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Aerobic alcohol oxidation catalyzed by a new, oxygen-bridged heterometallic compound [PPh_4][Ru(N)Me_2(μ_2-O)$_2$Pd((−)-sparteine)]

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Abstract

The reaction between the new hydroxy compound [PPh_4][Ru(N)$(OH)_2Me_2$] and Pd$(OSiMe_3)_2$((−)-sparteine) produces $(Me_3Si)_2O$, H_2O and a new heterobimetallic compound [PPh_4][Ru(N)Me_2(μ_2-O)$_2$Pd((−)-sparteine)] in good yield. The Ru/Pd bimetallic compound catalyzes the oxidation of aryl and allyl alcohols to the corresponding carbonyl compound in air and the rearrangement of allylic alcohols unsaturated aldehydes. It also oxidizes PPh_3 to O–PPh_3 under O_2.

Keywords: Oxidation catalysis; Molecular oxygen; Aerobic oxidation; Heterobimetallic complex; Alcohol

1. Introduction

Because of cooperativity between the metal centers, compounds containing more than one type of metal center have the potential to be superior to monometallic catalysts. This may be especially important for aerobic oxidation catalysts where different metals could selectively coordinate O_2 and the organic substrate. Several enzymes for oxidation reactions demonstrate this with active sites that contain and use multiple metal centers [1], and binuclear compound of iron and copper can model the oxidation reactions of enzymes [2]. The interaction between metal centers can also impede catalysis at a single metal center as it does in the oxidation of styrene with O_2 by *trans*-[IrCl(CO)(L-M′)$_2$] [3]. Most synthetic heterometallic inorganic or organometallic compounds are poor catalysts for oxidation and other reactions because they are either coordinatively saturated and lack a site for substrate binding, or because they are not robust to the reaction conditions.

There is a need for general methods for the preparation of reactive heterometallic compounds from a range of metal precursors. We have previously prepared heterobimetallic and heterotrimetallic with bridging oxo or sulfido groups through specific bridge-building reactions such as the reaction of organoosmium(VI) and organoruthenium(VI) chloro compounds [N(*n*-Bu)$_4$][M(N)R_2Cl_2] with Ag_2CrO_4 [4], $AgReO_4$ [5], or K_2WS_4 [6]. The ruthenium compounds [N(*n*-Bu)$_4$][Ru(N)Me_2Cl_2] also react with (trimethylsilyl)sulfido compounds M′$(SSiMe_3)_2L_2$ (M′ = Ni, Pd, Pt; L_2 = dppe, COD) to form the trimetallic species {Ru(N)Me_2}(μ_3-S)$_3${M′L_2} [7,8]. These compounds contain coordinately unsaturated metals and some of them are active for the aerobic oxidation of alcohols.

Although {Ru(N)Me_2}(μ_3-S)$_3${Pd(dppe)} catalyzes the oxidation of alcohols with O_2, the compound is not stable under reaction conditions due to the oxidation of the bridging sulfido groups. In this paper, we report the synthesis of a new, oxo-bridged Ru(VI)–Pd(II) compound that does not contain sensitive sulfido or organophosphine ligands.

2. Experimental

All reactions were conducted under an N_2 atmosphere using standard air-sensitive techniques in a Vacuum Atmospheres drybox unless otherwise stated. NMR spectra were recorded on Varian Unity-500 and Varian Unity-400 FT

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NMR spectrometers at ambient temperature. IR spectra were recorded on a Perkin–Elmer 1600 series FTIR. UV–visible spectra were recorded on a Hewlett–Packard 8452A spectrometer. Elemental analyses were performed by the University of Illinois microanalytical service. Toluene, diethyl ether and hexane were distilled from Na/benzophenone under N_2. Dichloromethane was distilled from CaH_2 under N_2. Acetonitrile was distilled first from P_2O_5, then from CaH_2 under N_2. Sodium trimethylsilanolate and pyridinium hydrochloride were sublimed under vacuum at 210 °C in a temperature controlled oil bath. Sodium hydroxide was dried under vacuum at 210 °C for 4 days. HPLC-grade acetonitrile was obtained from Fisher Scientific. The compounds $[N(n\text{-}Bu_4)][Ru(N)Cl_2Me_2]$, $[PPh_4][Ru(N)Cl_2Me_2]$ [9], and $PdCl_2$(−)-sparteine [10], were prepared according to literature procedure.

2.1. Preparation of $Pd(OSiMe_3)_2$ ((−)-sparteine) (2)

To a solution of $NaOSiMe_3$ (0.21 g, 1.89 mmol) in 4 mL of diethyl ether at −30 °C was added $PdCl_2$((−)-sparteine) (0.194 g, 0.472 mmol). The suspension was stirred as the reaction was warmed to room temperature. After 1 h, the mixture was filtered and solvent was removed from the filtrate under vacuum. The resulting orange solid was crystallized from ether/hexane at −30 °C. Yield = 0.170 g (0.287 mmol, 67.3%). ^{1}H NMR (500 MHz, d_6-benzene) δ 4.03–0.71 (m, 26H, (−)-sparteine), 0.66 (s, 9H, OSi(CH_3)$_3$), 0.64 (s, 9H, OSi(CH_3)$_3$). $^{13}C\{^1H\}$ NMR (125.7 MHz, d_6-benzene) δ 69.0 ((−)sparteine-C6), 64.0 ((−)sparteine-C11), 62.0 ((−)sparteine-C10), 58.2 ((−)sparteine-C2), 57.7 ((−)sparteine-C15), 48.5 ((−)sparteine-C17), 34.7 ((−)sparteine-C7), 34.3 ((−)sparteine-C9), 30.1 ((−)sparteine-C5), 27.4 ((−)sparteine-C8), 26.0 ((−)sparteine-C14), 24.5 ((−)sparteine-C3), 24.2 ((−)sparteine-C4), 23.2 ((−)sparteine-C12), 19.2 ((−)sparteine-C13), 5.7 (OSi(CH_3)$_{3(A)}$), 5.6 (OSi(CH_3)$_{3(B)}$). IR (KBr pellet; cm^{-1}) 2942, 2885 (νC–H), 1474, 1458, 1438, 1253, 1239, 994, 939, 822, 736, 660, 619. UV–visible (ε): 248 nm (3 655), 294 (728), 358 (845). Anal. Calc. for $C_{21}H_{44}N_2O_2PdSi_2$: C, 48.58; H, 8.54; N, 5.40. Found: C, 48.64; H, 8.90; N, 5.51.

2.2. Preparation of $[PPh_4][Ru(N)(OH)_2Me_2]$ (4)

To a solution of $[PPh_4][Ru(N)Cl_2Me_2]$ (0.168 g, 0.293 mmol) in 10 mL of diethyl ether was added excess NaOH (0.150 g, 3.751 mmol) and the orange suspension was stirred for 5 h. White solid precipitated from the yellow solution and this was separated by filtration. Solvent was removed from the filtrate under vacuum to yield a yellow solid. Yield = 0.101 g, 66.4%. ^{1}H NMR (500 MHz, C_6D_6) δ 7.67-6.99 (m, 20H, P(C_6H_5)$_4$), 1.64 (s, 2H, Ru(OH)$_2$), 1.52 (s, 6H, Ru(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (125.7 MHz, D_8-toluene) δ 132.4 (s, PC_6H_5), 128.8 (s, PC_6H_5), 127.9 (s, PC_6H_5), 127.3 (s, PC_6H_5), 127.2 (s, PC_6H_5), 126.8 (d, PC_6H_5), −0.1 (s, Ru(CH_3)$_2$). ^{31}P NMR (500 MHz, C_6D_6) δ 26.5 (s, $P(C_6H_5)_4$). IR (KBr pellet cm^{-1}) 3607 (s, νO–H), 3421 (wb, νO–H), 3055 (w, ν-arC–H), 2968 (w, νC–H), 2882 (w, νC–H), 1590 (w, νC=C) 1483 (s, νC=C), 1437 (s, νC=C), 1193 (s, δipO–H), 1119 (s, δipC–H), 1096 (s, νRu≡N), 882 (w), 721 (s, δoopC–H), 694 (s, δoopC–H), 539 (s). UV–visible (ε): 212 nm (37 945), 252 nm (70 491), 286 nm (350 727), 378 nm (46 104). Anal. Calc. for $C_{26}H_{28}NO_2PRu11/2NaOH$: C, 53.98; H, 5.14; N, 2.42. Found: C, 53.47; H, 4.43; N, 2.54.

2.3. Preparation of $[PPh_4][Ru(N)Me_2(\mu_2\text{-}O)_2Pd((-)\text{-sparteine})]$ (5)

A solution of $[PPh_4][Ru(N)(OH)_2Me_2]$ (0.022 g, 0.042 mmol) in 2 mL of diethyl ether at −30 °C was added dropwise to a solution of $Pd(OSiMe_3)$((−)-sparteine) (0.022 g, 0.042 mmol) that was also cooled to −30 °C. The reaction mixture was stirred for 1 h at room temperature, then filtered, and the solvent was removed from the filtrate under vacuum. The residue was crystallized from CH_2Cl_2/ether. Yield = 0.033 g (91.7%) red crystals. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74–6.93 (m, 20H, P(C_6H_5)$_4$), 3.11–0.52 (m, 26H, (−)-sparteine), 1.62 (s, 3H, RuCH_3), 1.57 (s, 3H, RuCH_3). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ 132.4 (P(C_6H_5)$_4$), 132.3 (P(C_6H_5)$_4$), 132.1 (P(C_6H_5)$_4$), 128.8 (P(C_6H_5)$_4$), 66.8 ((−)sparteine-C6), 64.7 ((−)sparteine-C11), 62.2 ((−)sparteine-C10), 56.5 ((−)sparteine-C2), 55.6 ((−)sparteine-C15), 53.8 ((−)sparteine-C17), 34.9 ((−)sparteine-C7), 32.1 ((−)sparteine-C9), 29.5 ((−)sparteine-C5), 26.2 ((−)sparteine-C8), 26.1 ((−)sparteine-C14), 25.1 ((−)sparteine-C3), 25.0 ((−)sparteine-C4), 24.9 ((−)sparteine-C12), 22.8 ((−)sparteine-C13), 2.0 (RuCH_3), 1.8 (RuCH_3). ^{31}P NMR (500 MHz, $CDCl_3$) δ 29.4. IR (KBr pellet; cm^{-1}) 3056 (w, ν-arC–H), 2940 (s, νC–H), 2885 (s, νC–H), 1438 (s, νC=C), 1239, 1197, 1119 (s), 1070 (m, νRu≡N), 1011, 932, 824, 721 (s, δoopC–H), 695 (s, δoopC–H), 541. UV–visible (ε) 266 nm (8 442), 372 nm (1 947): Calcd for $C_{41}H_{52}N_3O_2PPdRu$: C, 57.44; H, 6.11; N, 4.70. Found: C, 57.02; H, 6.39; N, 4.04. ESI-MS (CH_3CN): m/z 860.2 (M^++3H).

2.4. Mass spectrometry

A few crystals of **5** were dissolved in HPLC-grade acetonitrile and directly infused into an LCQ Deca electrospray ionization-ion trap-mass spectrometer at 3 μL/min. The concentration of the solution was estimated to be ~100 μM. In order to obtain the optimal signal, the parent mass was subjected to an automatic lens optimization using the AutoTune feature of the Xcalibur software. A capillary voltage of 3.0 V, a tube lens offset of −60.0 V, a second octopole offset of −14.5 V, a first octopole offset of −2.75 V, an inter-octopole lens setting of −74.0 V and an entrance lens setting of −76.0 V were found to be optimal. Sheath and auxiliary gas flow rates of 60 and 30 units, respectively, were utilized. Lastly, a spray voltage of 4.3 kV and a capillary temperature of 180 °C were used.

A ZoomScan, high resolution profile experiment was performed, averaging 31 scans for the data presented. Simulated spectra of input elemental formulas were created using the Isotope Viewer feature of the Xcalibur software. Collisionally-induced dissociation (CID) at 35% collisional energy and a 3.0 *m/z* isolation width was performed. Comparison of the observed fragments in the CID spectrum to the full mass spectrum showed that in-source fragmentation was minimal.

2.5. Reaction of **5** and O_2 with benzyl alcohol

A sample of **5** (0.011 g, 0.013 mmol) was placed in an NMR tube along with 1 mL of $CDCl_3$ and capped with a septum. Benzyl alcohol (1.3 μL, 0.013 mmol) was added and a ^{1}H NMR spectrum was acquired. The NMR tube was purged with O_2 for 5 min, then heated at 60 °C for 24 h in a temperature regulated oil bath. A second ^{1}H NMR spectrum was acquired. ^{1}H NMR (500 MHz, $CDCl_3$), 0 h: δ 10.02 (s, 0.01H, C_6H_5CHO) 7.68–7.64 (m, 8H, $P(C_6H_5)_4$), 7.56–7.53 (m, 4H, $C_6H_5CH_2OH$), 7.48–7.44 (m, 8H, $P(C_6H_5)_4$), 7.37–7.36 (m, 6H, $P(C_6H_5)_4$), 7.29 (s, 1H, $C_6H_5CH_2OH$), 4.70 (s, 2H, $C_6H_5CH_2OH$) 4.50–1.23 (m, 32H, (−)-sparteine and $Ru(N)(CH_3)_2$), 24 h: ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.03 (s, 0.62H, C_6H_5CHO) 8.09–7.28 (m, 21.8H, $P(C_6H_5)_4$, $C_6H_5CH_2OH$ and $C_6H_5CH_2OH$), 4.70 (s, 1H, $C_6H_5CH_2OH$) 4.52–1.00 (m, 32H, (−)-sparteine and $Ru(N)(CH_3)_2$) 1.20 (s, 1H, H_2O).

2.6. Reaction of **5** and O_2 with triphenylphosphine

A sample of **5** (0.008 g, 0.009 mmol) was added to an NMR tube along with 1 mL of $CDCl_3$ and PPh_3 (0.002 g, 0.009 mmol). The tube was capped under N_2 and a ^{31}P NMR spectrum was acquired. The NMR tube was purged with O_2 for 5 min, then heated at 60 °C for 24 h in a temperature regulated oil bath. A second ^{31}P NMR spectrum was acquired. ^{31}P NMR (500 MHz, $CDCl_3$), 0 h: δ 29.4 (s, $P(C_6H_5)_4$), −5.4 (s, PPh_3), 24 h: ^{31}P NMR (500 MHz, $CDCl_3$) δ 29.5 (s, $P(C_6H_5)_4$), 23.5 (s, $O{=}PPh_3$), 17.2 (s, $Ru{-}PPh_3$).

2.7. Reaction of **5** and O_2 with allyl alcohol

A sample of **5** (0.009 g, 0.010 mmol) was added to an NMR tube along with 1 mL of $CDCl_3$. The tube was capped a septum under N_2. Allyl alcohol (0.7 μL, 0.010 mmol) was added via syringe and a ^{1}H NMR spectrum was acquired. The NMR tube was purged with O_2 for 5 min, then heated at 60 °C for 24 h in a temperature regulated oil bath. A second ^{1}H NMR spectrum was acquired. ^{1}H NMR (500 MHz, $CDCl_3$), 0 h: δ 7.72–6.94 (m, 20H, $P(C_6H_5)_4$), 5.80 (m, 1H, $CH_2{=}CH{-}CH_2OH$), 5.17 (dd (J_{HH} = 17.2, 1.8 Hz), 1H, $CH_2{=}CH{-}CH_2OH$), 4.93 (dd, J_{HH} = 10.5, 1.8 Hz, 1H, $CH_2{=}CH{-}CH_2OH$) 3.86 (d, J_{HH} = 4.9 Hz, 2H, $CH_2{=}CH{-}CH_2OH$), 3.56–0.56 (m, 32H, (−)-sparteine and $Ru(N)(CH_3)_2$), 0.28 (s, 1H, $CH_2{=}CH{-}CH_2OH$), 24 h: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.80 (t (J_{HH} = 1.4 Hz) 0.10H, CH_2CH_2CHO) 9.58 (d (J_{HH} = 7.4 Hz), 0.05H, $CH_2{=}CH{-}CHO$), 8.00–7.28 (m, 20H, $P(C_6H_5)_4$), 6.00 (m, 0.68H, $CH_2{=}CH{-}CH_2OH$), 5.30 (dd, J_{HH} = 10.5, 1.8 Hz, 0.78H, $CH_2{=}CH{-}CH_2OH$) 5.30 (dd, J_{HH} = 10.5, 1.8 Hz, 0.71H, $CH_2{=}CH{-}CH_2OH$), 4.15 (d, J_{HH} = 4.9 Hz, 2H, $CH_2{=}CH{-}CH_2OH$), 3.56–0.56 (m, 32H, (−)-sparteine and $Ru(N)(CH_3)_2$), 0.28 (s, 1H, $CH_2{=}CH{-}CH_2OH$).

2.8. Reaction of **5** with allyl alcohol

A sample of **5** (0.010 g, 0.012 mmol) was added to an NMR tube along with 1 mL of $CDCl_3$ and the tube was capped with a septum. Allyl alcohol (0.9 μL, 0.012 mmol) was added by syringe and a ^{1}H NMR spectrum was acquired. The NMR tube was heated at 60 °C for 24 h in a temperature regulated oil bath. A second ^{1}H NMR spectrum was acquired. ^{1}H NMR (500 MHz, $CDCl_3$), 0 h: δ 7.79–6.93 (m, 20H, $P(C_6H_5)_4$), 5.78 (m, 1H, $CH_2{=}CH{-}CH_2OH$), 5.19 (dd (J_{HH} = 17.0, 1.9 Hz), 1H, $CH_2{=}CH{-}CH_2OH$), 4.93 (dd, J_{HH} = 10.6, 1.9 Hz, 1H, $CH_2{=}CH{-}CH_2OH$) 3.86 (d, J_{HH} = 4.9 Hz, 2H, $CH_2{=}CH{-}CH_2OH$), 3.56–0.56 (m, 32H, (−)-sparteine and $Ru(N)(CH_3)_2$), 0.28 (s, 1H, $CH_2{=}CH{-}CH_2OH$), 24 h: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.80 (t (J_{HH} = 1.4 Hz) 0.12H, CH_2CH_2CHO) 9.58 (d (J_{HH} = 7.5 Hz), 0.04H, $CH_2{=}CH{-}CHO$), 7.91–7.33 (m, 20H, $P(C_6H_5)_4$), 6.00 (m, 0.68H, $CH_2{=}CH{-}CH_2OH$), 5.30 (dd, J_{HH} = 10.4, 1.8 Hz, 0.78H, $CH_2{=}CH{-}CH_2OH$) 5.30 (dd J_{HH} = 10.4, 1.8 Hz, 0.71H, $CH_2{=}CH{-}CH_2OH$), 4.15 (d, J_{HH} = 4.9 Hz, 2H, $CH_2{=}CH{-}CH_2OH$), 0.28 (s, 0.60H, $CH_2{=}CH{-}CH_2OH$).

2.9. Oxidation of alcohols, Method 1

In the dry box, a sample of **5** (60 mg. 0.070 mmol) was dissolved in 50 mL of C_6D_6 (1.4×10^{-3} M). The solution was removed from the drybox and anisole (138 μL, 0.350 mmol, 50 equiv) was added as an internal standard. Next, a reaction tube was equipped with a stir bar and cap, then charged with 50 equiv of substrate (see Table 1). A 1 mL aliquot of the solution of **5** was placed in the reaction tube and a ^{1}H NMR spectrum was acquired. The reaction mixture was heated to 60 °C with stirring for 24 h, then cooled to room temperature. Another ^{1}H NMR spectrum was acquired. Results were calculated by comparison of the integrated values for peaks resulting from starting materials and products to the integrated values of peaks resulting from the internal standard, anisole.

2.10. Oxidation of alcohol and alkene substrates in solution, Method 2

A sample of **5** (0.007 g, 8×10^{-3} mmol) was dissolved in 25 mL chlorobenzene. An aliquot of this solution (2 mL, 6×10^{-4} mmol catalyst) were added to a mixture of benzyl

Table 1
Aerobic oxidations catalyzed by **5**, method 1

Substrate	Product	% Conversion	Turnovers	TON (h^{-1})
Benzyl alcohol	Benzaldehyde	12.7	6.4	0.26
4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	12.2	6.1	0.25
3-Methylbenzyl alcohol	3-Methylbenzaldehyde	9.1	4.5	0.19
4-Trifluoromethylbenzyl alcohol	4-Trifluoromethylbenzaldehyde	8.5	4.3	0.18
4-Methylbenzyl alcohol	4-Methylbenzaldehyde	7.9	3.9	0.16
4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	6.5	3.2	0.13
4-Nitrobenzyl alcohol	4-Nitrobenzaldehyde	4.7	2.3	0.10
Allyl alcohol	Propionaldehyde	30.0	15.0	0.63
	Acrolein	10.5	5.3	0.22
2-Octen-1-ol	2-Octenal	7.6	3.8	0.16
2-Cyclohexen-1-ol	2-Cyclohexanone	15.4	7.7	0.32
Geraniol	Geranial	6.3	3.2	0.13
Cinnamyl alcohol	Cinnamylaldehyde	6.7	3.3	0.14
1-Octen-3-ol	1-Octen-3-one	9.0	4.5	0.19
n-Decanol	*n*-Decanal	5.8	2.9	0.12
n-Heptanol	*n*-Heptanal	8.2	4.1	0.17

alcohol (50 μL, 0.48 mmol) and anisole (5 μL, 0.018 mmol) in a reaction vessel. To half of the aliquots was added 0.2 g of 3 Å molecular sieves. The reaction mixtures were heated to between 95 and 100 °C under 1 atm O_2 for 20 h, then cooled in ice. The product mixture were analyzed by gas chromatography.

3. Results

The palladium compound, $PdCl_2$((−)-sparteine) **1**, results from the addition of Na_2PdCl_4 to a stirring solution of (−)-sparteine in CH_2Cl_2 [10]. It reacts with 2 equiv of NaO-$SiMe_3$ in diethyl ether to produce $Pd(OSiMe_3)_2$((−)-sparteine), **2**, in 65–70% yield. The trimethylsiloxy compound is very soluble in most organic solvents is insoluble in hexane. It crystallizes from diethyl ether and hexane at −30 °C as dark yellow crystals.

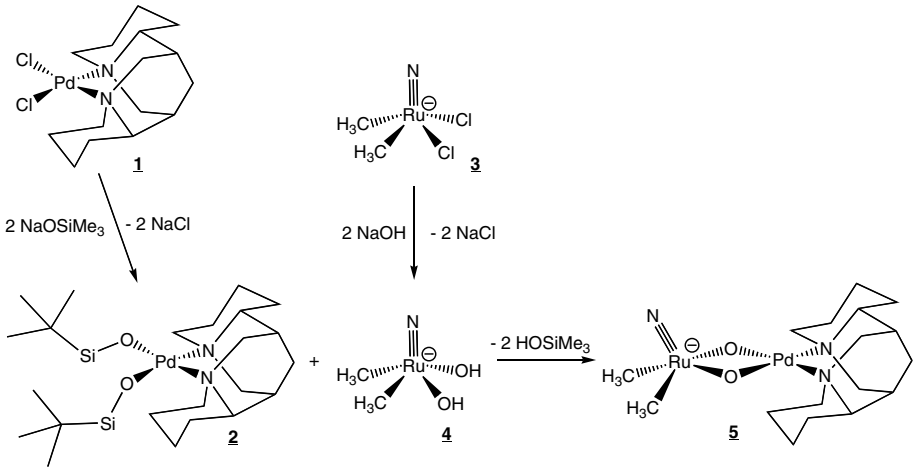
Compound **2** is sensitive to water and acids. It is diamagnetic in all solvents. The ^{13}C NMR spectrum includes 17 resonances, 15 between 69.0 ppm and 19.2 ppm for coordinated sparteine and two at 5.7 and 5.6 for the inequivalent trimethylsiloxy groups. Along with resonances for coordinated (−)sparteine in the ^1H NMR spectrum, there are resonances at 0.66 and 0.64 ppm for the inequivalent trimethylsiloxy groups.

The reaction of $[PPh_4][Ru(N)Cl_2Me_2]$, **3**, with excess sodium hydroxide in diethyl ether at ambient temperature produces the yellow compound $[PPh_4][Ru(N)(OH)_2Me_2]$, **4**. The reaction requires 4 h for completion. After filtering the reaction mixture to remove the NaCl, the product can be isolated as a yellow oil by concentrating the solution and adding hexane. Drying the oil under vacuum forms a glassy yellow solid. The solid contains some sodium hydroxide and analyzes as $[PPh_4][Ru(N)(OH)_2Me_2]$11/2 NaOH. The ^1H NMR spectrum of **4** contains resonances between 7.7 and 7.0 ppm that integrate to 20 protons for the PPh_4 ion as well as a broad resonance at 1.6 ppm for the hydroxyl protons and a resonance at 1.5 that integrates to six protons for the methyl groups. The ^{13}C NMR spectrum of this compound has six resonances between 133 and 128 ppm for the $[PPh_4]$ ion and a single resonance at 4 ppm for the equivalent methyl carbons. There are absorbances at 3607 and 3421 cm^{-1} corresponding to the symmetric and asymmetric O–H stretching vibrations and at 1096 cm^{-1} for the Ru≡N stretching vibration in the IR spectrum.

The reaction between **3** and **4** in a solution of THF/diethyl ether at room temperature produces Me_3SiOH, $Me_3SiOSiMe_3$, and the heterobimetallic compound $[PPh_4]$ $[Ru(N)Me_2(\mu_2\text{-}O)_2Pd((-)\text{-sparteine})]$, **5** (Scheme 1). Within 10 min, the yellow solution turns dark red. Filtering the solution and removing solvent from the filtrate gives the crude product as a red solid. The crude product crystallizes slowly crystallizes from CH_2Cl_2 and diethyl ether at −30 °C in 63% yield. It is soluble in $CDCl_3$, CH_2Cl_2, THF, benzene, CH_3CN and toluene and is insoluble in diethyl ether and hexane.

Along with fives resonances for the carbons of the $[PPh_4]^+$ ion and 15 resonances for carbons of the (−)-sparteine ligand in the ^{13}C NMR spectrum of **5**, there are two resonances for the inequivalent methyl groups at 2.0 and 1.8 ppm. Electrospray ionization-mass spectrometry of this compound (Fig. 1) shows a singly-charged molecular ion peak (+ 3H) at 860.1 *m/z* and the isotopic ratio matches with the predicted distribution (Fig. 1). There are no peaks that do not result from **5** in the mass spectrum. Infrared spectroscopy has key absorbances for the sparteine ligand C–H stretch at 2940 cm^{-1} and the ruthenium-nitrido stretch at 1119 cm^{-1}.

The Ru/Pd heterometallic compound oxidizes both benzyl alcohol and triphenylphosphine in 60 °C in the presence of O_2. We monitored the reaction of **5** and 1 equiv of benzyl alcohol in $CDCl_3$ under one atmosphere of oxygen by ^1H NMR spectroscopy. After 24 h, the benzyl alcohol had been completely converted



Scheme 1.

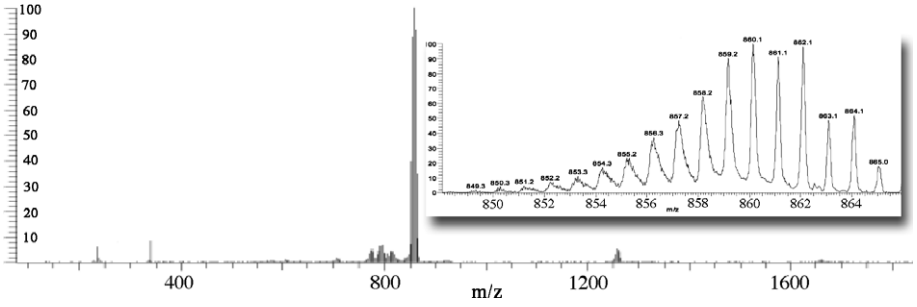


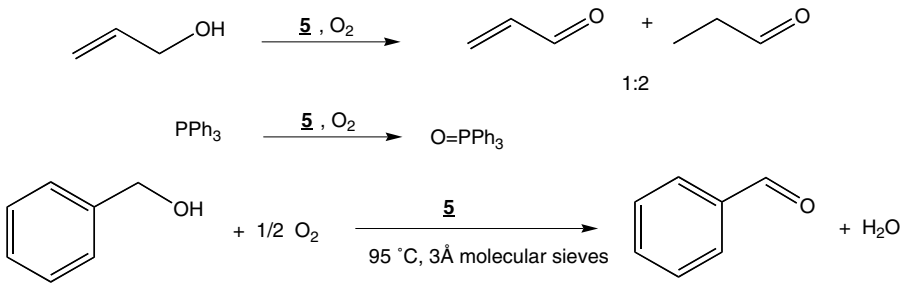
Fig. 1. Electrospray mass spectrum of **5**.

to benzaldehyde and water and the concentration of **5** was unchanged from its original concentration. Under the same reaction conditions, we monitored the conversion of PPh_3 to O–PPh_3 by **5** in O_2 by ^{31}P NMR spectroscopy. After 24 h the resonance for PPh_3 had completely disappeared and was replaced by a resonance for O–PPh_3. There was also a very small peak at 17.2 ppm in the spectrum which could correspond to a metal–phosphine compound as a byproduct in the reaction.

Interestingly, treatment of allyl alcohol with **5** and O_2 produced propionaldehyde, a rearrangement product, as well as acrolein, the oxidation product, in a ratio of 2:1 by ^1H NMR spectroscopy. In the absence of air, the bimetallic compound decomposed to an insoluble black solid in the presence of allyl alcohol.

We investigated the catalytic oxidation of aryl, allylic, and primary by O_2 in the presence of **5**. The standard reaction conditions were 24 h reaction time at 60 °C, in air with 2 mol % catalyst, in C_6D_6 with anisole as an internal standard. The products were analyzed by ^1H NMR spectroscopy (Table 1).

Similar to other Pd-containing aerobic oxidation catalysts, the catalytic oxidation of alcohols is very sensitive to temperature and the presence of water in the solution. At 60 °C under O_2, compound **5** converts only 6.4 equiv of benzyl alcohol to benzaldehyde in a 20 h period. At 95 °C, 21 turnovers of benzaldehyde are produced and, in



Scheme 2.

the presence of 3 Å molecular sieves to scavenge the water produced in the reaction, 53 turnovers of benzaldehyde are produced (Scheme 2).

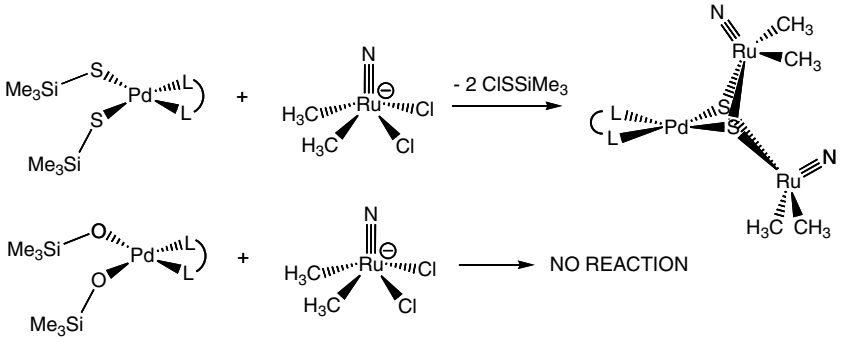
4. Discussion

Because the sulfido ligands groups in $\{Ru(N)Me_2\}(\mu_3\text{-}S)_3\{Pd(dppe)\}$ were sensitive to oxidizing conditions, an improved heterometallic oxidation catalyst would have bridging oxo groups in place of the sulfido groups. Initially, we tried to synthesize the μ-O analog by substituting $Pd(dppe)(OSiMe_3)_2$ for $Pd(dppe)(SSiMe_3)_2$ in the reaction with $[PPh_4][Ru(N)Me_2Cl_2]$ but this was not successful (Scheme 3).

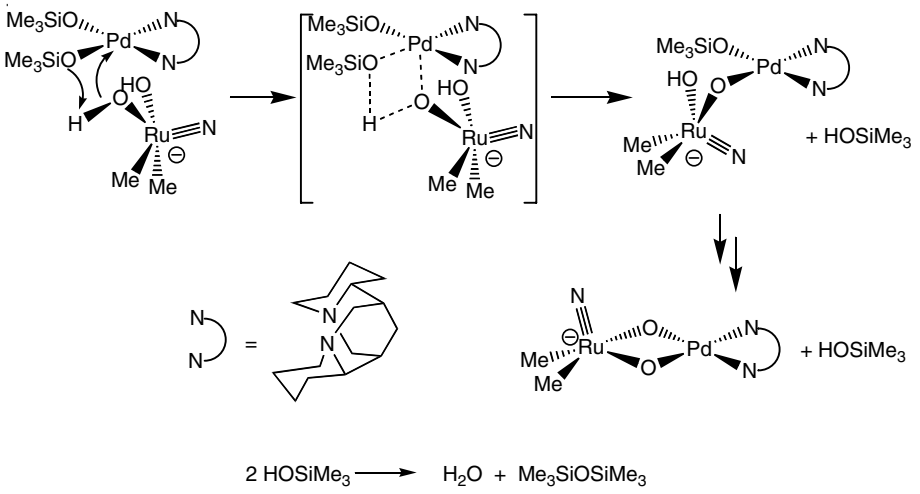
The formation of the μ-sulfido compound is favored because the more stable Cl–Si bond forms as the S–Si bond breaks. However the energy difference between the Cl–Si bond (90 kcal/mol) and the O–Si (110 kcal/mol) bond disfavors formation of the μ-oxo by this route.

Better precursors to a new heterometallic oxygen-bridged compound are $[PPh_4][Ru(N)(OH)_2Me_2]$ and $Pd(OSiMe_3)_2$((−)-sparteine) which react cleanly to form **5**. This compound with large, organic diamine and alkyl ligands is very soluble in non-polar organic solvents. In the synthesis, one hydroxyl group from **4** may react with **2** in a concerted fashion, forming the intermediate $[PPh_4]$-$[Ru(N)(OH)Me_2(\mu\text{-}O)Pd(OSiMe_3)$((−)-sparteine)] and an equivalent of trimethylsilanol. The new, bridged intermediate is set for a second displacement reaction, forming the μ-dioxo heterometallic compound and another molecule of trimethylsilanol. Two molecules of trimethylsilanol rapidly condense and produce hexamethyldisiloxane and an equivalent of water (Scheme 4). The bimetallic $[PPh_4][Ru(N)Me_2(\mu_2\text{-}O)_2Pd$((−)-sparteine)] is favored over the trimetallic $\{Ru(N)Me_2\}(\mu_3\text{-}O)_2\{Pd$((−)-sparteine)} even with an excess quantity of the palladium precursor probably because of the steric bulk of the chelating sparteine ligand.

Nuclear magnetic resonance spectra show that the chiral (−)-sparteine ligand on palladium influences the symmetry of the heterometallic compound. The methyl groups on the ruthenium in **5** are inequivalent in the ^1H and ^{13}C NMR spectra. Because of the asymmetry of the Pd(−)-sparteine compound **2**, the reaction between **2** with **4** could form two diastereomers but we observe only one of them by ^{13}C NMR spectroscopy.



Scheme 3.



Scheme 4.

Electrospray ionization-mass spectrometry data for compound **5** confirms its composition. The ESI-MS spectrum shows an envelope of singly-charged peaks with an average mass of 860.1 *m*/*z*, closely matching the predicted isotopic distribution for $C_{41}H_{55}N_3O_2PPdRu + 3H$ as seen in Fig. 1. The nearly identical appearance of the isotopic distribution between the observed and predicted compound both in terms of the intensity distribution and mass match provide exceptionally strong evidence that the compound of interest formed. Also, the full mass spectrum from 75 to 2000 *m*/*z* demonstrates that the compound is very pure relative to volatile material with a mass greater than 75 Da. Other peaks in the spectrum correspond to the counter-ion, [PPh_4] (e.g. *m*/*z* 339.4) and in-source fragments (e.g. *m*/*z* 795.3, 706.5).

In-source fragments were identified through analysis of a collisionally-induced dissociation, or MS/MS, spectrum of the molecular ion using 35% collisional energy and an isolation width of 3 *m*/*z*. Collectively, this data illustrates the power of mass spectrometric techniques for assessing the identity of organometallic compounds as well as relative purity of the compound solution. Even when mass spectrometry is not coupled a with separation technique, can be a measure of purity [11]. However, non-volatile impurities (i.e. silica, glass) may not be ionized. Even though mass spectrometry is an information-rich analytical technique, few research groups currently use mass spectrometry as a method for identification of inorganic and organometallic compounds [12].

Compound **5** oxidizes alcohols, with a preference for benzylic and allylic alcohols. The turnover number for the oxidation of benzyl alcohol is much higher when molecular sieves are added to remove water as it is formed. The competition between rearrangement and oxidation of allyl alcohol suggests that oxidation reactions of alcohols occur with alcohol binding to the ruthenium center. Compound **5** includes both ruthenium(VI) and palladium(II) centers that are each capable of oxidizing an alcohol [13]. Coordination of the hydroxy group of allyl alcohol to the ruthenium center allows the C–C double bond to interact with the neighboring palladium(II) center and rearrange through a palladium-allyl intermediate [14]. If the alcohol initially coordinated to the palladium, a rearrangement of the alkene at the ruthenium(VI) center would be unlikely.

5. Conclusion

This work demonstrates a new method for the preparation of μ_2-oxygen-bridged heterometallic compounds. Displacement of proton-sensitive leaving groups by metal-hydroxides produces μ-oxo heterometallic compounds. We prepared the heterometallic compound **4** by the reaction of **2** with **3**. Spectroscopic analysis confirms the existence of compound **5** and establishes its structure. It is likely that a diastereomeric mixture of the compound exists and that this mixture complicates crystallization of the compound, thus precluding further structural analysis. Compound **4** preferentially oxidizes allyl and aryl alcohols. Likely, coordination occurs at the ruthenium center as indicated by the allylic rearrangement.

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