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Preliminary communication

$Ru_3(CO)_9(PPh_3)_3$: a convenient starting material for the synthesis of binuclear ruthenium(I) complexes. Crystal structure of $Ru_2(\mu\text{-}L_2)(CO)_4(PPh_3)_2$ (H_2L_2 = 1,8-diaminonaphthalene)

Pedro L. Andreu, Javier A. Cabeza *, Victor Riera,

Departamento de Química Organometálica, Facultad de Química, Universidad de Oviedo, E-33071 Oviedo (Spain)

Francis Robert and Yves Jeannin

Université Pierre et Marie Curie, Laboratoire de Chimie des Métaux de Transition, 4 Place Jussieu, F-75252 Paris Cedex 05 (France)

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Abstract

The thermal reaction of $Ru_3(CO)_9(PPh_3)_3$ with precursors (HL) of binucleating anionic ligands affords the ruthenium(I) dimers $Ru_2(\mu\text{-}L)_2(CO)_4(PPh_3)_2$ in high yield [HL = 2-pyridone (**1**), *N*-methyl-2-mercaptoimidazole (**2**), pyrazole (**3**), t-butylmercaptane (**4**); H_2L_2 = 1,8-diaminonaphthalene (**5**)]. The crystal structure of complex **5** shows that each nitrogen of the 1,8-diiminonaphthalene ligand bridges the two ruthenium atoms, leading to a very distorted octahedral arrangement of the ligands and a very short Ru–Ru distance, 2.5788(3) Å.

Introduction

Ruthenium(I) compounds are still uncommon [1]. Until recently [2–4] they were practically limited to derivatives of $Ru_4H_4(CO)_{12}$ [5], $Ru_2Cp_2(CO)_4$ [6] and to carboxylate-bridged complexes such as $Ru_2(\mu\text{-}RCO_2)_2(CO)_4L_2$ [7–11], which are the only types of complex that could be obtained in high yield. This apparent lack of attention to ruthenium(I) compounds is probably due to the low yields in which they are made from the usual starting material, $Ru_3(CO)_{12}$ [12]. Recently, we extended the known types of ruthenium(I) dimers by the synthesis of a series of pyrazolate-bridged complexes starting from $RuCl_3 \cdot nH_2O$ [2], and we studied their structure and reactivity [3]. We now report a general method for the synthesis of ruthenium(I) dimers starting from a readily available substrate $Ru_3(CO)_9(PPh_3)_3$ [13].

While this work was underway, there were two significant developments which increased interest in ruthenium(I) compounds: (a) the carboxylate complexes

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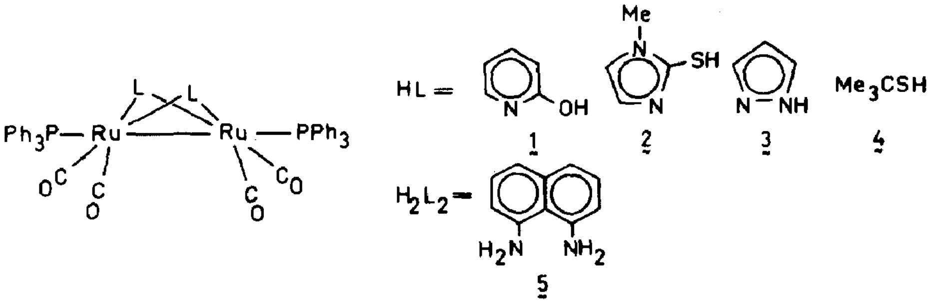

Scheme 1

$Ru_2(\mu\text{-}RCO_2)_2(CO)_4L_2$ (R = alkyl, aryl; L = P-donor ligands) were found to catalyse the hydroformylation of olefins under very mild conditions (1 MPa of syn-gas) [14], and (b) it was shown that the acetate groups of $Ru_2(\mu\text{-}MeCO_2)_2(CO)_4L_2$ (L = MeCN, PPh_3) can be replaced by pyrazolate, pyridonate and mercaptothiazolidinate ligands [4].

Results and discussion

The reaction of $Ru_3(CO)_9(PPh_3)_3$ with four equivalents of 2-pyridone, *N*-methyl-2-mercaptoimidazole, t-butylmercaptane, or 1,8-diaminonaphthalene in a

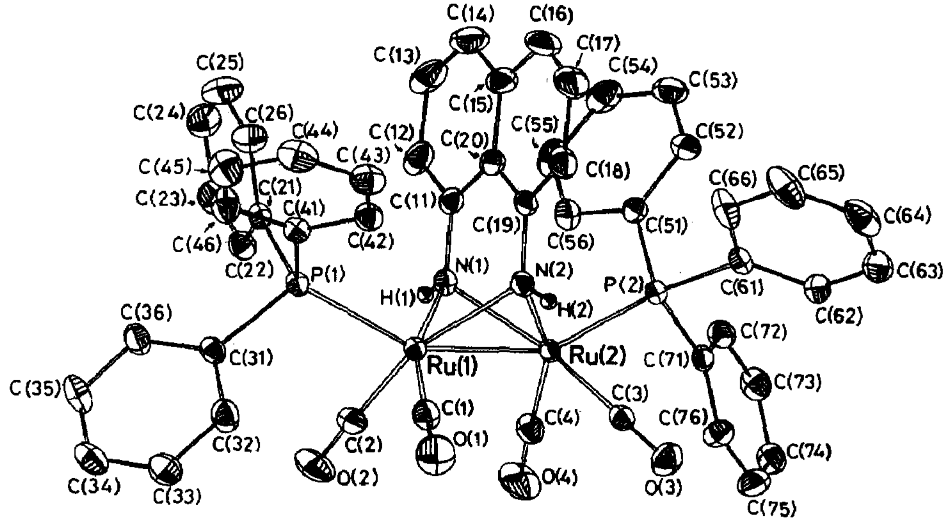

Fig. 1. Perspective view of complex 5. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.5788(3), Ru(1)–N(1) 2.151(3), Ru(1)–N(2) 2.132(3), Ru(1)–C(1) 1.871(3), Ru(1)–C(2) 1.865(4), Ru(1)–P(1) 2.3786(8), Ru(2)–N(1) 2.163(3), Ru(2)–N(2) 2.144(3), Ru(2)–C(3) 1.863(3), Ru(2)–C(4) 1.853(3), Ru(2)–P(2) 2.3905(8); C(2)–Ru(1)–C(1) 90.5(2), Ru(2)–Ru(1)–C(2) 107.1(1), N(1)–Ru(1)–Ru(2) 53.51(7), N(1)–Ru(1)–N(2) 73.3(1), P(1)–Ru(1)–C(1) 90.4(1), P(1)–Ru(1)–Ru(2) 151.57(2), P(1)–Ru(1)–N(2) 101.49(7), Ru(2)–N(1)–Ru(1) 73.41(8), Ru(2)–Ru(1)–C(1) 103.6(1), N(1)–Ru(1)–C(2) 93.8(1), P(1)–Ru(1)–N(1) 111.45(7), P(2)–Ru(2)–Ru(1) 153.74(2).

refluxing toluene solution gave the binuclear ruthenium(I) compounds **1**–**5** (Scheme 1) in yields of 70 to 90%. Their $^{31}P\{^{1}H\}$ NMR spectra[*] are singlets, indicating that the bridging ligands in the complexes **1** and **2** are in a head-to-tail arrangement, since a head-to-head disposition would give two doublets. The IR spectra in the carbonyl stretching region[**] of complexes **1** and **2** (C_2 symmetry) show four bands, whereas those of complexes **3**–**5** (C_{2v} symmetry) display three bands, as expected from their symmetry. The X-ray crystal structures of complexes **1** and **3** were reported [4] while this manuscript was being prepared; they confirm the proposed structures.

The X-ray crystal structure[***] of complex **5**, depicted in Fig. 1, shows that the doubly-deprotonated form of 1,8-diaminonaphthalene bridges symmetrically two $Ru(CO)_2(PPh_3)$ units, with the carbonyl groups *trans* to the nitrogen atoms and the PPh_3 ligands *trans* to the Ru–Ru bond. Overall, the compound has the sawhorse arrangement observed in other ruthenium(I) dimers [2,4,9,10,12a,12e,15], but two significant differences should be noted: (a) the coordination about the ruthenium atoms is a very distorted octahedral, with angles P(1)–Ru(1)–Ru(2) (151.57(2)°) and P(2)–Ru(2)–Ru(1) (153.74(2)°) which differ by ca. 28° from the ideal 180°; and (b) the Ru–Ru separation of 2.5788(3) Å is considerably shorter than all other Ru–Ru distances reported for ruthenium(I) dimers, which average ca. 2.70 Å. These differences from other ruthenium(I) dimers must be caused by the strain imposed by the bridging ligand, with angles Ru(1)–N(1)–Ru(2) (73.41(8)°), Ru(1)–N(2)–Ru(2) (74.18(9)°) and N(1)–Ru(1)–N(2) (73.3(1)°), N(1)–Ru(2)–N(2) (72.8(1)°) deviating by ca. 35 and 16° from the ideal 109.5 and 90°, respectively.

We expect that the synthetic strategy described above will lead to a variety of ruthenium(I) dimers which will show significantly different chemical and catalytic properties arising from different combinations of bridging and terminal ligands. Further work in this area is in progress.

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[*] *NMR Data ($CDCl_3$).* ^{1}H NMR (δ, ppm, 300 MHz): **1**: 7.53–7.27 (m, 30H), 6.98 (ddd, *J* 8, 7 and 1.5 Hz, 2H), 5.98 (dd, *J* 8 and 1.3 Hz, 2H), 5.66 (ddd, *J* 8, 7 and 1.5 Hz, 2H); **2**: 7.53–7.25 (m, 30H), 6.20 (s, br, 2H), 5.96 (s, br, 2H), 3.41 (s, 6H); **3**: 7.60–7.20 (m, 30H), 6.64 (d, *J* 1.9 Hz, 4H), 5.73 (t, *J* 1.9 Hz, 2H); **4**: 7.54–7.25 (m, 30H), 0.60 (s, 18H); **5**: 7.55–7.24 (m, 30H), 6.86 (d, *J* 8 Hz, 2H), 6.40 (t, *J* 8 Hz, 2H), 5.97 (d, *J* 8 Hz, 2H), 4.27 (s, br, 2H). $^{31}P\{^{1}H\}$ NMR (δ, ppm, 121.5 MHz): **1**: 14.69 (s); **2**: 15.07 (s); **3**: 19.56 (s); **4**: 23.87 (s); **5**: 27.20 (s).

[**] *IR Data.* $\nu(CO)(CH_2Cl_2$, $cm^{-1})$: **1**: 2019vs, 1978m, 1945s, 1917w; **2**: 2018vs, 1976m, 1945s, 1923w; **3**: 2024vs, 1983m, 1956s; **4**: 2000vs, 1964m, 1930s; **5**: 1998vs, 1968m, 1926s. $\nu(NH)$(Nujol, cm^{-1}): **5**: 3342w, 3333w.

[***] *Crystal data for 5*: $C_{50}H_{38}N_2O_4P_2Ru_2$, $M = 994.96$, space group $P\bar{1}$, a 9.528(1), b 13.049(2), c 18.550(2) Å, α 68.71(1), β 82.00(1), γ 86.56(1)°, U 2131 Å^3, $Z = 2$, D_c 1.55 g cm^{-3}, $F(000) = 1004$, λ 0.71069 Å, $\mu(\text{Mo-}K_\alpha)$ 8.13 cm^{-1}. The intensities of 8049 reflections were collected with a CAD-4 Enraf–Nonius diffractometer ($1 < \theta < 25°$, scan width $1.20 + 0.34 \tan \theta$) using the $\theta/2\theta$ scan technique and Mo-K_α radiation (graphite monochromator). 6007 reflections with $F > 3\sigma(F)$ were used for computations. No absorption correction was made. The structure was solved by Patterson and subsequent Fourier maps and refined by least squares with an approximation, in three blocks, to the normal matrix, with anisotropic thermal parameters for the non hydrogen atoms. All the hydrogen atoms were found from difference maps, but only the parameters of those attached to the nitrogen atoms were refined, with an isotropic thermal parameter of 0.08 Å^2. The coordinates of the other hydrogen atoms were not refined, being placed at their geometrically calculated positions after each cycle. Final R and R_w values are 0.022 and 0.027. The atomic coordinates and a complete list of bond lengths and the angles have been deposited at the Cambridge Crystallographic Data Centre.

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