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Journal of Organometallic Chemistry 498 (1995) C20–C22

Journal of Organometallic Chemistry

Preliminary communication

Hydridosulphonato, hydridocarboxylato and cationic hydrido complexes of carbonylpyridine ruthenium(II)

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Received 15 March 1995

Abstract

The oxidative addition of pyridinium salts of Brønsted acids to $[Ru_3(CO)_{12}]$ provides a straightforward and easy way to a new class of H-RuII complexes. These have the H *trans* to either N or O donors which increases their hydridic character.

Keywords: Ruthenium; Pyridine; Oxidative addition; Hydrido complexes; Sulphonato complexes; Carboxylate complexes

1. Introduction

Since the first report by Lewis et al. in 1969, the reactions between $[Ru_3(CO)_{12}]$ and sulphonic or carboxylic acids have been studied by a number of workers [1]. The initial reaction produces dihydrogen and μ_2-η^2-sulphonato or μ_2-η^2-carboxylato dinuclear RuI complexes as primary products. Pyridine (py) can also be orthometallated upon reaction with $[Ru_3(CO)_{12}]$ [2]. Nevertheless, neither reaction is observed when $[Ru_3(CO)_{12}]$ is treated with acids in py and a novel reaction without dihydrogen evolution takes place in minutes at 95°C. Analysis of the products isolated in nearly quantitative yields, and gas volumetric measurements of the CO evolved, indicate the stoichiometry of Eq. 1 for such an oxidative addition of Brønsted acids to $[Ru_3(CO)_{12}]$ in py solution.

$$[Ru_3(CO)_{12}] + 3HX \xrightarrow{py,95^\circ C} 3[RuHX(CO)_2(py)_2] + 6CO \qquad (1)$$

$$X = OOS(O)Tol,\ OOCF_3$$

In the solid state, the *p*-toluensulphonate complex displays three IR absorptions in the CO stretching region. The two of higher intensity at 2038(s) and 1968(vs) indicate *cis* carbonyls, while that at 2009 cm^{-1} (absent in the product obtained with deuterated acid) is attributed to the (Ru–H). A crystallographic analysis of $[RuH(OOS(O)Tol)(CO)_2(py)_2]$ **1** proves the *trans,cis, cis* geometry (Fig. 1) [3].

However, in solution rearrangements can occur. In CH_2Cl_2 solution, **1** exhibits a dynamic behaviour over an hour at room temperature. The IR difference spectrum between a freshly prepared solution (2048(s), 1974(vs) cm^{-1}) and the same after equilibration shows that the two ν(CO) bands of **1** are reduced in intensity and are accompanied by two new absorptions at 2043 and 1961 cm^{-1}. Correspondingly, in CD_2Cl_2 the resonance of the hydride ligand of **1** at -14.10 ppm decreases in intensity, while a new singlet arises at -11.30 ppm. At the equilibrium, the integration ratio shows that 10% of the original **1** has been converted into another isomer, **2**. Based on the two ν(CO) bands of the latter (see above), the presence of *cis* carbonyls is inferred. However, the hydride chemical shift of less than -10 ppm excludes a carbonyl *trans* to hydrido [4] and the geometry of Fig. 2 is indicated.

On dissolving **1** in deuterated py, a fast equilibration occurs and three hydride resonances (-10.40, -11.0, -13.30 ppm) are observed. The two at -13.30 and -10.40 can be tentatively attributed to **1** still present in the equilibrium mixture and to isomer **2**, respectively. The integration ratios at room temperature show that these two components are present in ca. 3 : 1 ratio and that they constitute 50% of total hydrides. The third resonance at -11.0 ppm is attributed to a cationic complex whose relative concentration is probably af-

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SSDI 0022-328X(95)05577-0

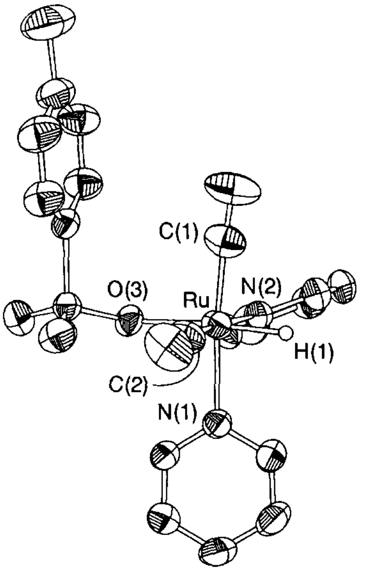


Fig. 1. Projection of the molecular structure of **1**. Ru–C(1) 1.852(3), Ru–C(2) 1.861(3), Ru–N(1) 2.159(2), Ru–N(2) 2.161(2), Ru–O(3) 2.217(2), Ru–H(1) 1.60 Å, C(1)–Ru–C(2) 89.1(1), C(1)–Ru–N(1) 174.2(1), C(2)–Ru–N(1) 91.4(1), C(1)–Ru–N(2) 93.3(1), C(2)–Ru–N(2) 175.8(1), N(1)–Ru–N(2) 85.83(8), C(1)–Ru–O(3) 99.6(1), C(2)–Ru–O(3) 98.9(1), N(1)–Ru–O(3) 86.11(7), N(2)–Ru–O(3) 84.07(8)°.

fected by the dielectric constant of the medium, so that only this resonance is observed in D_2O pyridine-d_5 1:5 vol:vol. The tetraphenylborate salt of this cationic complex, $[RuH(CO)_2(py)_3][BPh_4]$ **3**, was precipitated in quantitative yield by addition of CH_3OH to a py solution of **1** and $NaBPh_4$. When redissolved in deuterated py, this product, exhibits a single hydride resonance at −11.0 ppm, confirming that **3** the major component in the equilibrium mixture generated from **1** in py. **3** displays two νCO bands, both in CH_2Cl_2 (2053(s), 1984(vs) cm^{-1}) and in the solid state (2037(s), 1968(vs) cm^{-1}), while ν(Ru–H) is at 2016 cm^{-1} in the solid state. These ^1H NMR and IR spectra indicate the *fac* disposition of py (Fig. 3).

A preliminary crystallographic analysis of 3 confirms this conclusion [5].

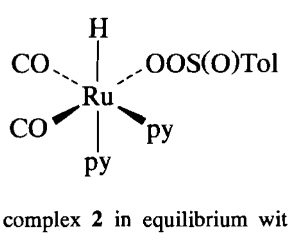


Fig. 2. Geometry of complex **2** in equilibrium with **1** in CH_2Cl_2 solution.

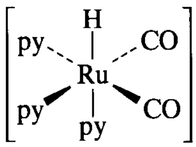
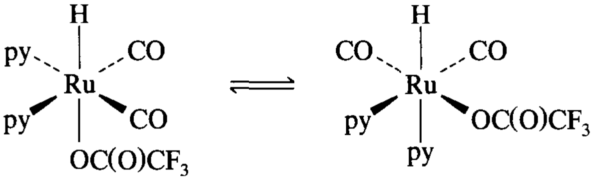


Fig. 3. Geometry of the cationic complex **3** generated from **1** in py/H_2O solution.

As expected (Eq. 1), pyridinium trifluoroacetate adds oxidatively to $[Ru_3(CO)_{12}]$ in a fashion analogous to pyridinium 4-toluensulphonate and so reaction 1 seems to be applicable to a wide range of Brønsted acids. The analysis of the colourless solid product, $[RuH(OC(O)CF_3)(CO)_2(py)_2]$, corresponds however to two different geometric isomers, neither of which was obtained in pure form. The IR spectrum in the solid state displays absorptions at 2042(s), 1960(vs. broad) cm^{-1} due to *cis* carbonyls, at 2000(m) cm^{-1} (shifted to 1440 when CF_3COOD is employed) due to ν(Ru–H) and at 1689 cm^{-1} due to the asymmetric vibration of the monodentate carboxylate [6]. The ^1H NMR spectrum of a freshly prepared CD_2Cl_2 solution shows two resonances at −11.3 and −12.6 ppm with their integral ratio equal to 2 in favour of the lower chemical shift resonance. On standing, equilibration occurs within an hour and a ratio of nearly 1 is obtained at room temperature. Such an equilibration between two isomers can be followed also by IR spectroscopy and two new bands at 2045 and 1970 cm^{-1} can be seen in the difference spectrum. These spectroscopic features imply equilibrium (2) between the two isomeric (hydrido)-trifluoroacetato complexes of carbonylpyridine ruthenium(II), **4** and **5**.



4 **5**

(2)

Compounds **1**–**5** are rare examples of hydrido complexes of RuII without P or As ligands [7]. When these are present, the H atom is generally *trans* to tertiary phosphines or arsines, or *trans* to CO if this π-acid ligand is also present [8]. With only sulphonato or carboxylato, py and CO coligands, the H is found *trans* to N or O hard σ-donor atoms. This is expected to increase the hydridic nature of H–Ru bond, and a novel coordination chemistry can be envisaged. In contrast, *cis*-$[Ru(bpy)_2(CO)H]^+$ [9] (bpy = 2,2′ bipyridine), where a similar H–Ru–N *trans* configuration exists, is attracting much attention, because it is implicated as an intermediate in the homogeneous WGS reaction [10] and in the photochemical [11] and electrochemical [12] reduction of CO_2 to formate.

Preliminary investigations confirm the hydridic nature of **1**–**5**, since dihydrogen is evolved on treating with 4-toluensulphonic or trifluoroacetic acid in CH_2Cl_2 solution.

2. Experimental details

$[Ru_3(CO)_{12}]$ (3.2 g) and *p*-toluensulphonic acid (2.7 g) were heated at 95°C in py (25 ml) for 10 min. The pale yellow solution, when evaporated to dryness under reduced pressure, left an oil which was dissolved in 30 ml of EtOH. Upon addition of 300 ml of Et_2O to this solution cooled at 0°C, 6 g of **1** (82% yield) were obtained as colourless crystals, suitable for structure determination. The same procedure was followed for the reaction with CF_3COOH.

Full X-ray structural parameters have been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgements

This work was supported by MURST Roma. We thank Prof. B.R. James, Prof. S. Merlino and Dr. G. Fochi for helpful discussions and CHIMET SpA for a gift of ruthenium.

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[3] X-ray structure of **1**: $[C_{19}H_{18}N_2O_5RuS]$, $M = 487.5$. Siemens P4 diffractometer, room temperature, Mo Kα radiation, $\lambda = 0.71069$ Å, triclinic, space group $P\bar{1}$, $a = 8.8758(3)$, $b = 9.5378(3)$, $c = 13.5377(6)$ Å, $\alpha = 95.127(4)$, $\beta = 106.403(4)$, $\gamma = 108.867(4)°$, $V = 1019.51(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.588$ g.cm^{-3}, 3496 independent reflections. The structure was solved by standard Patterson and Fourier methods and the hydrogen atoms were localized on difference Fourier map. Full-matrix refinement, with constraints on organic hydrogens geometry. Final R factor 0.0282, 282 parameters, final largest differential peak 0.62 e.Å^3. Structure solution and refinement was made by SHELX86 and SHELX93 programs.

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[5] X-ray structure of **3**: $[(C_{17}H_{16}N_3O_2Ru)\ (C_{24}H_{20}B)]$, $M = 714.6$, Crystals of **3** obtained from py/CH_3OH are colorless, with prismatic hexagonal habit terminated with hexagonal pyramidal faces. The Weissenberg photographs indicated the Laue symmetry $6/m$, the systematic absences pointed to the presence of a 6_1 axis. Intensities were measured on a Philips PW1100 diffractometer, room temperature, Cu Kα radiation, $\lambda = 1.54178$, space group $P6_1$, $a = 9.762(7)$, $c = 64.30(2)$ Å, $V = 5306(8)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.342$ g.cm^{-3}, 2549 independent reflections. Owing to the length of c axis, the intensity measurements are probably affected by some degree of superposition. This can explain the high value of $R_{int} = 0.11$ between the equivalent reflections. The structure was solved by standard Patterson and Fourier methods. All heavy atoms were localized except one carbonyl group. The cationic moiety contains a Ruthenium atom in octahedral coordination. The pyridine ligands are *fac* with two Ru–N distances shorter than the third. Opposite to one of the nearer nitrogen atoms was the CO group. The missing carbonyl was introduced in a calculated position, opposite the other closer nitrogen atom. The refinement was made without hydrogen atoms, with anisotropic thermal factors for the Ru atom and restraining the carbon cycles to regular hexagons:final R value 0.096 (for 1098 reflections with $F_0 > 4\sigma(F_0)$), 115 parameters. All thermal factors appeared unusually high. This is probably an artefact due to the low quality of the data. We are now trying to improve the data collection using a diffractometer with a longer detector arm. The quality of the described determination is however sufficient to establish that the three pyridine ligands are *fac*. Calculations have been made with SHELX86 and SHELX93 programs.

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