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Synthesis of Monomeric Ruthenium Hydroxo Complexes $(PMe_3)_4Ru(R)(OH)$ (R = H, Me) and a Unique Dimeric Ruthenium Hydroxo–Water Complex $[\textit{trans}\text{-}Ru(H)(OH)(DMPE)_2{\cdot}H_2O]_2$

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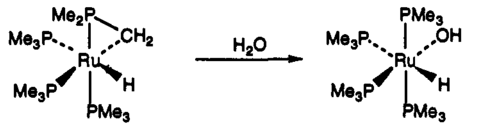
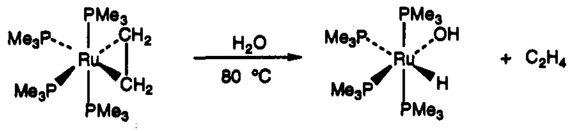
Hydroxo complexes of transition metals have been postulated as critical intermediates in a number of catalytic reactions involving water as a substrate.[1-7] However, there exist very few examples of monomeric transition-metal hydroxides.[1,8-19] Alkyl and hydrido hydroxo complexes are especially rare. We wish to report the syntheses of two monomeric ruthenium hydroxo complexes $(PMe_3)_4Ru(R)(OH)$ (**1**, R = H; **2**, R = Me) prepared via the addition of water to a Ru(II) complex. In addition, we have prepared and structurally characterized a novel ruthenium hydroxo–water complex in which two ruthenium hydrido hydroxo molecules are bound together by two hydrogen-bonded water bridges, $[\textit{trans}\text{-}Ru(H)(OH)(DMPE)_2{\cdot}H_2O]_2$ (**3**).

The (hydrido)hydroxoruthenium complex $(PMe_3)_4Ru(H)(OH)$ (**1**) has been prepared via two methods. Cyclometalated hydride $(PMe_3)_3(Me_2PCH_2)Ru(H)$ (**4**)[20] reacted with H_2O at room temperature to form complex **1** in low yield (eq 1). More conveniently, treatment of $(PMe_3)_4Ru(C_2H_4)$[21] (**5**) with 1 equiv of H_2O at room temperature resulted in the formation of $(PMe_3)_4Ru(H)(OH)$ (**1**) (eq 2) in 80% yield by NMR spectroscopy. Due to its high solubility, even at low temperatures, compound **1** was isolated by recrystallization from pentane at −30 °C in only 30% yield. It was characterized by standard spectroscopic and analytical techniques.[22] Addition of excess H_2O (>2 equiv) to hydride **1** resulted in the formation of a white precipitate (**6**). Spectroscopic and analytical data indicate that this material can be formulated as the hydroxide salt $[(PMe_3)_3Ru(\mu\text{-}OH)_3Ru(PMe_3)_3]^+OH^-$, but we cannot rule out a prototropic isomer containing two hydroxide and one oxo bridges associated with a molecule of water.[23,24]

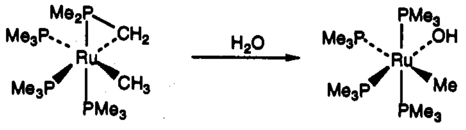


4 **1** (1)



5 **1** (2)

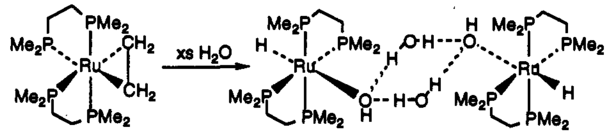
It was hoped that replacement of the ruthenium hydride ligand by an alkyl group would increase the thermal stability of a monomeric hydroxo complex. The methyl hydroxo monomer **2** was formed over 2 days from the room temperature reaction of the cyclometalated complex $(PMe_3)_3(Me_2PCH_2)Ru(Me)$[25] (**7**) with a slight excess (1.5 equiv) of H_2O (eq 3). Compound **2** was isolated by pentane extraction and purified by crystallization at −30 °C to yield the product in 60% yield. Analysis of the crude reaction mixture showed the hydroxo dimer **6** as a minor side product.



7 **2** (3)

Hydroxo methyl complex **2** was thermally more stable than hydroxo hydride **1**. In both cases, thermolysis of a benzene solution of the hydroxo complex led to the formation of a complex mixture containing mainly dimer **6**, PMe_3, and $OPMe_3$. However, **2** did not decompose until 70 °C, whereas hydroxo hydride **1** began to decompose at 45 °C.

In an attempt to obtain an analogue of hydroxo hydride **1** containing a bidentate ligand, $(DMPE)_2Ru(C_2H_4)$ (**8**) was treated with an excess of H_2O at 90 °C. This led to **3**, an unusual ruthenium hydroxo dimer bridged by two hydrogen-bound water molecules (eq 4). Dimer **3** was purified by recrystallization to yield 28% pure product. Variable-temperature ^1H NMR studies performed on complex **3** indicated an intimate interaction between the two water molecules and the ruthenium-bound OH ligands. At room temperature, a single broad resonance at δ 2.30 (C_6D_6) in the ^1H NMR spectrum demonstrated that the protons on the hydroxide ligands were rapidly exchanging with those on the water molecules. At −92 °C, the exchange process slowed enough on the NMR time scale to distinguish distinct resonances for the



8 **3** (4)

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(1) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980,** *199,* 119.

(2) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978,** *100,* 1750.

(3) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1973,** *95,* 3030.

(4) Jensen, C. M.; Trogler, W. C. *J. Am. Chem. Soc.* **1986,** *108,* 723.

(5) Jensen, C. M.; Trogler, W. C. *Science* **1986,** *233,* 1069.

(6) Masters, C. *Homogeneous Transition Metal Catalysis*; Chapman & Hall: New York, 1981.

(7) Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979,** *101,* 2027.

(8) Bennett, M. A.; Appleton, T. *Inorg. Chem.* **1978,** *17,* 739.

(9) Bryndza, H. E. *Chem. Rev.* **1988,** *88,* 1163.

(10) Cole-Hamilton, D. J.; Young, R. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976,** 1995.

(11) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1989,** *111,* 2717.

(12) Milstein, D.; Calabrese, J. C.; Williams, I. D. *J. Am. Chem. Soc.* **1986,** *108,* 6387.

(13) Mehrotra, R. C.; Agarwal, S. K.; Singh, Y. P. *Coord. Chem. Rev.* **1985,** *68,* 101.

(14) Ros, R.; Michelin, R. A.; Bataillard, R.; Roulet, R. *J. Organomet. Chem.* **1978,** *161,* 75.

(15) James, B. R.; Preece, M.; Robinson, S. D. *ACS Adv. Chem. Ser.* **1982,** *196,* 145.

(16) Vaska, L.; J. Peone, J. *J. Chem. Soc. D* **1971,** 418.

(17) Stevens, R. C.; Bau, R.; Milstein, D.; Blum, O.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1990,** 1429.

(18) Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Dalton Trans.* **1976,** 993.

(19) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978,** *100,* 3941.

(20) Werner, H.; Werner, R. *J. Organomet. Chem.* **1981,** *209,* C60.

(21) Wong, W. K.; Chiu, K. W.; Statler, J. A.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *Polyhedron* **1984,** *3,* 1255.

(22) All spectroscopic and analytical data for isolable complexes have been provided as supplementary material.

(23) For a similar type of dimer, see: Nutton, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981,** 1997.

(24) A complex assigned the formula $(PMe_3)_6(OH)_4Ru_2$ that may be identical to **6** was reported earlier by Wilkinson and co-workers: Jones, R. A.; Wilkinson, G.; Colquohoun, I. J.; McFarlane, W.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1980,** 2480.

(25) Hartwig, J. H.; Bergman, R. G.; Andersen, R. A. *J. Organomet. Chem.* **1990,** *394,* 417.

0002-7863/93/1515-5875$04.00/0

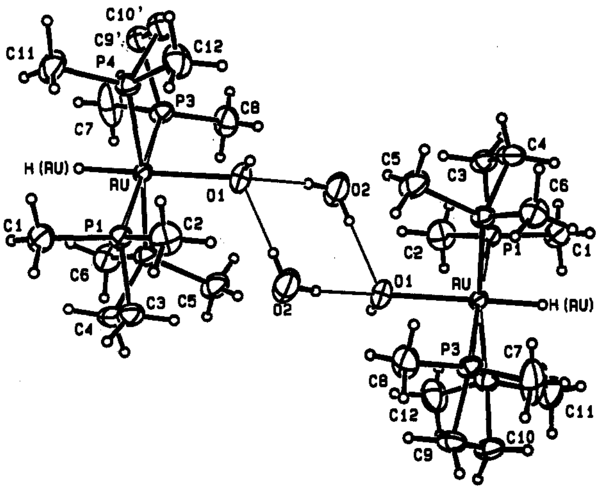


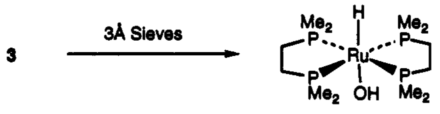
Figure 1. ORTEP Diagram of $[(DMPE)_2Ru(H)(OH)(\mu\text{-}OH_2)]_2$ (3).

hydroxide protons (δ −4.55, THF-d_8) and water protons (δ 5.70, THF-d_8) with an intensity ratio of 1:2.2, respectively.

A suitable single crystal of complex **3** was obtained, and its structure was determined by an X-ray diffraction analysis (Figure 1).[26] The X-ray structure shows two 18-electron $(DMPE)_2Ru(H)(OH)$ moieties bridged by hydrogen-bonding to two water molecules. An unusual aspect of the hydrogen-bonding bridge is that the OH proton is not involved; only the hydrogens of the water molecules form the hydrogen bonds between water and hydroxide. Selected structural data for **3** are given in Table I. The Ru–O bond distances of 2.230(2) Å and Ru–H bond distances of 1.47(3) Å are comparable to those of other known late-transition-metal complexes containing H and OH ligands.[12] The O···O bond distances in complex **3** of 2.758(3) and 2.768(3) Å are slightly longer than O···O bond distances in the related $H_3O_2^-$ ligands[27–29] and are indicative of a moderately strong hydrogen bond. We are uncertain as to the actual solution structure of complex **3** at this time. It does not appear to fragment or lose water even at temperatures as high as 70 °C in solution; however, we were able to remove the hydrogen-bound water by molecular sieves, yielding the monomeric *trans*-$Ru(H)(OH)(DMPE)_2$ (**7**) (eq 5).

Table I. Selected Structural Data for $[(DMPE)_2Ru(H)(OH)(\mu\text{-}OH_2)]_2$ (3)

interatomic distances (Å)			selected bond angles (deg)			
atom 1	atom 2	distance	atom 1	atom 2	atom 3	angle
Ru	P1	2.297(1)	P1	Ru	P2	84.36(2)
Ru	P2	2.290(1)	P1	Ru	P3	178.12(2)
Ru	P3	2.291(1)	P1	Ru	P4	96.10(2)
Ru	P4	2.295(1)	P1	Ru	O1	92.11(5)
Ru	O1	2.230(2)	P1	Ru	H(Ru)	88.3(10)
Ru	H(Ru)	1.47(3)	P2	Ru	P3	95.21(2)
			P2	Ru	P4	172.53(2)
O1	O2	2.758(3)	P2	Ru	O1	91.89(5)
O1	O2	2.768(3)	P2	Ru	H(Ru)	88.8(10)
O1	H–O	0.61(2)	P3	Ru	P4	84.08(2)
O1	HW1	1.94(3)	P3	Ru	O1	89.73(5)
O1	HW2	2.00(3)	P3	Ru	H(Ru)	89.8(10)
O2	HW1	0.82(3)	P4	Ru	O1	95.54(5)
O2	HW2	0.78(3)	P4	Ru	H(Ru)	83.8(10)
			O1	Ru	H(Ru)	179.3(10)
P1	C1	1.830(2)				
P1	C2	1.823(2)	Ru	O1	O2	117.09(8)
P1	C3	1.848(2)	Ru	O1	O2	134.80(9)
P2	C4	1.848(2)	Ru	O1	H–O	114.4(27)
P2	C5	1.827(2)	O2	O1	O2	79.78(7)
P2	C6	1.829(2)	O2	O1	H–O	100.8(27)
C3	C4	1.525(3)	O2	O1	H–O	101.4(27)
			O1	O2	O1	100.22(7)
			HW1	O2	HW2	108.1(27)
			O2	HW1	O1	176.3(32)
			O2	HW2	O1	168.9(29)



7

(5)

In summary, we have prepared three new examples of ruthenium hydroxo complexes generated from the reaction of H_2O and Ru(II) complexes. The monomeric complexes **1** and **2** have shown some tendency to decompose thermally; in contrast, water-bridged dimer [*trans*-$Ru(H)(OH)(DMPE)_2{\cdot}H_2O]_2$ (**3**) is surprisingly resistant toward decomposition. Efforts are currently underway to explore the chemistry of complexes **1** and **2** as well as **3** and its anhydrous form **7**.

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Supplementary Material Available: Spectroscopic and analytical data for complexes **1**, **2**, **3**, **6**, and **7**; X-ray diffraction data (ORTEP diagrams, crystal and data collection parameters, positional and anisotropic thermal parameters) for complex **3** (13 pages). This material is provided with the archival edition of the journal, available in many libraries. Alternatively, ordering information is given on any current masthead page.

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[26] Complex **3** crystallized as triclinic, pale yellow crystals: $a = 9.128(1)$ Å, $b = 9.659(2)$ Å, $c = 12.860(2)$ Å, $\alpha = 74.38(1)°$, $\beta = 82.75(1)°$, $\gamma = 67.58(1)°$, $V = 1009.1(2)$ Å^3, $T = -90$ °C, $R = 2.0\%$, $R_w = 2.42\%$, no. of reflections $(F2 > 3\sigma(F2)) = 3985$, GOF = 1.467, $R_{all} = 2.68\%$, no. of reflections = 4619.

[27] Ardon, M.; Bino, A. *Struct. Bonding* **1987**, *65*, 1.

[28] Eldik, R. V.; Roodt, A.; Leipoldt, J. G. *Inorg. Chim. Acta* **1987**, *129*, L41.

[29] Galsbol, F.; Larsen, S.; Rasmussen, B.; Springborg, J. *Inorg. Chem.* **1986**, *25*, 290.