ru metal atom ring [Ru, N(1), N(2), C(1), H(1)] was also tested for planarity, mean deviation 0.023 Å. The dihedral angles between the Ru ring and the 4-picoline rings, N(1) and N(2) rings, are 148.6 and 150.2°, respectively. Finally, the dihedral angle between the two pyridine rings is 55.5°.

4. Supplementary material

Structure factors, anisotropic thermal parameters, hydrogen atom parameters, and complete bond distances and angles are available from the authors.

Acknowledgements

We thank the Robert A. Welch Foundation (Grants No. AA-0668 and AA-1083) and Baylor University, in part, for support of this research. M.S.W. thanks the National Science Foundation for support through the REU Program.

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