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Nitrous Oxide Mediated Oxygen Atom Insertion into a Ruthenium−Hydride Bond. Synthesis and Reactivity of the Monomeric Hydroxoruthenium Complex $(DMPE)_2Ru(H)(OH)$

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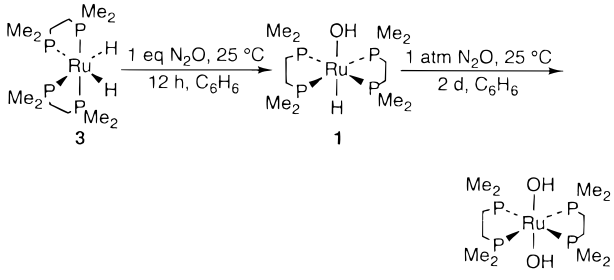
*Summary: Treatment of $(DMPE)_2Ru(H)_2$ with 1 equiv of N_2O affords the hydroxoruthenium complex $(DMPE)_2Ru(H)(OH)$ (**1**) in 41% yield; further treatment with an atmosphere of N_2O affords the bis(hydroxo) complex $(DMPE)_2Ru(OH)_2$ (**4**) in 17% yield. The addition of protic reagents to **1** results in the replacement of the OH group with several other ligands, including aryloxo, thiolato, siloxo, C-bound enolate, acetylide, and triphenylstannyl; more deep-seated changes take place when **1** reacts with p-tolualdehyde and hexafluoroacetone.*

We wish to report the first observation of oxygen atom transfer from N_2O into a late transition metal−hydrogen bond and the chemistry of the hydroxohydridoruthenium complex produced in this reaction.

Many catalytic processes involve intermediates that are proposed to contain late transition metal−heteroatom (N, O, S) bonds.[1−3] Recent work has been directed toward the synthesis of these potentially reactive species, but there remain few examples of monomeric late metal hydroxide complexes,[3−18] species which are thought to be important in the hydration of olefins to alcohols, the hydration of nitriles to carboxamides, and the Wacker process.[3,19−22]

We recently reported the preparation and characterization of the monomeric hydroxoruthenium complex $(DMPE)_2Ru(H)(OH)$ (**1**) *via* the oxidative addition of water to the Ru(0) complex $(DMPE)_2Ru(C_2H_4)$ (**2**) and subsequent H_2O removal with 4 Å molecular sieves. Elevated temperatures and extended reaction times were necessary to effect this reaction,[23] so the possible use of N_2O to directly transfer an oxygen atom into a ruthenium hydride bond seemed like an attractive alternative. Hillhouse and co-workers have found that N_2O can be used to insert oxygen atoms into nickel−carbon and the relatively oxophilic (group 4) early metal−hydrogen bonds, but to our knowledge oxygenation of late metal−hydrogen bonds has not been observed.[24−28]

We have now found that N_2O may be used to mediate oxygen atom insertion into the Ru−H bond of $(DMPE)_2Ru(H)_2$[29] (**3**). Treatment of the dihydride with 1 equivalent of N_2O affords the hydroxoruthenium complex **1** in 41% yield after crystallization.[30] Treatment of either dihydride **3** or the isolated monoinsertion product **1** with an atmosphere of N_2O affords the bis(hydroxo) complex $(DMPE)_2Ru(OH)_2$ (**4**), which can be obtained 95% pure in 17% yield (eq 1).[31]



3 **1** **4** (1)

We have also studied the exchange chemistry of **1** and have demonstrated that a number of complexes containing ruthenium−heteroatom bonds are accessible by treatment with protic reagents at room temperature. Addition of phenols, thiols, and silanols to **1** yield the

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(29) An improved preparative method for **3** has been used which involves Na reduction of $(DMPE)_2RuCl_2$ in the presence of an atmosphere of H_2. This affords **3** in >95% yield. We thank Prof. L. Field for this suggestion.

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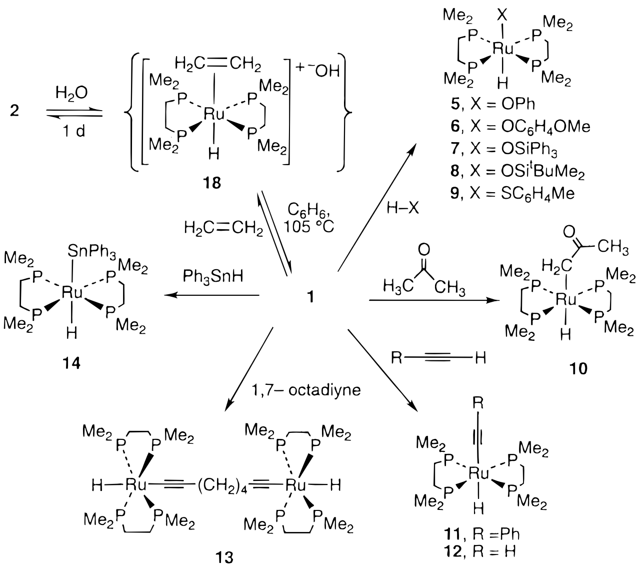
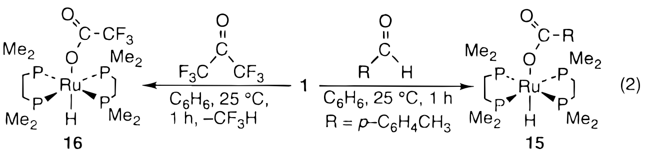
Scheme 1



corresponding (aryloxo)-,[32] (thiolato)-,[33] and siloxoruthenium complexes **5**–**9** in 25–40% yield (Scheme 1).[34] Complex **1** is also reactive toward molecules containing acidic C–H bonds. The treatment of **1** with acetone affords the C-bound enolate complex **10**[35] in 34% yield.[34] Terminal alkynes react with **1** to give the ruthenium acetylide complexes **11**[36] and **12** in *ca.* 30% yield.[34] Interestingly, reactivity can be affected at both ends of 1,7-octadiyne to give the bimetallic complex **13** (68% yield). The reactivity of the hydroxoruthenium complexes **1** and **4** toward the C–H bonds of conjugated alkynes could provide a convenient, controlled route into extended conjugated organometallic systems.[37–43]

While the aforementioned reactions may be thought of as proceeding by protonation of the hydroxide moiety, this is not the only mode of reactivity available to the hydroxoruthenium complex **1**. The addition of Ph_3SnH, which does not contain an acidic hydrogen, to **1** affords the stannyl hydride complex **14** in 86% yield (Scheme 1). Both Sn–P and Sn–H coupling are observed by NMR spectroscopy.[44]

An interesting reaction is observed when **1** is treated with 1 equiv of *p*-tolualdehyde (eq 2). The hydroxide



oxygen is retained, the aldehydic C–H bond is broken, and the ruthenium carboxylate complex **15** is obtained in 28% yield.[34] The structural assignment of **15** was confirmed by X-ray crystallography; an ORTEP diagram

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(30) An 800-mL thick-walled glass vessel fused to a vacuum stopcock was charged with a stir bar and a colorless solution of $(DMPE)_2Ru(H)_2$ (2.30 g, 5.71 mmol) in C_6H_6 (100 mL). The bomb was degassed via three freeze–pump–thaw cycles, and N_2O (6.29 mmol) was condensed in. The solution was warmed to 25 °C and stirred for 12 h. The resulting brown solution was concentrated *in vacuo* to a dark brown residue and washed with pentane (4 × 5 mL) to remove unreacted $(DMPE)_2Ru(H)_2$. The residue was dissolved in minimal toluene (10 mL) and layered with pentane (40 mL). After 1 d at 25 °C, the tan solution was decanted from a dark brown residue and the solution was cooled to −35 °C for 2 d. The tan crystals obtained were washed with pentane (3 × 1 mL) and dried *in vacuo* to afford 980 mg (41% yield) of **1**. Characterization data for **1** are identical with the literature values given in ref 23.

(31) The synthesis of **4** differs from the synthesis of **1** in that 1 atm of N_2O was used and the solution was stirred for 2 d. Analytically pure material was not obtained after repeated recrystallizations.

(32) Conditions for the synthesis and isolation of **5** listed below are general for complexes **6**, **7**, **8**, **9**, **14**, and **15**. To a solution of $(DMPE)_2Ru(OH)(H)$ (**1**) (89.3 mg, 0.10 mmol) in C_6H_6 (10 mL) was added phenol (20.9 mg, 0.11 mmol). After 1 h at 25 °C, the solution was concentrated to a beige powder, which was dissolved in toluene for crystallization by slow pentane vapor diffusion into the solution. Recrystallization afforded 24.8 mg (25% yield) of **5** as white crystals. ^1H NMR (C_6D_6): δ 7.35 (t, J_{HH} = 7.8 Hz, 2 H, *m*-OC_6H_5), 6.62 (t, J_{HH} = 6.8 Hz, 1 H, *p*-OC_6H_5), 6.43 (d, J_{HH} = 7.6 Hz, 2 H, *o*-OC_6H_5), 1.65 (m, 4 H, P–CH_2), 1.30 (s, 12 H, P–CH_3), 1.23 (m, 4 H, P–CH_2), 1.09 (s, 12 H, P–CH_3), −23.3 (qn, J_{HP} = 21.8 Hz, 1 H, Ru–*H*). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 45.4 (s). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 174.0 (C), 129.1 (CH), 120.5 (CH), 109.5 (CH), 31.3 (qn, J_{CP} = 12.3 Hz, CH_2), 22.9 (m, PCH_3), 15.5 (qn, J_{CP} = 5.4 Hz, PCH_3). IR (KBr): 3058 (w), 2958 (w), 2897 (m), 1928 (m), 1589 (m, br), 1562 (w, br), 1489 (m), 1479 (m, br), 1421 (w, br), 1290 (m, br), 1279 (m, br), 1164 (w, br), 1124 (w, br), 1101 (w, br), 1072 (w, br), 1020 (w, br), 989 (w, br), 935 (s, br), 910 (m, br), 889 (m), 841 (m), 795 (w), 760 (w), 727 (m), 698 (m), 644 (m), 523 (w), 459 (w) cm^{-1}. MS-EI: *m/z* = 496 [M^+]. HRMS (EI) (*m/z*): Calcd for $C_{18}H_{38}OP_4Ru$, 496.0917; obsd, 496.0924. Anal. Calcd for $C_{18}H_{38}OP_4Ru$: C, 43.64; H, 7.73. Found: C, 43.99; H, 8.22.

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(34) Yields refer to doubly recrystallized material and do not reflect percent conversions to spectroscopically pure material which are >90%.

(35) Conditions for the synthesis and isolation of **10** given in this footnote are applicable for the synthesis of **16**. A 50-mL thick-walled glass vessel fused to a vacuum stopcock was charged with a stir bar and a solution of $(DMPE)_2Ru(H)(OH)$ (104 mg, 0.25 mmol) in C_6H_6 (10 mL). The bomb was degassed via three freeze–pump–thaw cycles, and acetone (0.27 mmol) was condensed in. The solution was warmed to 25 °C and stirred for 1 h. Volatile materials were removed *in vacuo* to afford 108 mg (95% yield) of **10** as a tan powder which was pure by NMR spectroscopy. The product was washed with pentane (3 × 3 mL) and then dissolved in toluene for crystallization by slow pentane vapor diffusion into the solution. Recrystallization afforded 39 mg (34% yield) of **10** as tan crystals. ^1H NMR (C_6D_6): δ 2.13 (s, 3 H, C(O)CH_3), 1.57 (m, 6 H, Ru–CH_2 and P–CH_2), 1.38 (s, 12 H, P–CH_3), 1.21 (m, 4 H, P–CH_2), 1.14 (s, 12 H, P–CH_3), −16.67 (qn, J_{HP} = 22.2 Hz, 1 H, Ru–*H*); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 43.0 (s). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 210.7 (C), 31.0 (qn, J_{CP} = 13.7 Hz, *p*-CH_2), 30.6 (COCH_3), 25.7 (qn, J_{CP} = 7.6 Hz, *p*-CH_3), 18.0 (qn, J_{CP} = 4.2 Hz, Ru–CH_2), 15.2 (qn, J_{CP} = 5.0 Hz, *p*-CH_3). IR (KBr): 2958 (m), 2922 (m), 2897 (s), 1928 (s), 1713 (w), 1475 (m), 1444 (m), 1419 (s), 1365 (m), 1288 (w), 1279 (m), 1232 (w), 1074 (w), 991 (w), 935 (s), 889 (s), 862 (w), 840 (m), 795 (w), 727 (s), 702 (s), 683 (w), 644 (m), 459 (w) cm^{-1}. MS-EI: *m/z* = 459 [(M)$^+$]. Anal. Calcd for $C_{15}H_{38}OP_4Ru$: C, 39.21; H, 8.34. Found: C, 39.20; H, 8.32.

(36) Conditions for the synthesis and isolation of **11** given in this footnote are applicable for the synthesis of **13**. Complex **12** was synthesized by passing acetylene gas through a solution of **1** in benzene for 25 min. Complex **12** was isolated similarly to **11**. To a solution of $(DMPE)_2Ru(OH)(H)$ (**1**) (98 mg, 0.23 mmol) in C_6H_6 (5 mL) was added dropwise a solution of phenylacetylene (26 mg, 0.26 mmol) in C_6H_6 (5 mL). The tan solution turned peach after 0.5 h at 25 °C. Lyophilization of the reaction solution, followed by dissolution in pentane, filtration through Celite, and concentration *in vacuo* afforded 88 mg (74% yield) of **11** as an orange solid which was pure by NMR spectroscopy. Analytically pure yellow needles of **11** (33 mg, 28% yield) were obtained by two successive recrystallizations from pentane at −70 °C. ^1H NMR (C_6D_6): δ 7.47 (d, J_{HH} = 6.9 Hz, 2 H, *o*-C_6H_5), 7.18 (s, 2 H, *m*-C_6H_5), 6.95 (t, J_{HH} = 7.4 Hz, 1 H, *p*-C_6H_5), 1.50 (s, 12 H, P–CH_3), 1.51 (m, 4 H, P–CH_2), 1.29 (m, 4 H, P–CH_2), 1.24 (s, 12 H, P–CH_3), −11.95 (qn, J_{HP} = 20.0 Hz, 1 H, Ru–*H*). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 45.5 (s). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 133.5 (m, Ru–C), 132.5 (Ru–C*C*), 130.5 (CH), 127.9 (CH), 122.0 (CH), 109.3 (*ipso*-C), 31.6 (qn, J_{CP} = 14.1 Hz, *p*-CH_2), 23.7 (qn, J_{CP} = 7.0 Hz, *p*-CH_3), 17.1 (qn, J_{CP} = 7.0 Hz, *p*-CH_3). IR (KBr): 3064 (w), 2960 (w), 2926 (w), 2899 (m), 2058 (s), 1759 (w), 1632 (w), 1591 (m), 1479 (w), 1417 (m), 1290 (w), 1277 (w), 935 (s), 926 (s), 889 (m), 841 (w), 795 (w), 748 (m), 725 (m), 702 (m), 646 (m), 461 (w) cm^{-1}. MS-EI: *m/z* = 503 [(M − 1)$^+$]. Anal. Calcd for $C_{20}H_{38}P_4Ru$: C, 47.71; H, 7.61. Found: C, 47.50; H, 7.67.

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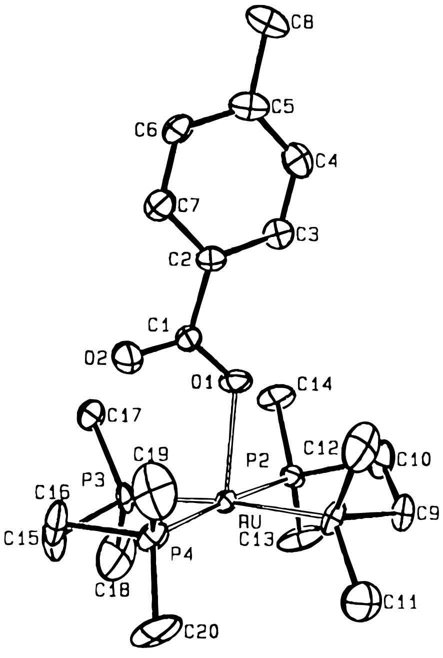
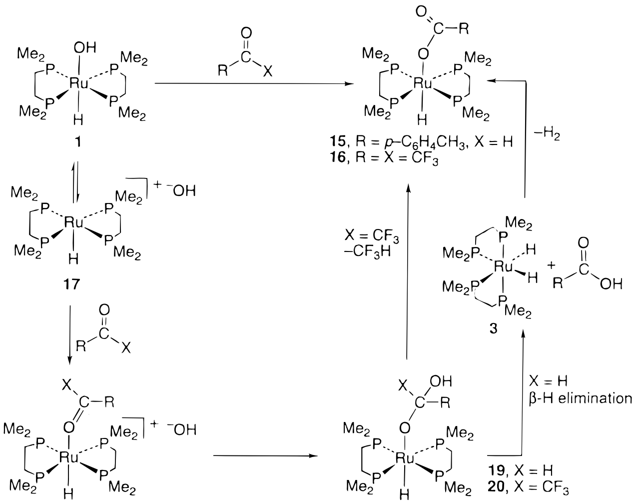


Figure 1. ORTEP diagram of $(DMPE)_2Ru(H)(OC(O)C_6H_4\text{-}Me)$ (**15**).

Scheme 2



of the complex is shown in Figure 1.[45] The structure reveals that there is no apparent interaction between the carbonyl oxygen and the ruthenium center in the solid state. We have found independently that **3** and *p*-toluic acid react to generate complex **15** with loss of dihydrogen (Scheme 2). Similar reactivity is observed when **1** is treated with hexafluoroacetone to afford **16** in 39% yield (eq 2).[34] In this case, the C−C bond is broken and the release of trifluoromethane is observed by NMR spectroscopy.

Much of the observed reactivity of **1** can be rationalized using the assumption that the first step involves reversible formation of a metal cation/OH^- ion pair (**17**). This is most easily applied to the reaction of **1** with weak protic acids H−X, perhaps including alkynes and acetone. In the reaction of triphenyltin hydride, we suggest that the Sn−H bond adds to the cationic ruthenium center and then hydroxide removes a proton from Ru to arrive at the observed product **14**.

Assuming the hydroxide ligand is labile, it should be possible to trap the resulting $[(DMPE)_2Ru(H)]^+$ cation **17**. When the hydroxoruthenium complex **1** is exposed to an atmosphere of ethylene in benzene at 105 °C for 1 d, the ruthenium ethylene complex **2** is formed (Scheme 1). There is strong evidence that the reverse reaction (treatment of **2** with an excess of water at elevated temperatures to form the hydroxoruthenium complex **1**) proceeds *via* a cationic hydridoruthenium ethylene complex **18** which loses ethylene and forms **2** by anion addition.[33] We believe that we are observing the microscopic reverse of this process: dissociation of hydroxide, coordination of ethylene, and deprotonation of the metal center to afford the observed product **2**.

Initial ion pair formation can also be used to rationalize the apparent oxidations of *p*-tolualdehyde and hexafluoroacetone to the corresponding carboxylate complexes. O-coordination of the aldehyde to the ruthenium center and subsequent hydroxide attack at the carbonyl carbon would form metallaacetal species **19** (Scheme 2). This species is likely to be unstable with respect to β-elimination, leading to the dihydride complex **3** and the carboxylic acid, which quickly react to give **15** (*vide supra*). Hexafluoroacetone leads to intermediate **20** which undergoes C−C cleavage followed by proton transfer to give **16**.

In summary, we have demonstrated that N_2O is capable of mediating oxygen atom insertion into a late metal−hydrogen bond to afford hydroxoruthenium complexes **1** and **4**. Additional complexes containing ruthenium−heteroatom bonds may be prepared *via* exchange reactions with **1**. Complex **1** has been shown to activate C−H, Sn−H, and C−C bonds under mild conditions, partially due to the lability of the hydroxide ligand. Further reactivity and mechanistic studies of the hydroxoruthenium complex **1** and its derivatives, as well as the bis(hydroxo)ruthenium complex **4**, are underway.

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Supporting Information Available: Text describing spectroscopic and analytical data for complexes **4**−**8** and **10**−**16**, tables of structural data for **15**, and NMR spectra for complexes **4**, **7**, **13**, and **14** (22 pages). Ordering information is given on any current masthead page.

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(44) $^2J_{PSn} = 174.6$ Hz; $^2J_{HSn} = 216.1$ Hz.

(45) Perutz and co-worker(s) have recently solved the X-ray structure for the related complex $(DMPE)_2Ru(H)(OCOH)$: *Organometallics* **1996**, *15*, 5166.