Reactivity of (dihydrogen)dihydridotris(triphenylphosphine)ruthenium. Dimerization to form (PPh3)2(H)Ru(.mu.-H)3Ru(PPh3)3 and decarbonylation of ethanol under mild conditions

Lori Stepan. Van der Sluys, Gregory J. Kubas, and Kenneth G. Caulton

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reaction might proceed to form a Me_3N complex after the release of CO_2.

Astruc found that **3** could be hydrogenated by using Pd/C with 1 atm of hydrogen in less than 1 h under ambient conditions to form a previously reported cyclohexadienyl complex.[5b] The hydrogenation of the exocyclic double bond of **2** using 2% Pd/C catalyst of established activity did not proceed even at 40 psi hydrogen over a 12-h period. This is a perplexing observation because **2** should be no more sterically hindered to hydrogenation than **3** and the anticipated product, **endo-4**, is a stable species.

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Supplementary Material Available: Table of general displacement parameter expressions and a least-squares plane drawing (2 pages); a table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

Reactivity of $Ru(H_2)(H)_2(PPh_3)_3$: Dimerization To Form $(PPh_3)_2(H)Ru(\mu\text{-}H)_3Ru(PPh_3)_3$ and Decarbonylation of Ethanol under Mild Conditions

Lori Stepan Van Der Sluys,[†,‡,§] Gregory J. Kubas,*[,†] and Kenneth G. Caulton*[,‡]

Inorganic and Structural Chemistry Group (INC-4), Los Alamos National Laboratory,
Los Alamos, New Mexico 87545, and Department of Chemistry, Indiana University,
Bloomington, Indiana 47405

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Loss of H_2 from $RuH_4(PPh_3)_3$ (**1**) leads to formation of $RuH_2(PPh_3)_3$; this intermediate has been shown to dimerize with loss of a phosphine to form $(PPh_3)_2(H)Ru(\mu\text{-}H)_3Ru(PPh_3)_3$ (**3**). Formation of $RuH_2(PPh_3)_3$ in the presence of ethanol leads to decarbonylation of the alcohol and formation of $RuH_2(PPh_3)_3(CO)$ (**7**), under the mild conditions of nonbasic solutions at 25 °C. Reaction of **1** with methanol, 1-propanol, or benzyl alcohol at 60 °C also results in decarbonylation and formation of **7**. The mechanisms of formation of these complexes are discussed.

Introduction

Recognition of the fact that a dihydrogen molecule can act as an intact metal-bound ligand[1] has resulted in many studies regarding the basic premises of oxidative addition of H_2. The kinetics and thermodynamics of rotation, dissociation, and oxidative addition of the H_2 molecule have been studied,[2] as well as deprotonation[3] and isotopic substitution.[1,4] However, one of the more valuable qualities of an H_2 ligand is its lability; dissociation of H_2 provides an extremely reactive unsaturated metal complex, in some cases retaining hydride ligands, which can act as reducing equivalents in subsequent reactions.[5]

We report here our observations regarding the facile and reversible dissociation of H_2 from $RuH_4(PPh_3)_3$[6] (postulated to be $Ru(H_2)(H)_2(PPh_3)_3$[7,8]), a process that leads to formation of the reactive 16-electron intermediate $RuH_2(PPh_3)_3$. We have found that dimerization and loss of a phosphine from this intermediate yields $(PPh_3)_2(H)Ru(\mu\text{-}H)_3Ru(PPh_3)_3$, while reaction with ethanol at 25 °C results in decarbonylation and formation of $RuH_2(CO)(PPh_3)_3$.[9]

Experimental Section

General Procedures. All manipulations were carried out under a prepurified atmosphere of the indicated gas, using standard Schlenk and drybox techniques. Solvents were dried and deoxygenated by using conventional procedures. $RuCl_2$-

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[†] Los Alamos National Laboratory.

[‡] Indiana University.

[§] Current address: 2700 Lyon Creek Road, Missoula, MT 59801.

(1) (a) Kubas, C. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451. (b) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (c) Henderson, R. A. *Transition Met. Chem.* **1988**, *13*, 474. (d) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299. (e) Ginzburg, A. G.; Bagatur'yants, A. A. *Organomet. Chem. USSR* **1989**, *2*, 111. (f) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95.

(2) (a) Eckert, J.; Kubas, G. J.; Dianoux, A. J. *J. Chem. Phys.* **1988**, *88*, 466. (b) Eckert, J.; Kubas, G. J.; Hall, J. H.; Hay, P. J.; Boyle, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 2324. (c) Khalsa, G. R. K.; Kubas, G. J.; Unkefer, C. J.; Van Der Sluys, L. S.; Kubat-Martin, K. A. *J. Am. Chem. Soc.* **1990**, *112*, 3855. (d) Gonzalez, A. A.; Zhang, K.; Nolan, S. P.; de la Vega, R. L.; Mukerjee, S. L.; Hoff, C. D.; Kubas, G. J. *Organometallics* **1988**, *7*, 2429. (e) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865. (f) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *111*, 5166.

(3) (a) Alvarez, D., Jr.; Lundquist, E. G.; Ziller, J. W.; Evans, W. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1989**, *111*, 8392. (b) Van Der Sluys, L. S.; Miller, M. M.; Kubas, G. J.; Caulton, K. G. Submitted for publication.

(4) For example: (a) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000. (b) Antoniutti, S.; Albertin, G.; Amendola, P.; Bordignon, E. *J. Chem. Soc., Chem. Commun.* **1989**, 229. (c) Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780. (d) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1661.

(5) (a) Lundquist, E. G.; Huffman, J. C.; Folting, K.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1165. (b) Marinelli, G.; Rachidi, I. E.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1989**, *111*, 2346. (c) Johnson, T. J.; Huffman, J. C.; Caulton, K. G.; Jackson, S. A.; Eisenstein, O. *Organometallics* **1989**, *8*, 2073.

(6) Harris, R. O.; Hota, N. K.; Sadavoy, L.; Yuen, J. M. C. *J. Organomet. Chem.* **1973**, *54*, 259.

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$(PPh_3)_3$ was prepared as described in the literature.[10] $NaBH_4$ was obtained commercially, used without further purification, and kept under Ar or N_2. ^1H NMR spectra were recorded on a Nicolet NT-360 spectrometer (at 360 MHz), a Varian UNITY-300 spectrometer (at 300 MHz), or an IBM AF-250 spectrometer (at 250 MHz) and referenced to toluene-d_8 at 6.98 ppm, THF-d_8 at 3.58 ppm, or benzene-d_6 at 7.15 ppm. ^{31}P NMR spectra were recorded on a Varian XL-100 spectrometer (40.5 MHz), a Varian UNITY-300 spectrometer (121.45 MHz), or an IBM AF-250 spectrometer (101 MHz) and referenced externally to 85% H_3PO_4 at 0 ppm. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer or a Digilab FTS-40 spectrophotometer with NaCl plates and referenced to polystyrene at 1601 cm^{-1}. Elemental analyses were recorded on a Perkin-Elmer 2400 CHN elemental analyzer. Mass spectral data were obtained from the University of California Berkeley Mass Spectrometry Laboratory.

Synthesis. $Ru(H_2)(H)_2(PPh_3)_3$ (1). The complex was made by a modification of the method of Harris et al.[6] All solvents must be saturated with H_2 prior to use and *all* manipulations carried out under H_2. Use of Ar results in lower yields and impure product. N_2 gas reacts reversibly to give $Ru(N_2)(H)_2(PPh_3)_3$.[11]

$RuCl_2(PPh_3)_3$ (0.762 g, 0.855 mmol) was dissolved in 112 mL of a 4:3 H_2-saturated EtOH/benzene mixture in a 250-mL flask. $NaBH_4$ (0.142 g, 3.745 mmol) was dissolved in 10 mL of EtOH, and the solution was added dropwise to the benzene solution over 30 min, during which time H_2 gas evolution was accompanied by a color change to red and then pink. Bubbling H_2 gas through the solution while the reaction was taking place was found to increase the yield of product. After ca. 1 h, a thick white precipitate had formed; after 2 h, cessation of gas evolution indicated completion of the reaction. The solid white product was collected on a coarse frit and washed with 3 × 5 mL of EtOH and 10 mL of pentane. The white product is soluble in benzene and toluene, insoluble in pentane and Et_2O, decomposes slowly in THF and immediately in chlorocarbons, and can be stored under H_2 or Ar. The ^1H NMR spectrum of 1 consists of a broad singlet in the hydride region, which broadens at low temperatures and coalesces and disappears into the baseline at −85 °C.

^1H NMR (25 °C, benzene-d_6): δ −7.0 (br s), 6.9 (t), 7.0 (t), 7.4 (br s). $^{31}P\{^1H\}$ NMR (25 °C, benzene-d_6): δ 57.0 (br s). $^{31}P\{^1H\}$ NMR (−95 °C, THF-d_8): δ 60.55 (d, 2 P, J_{PP} = 18.45 Hz), 49.35 (t, 1 P). IR (25 °C, Nujol, cm^{-1}): ν(M–H) = 1947; phenyl ν(C–C) = 1582, 1570; δ(C–H) = 1480, 1430.

$(PPh_3)_2(H)Ru(\mu\text{-}H)_3Ru(PPh_3)_3$ (3). (a) The EtOH/benzene filtrate saved from the isolation of 1 was allowed to sit at room temperature under Ar for a period of 2 weeks. Small red needles of 3 were formed (~10% yield based on $RuCl_2(PPh_3)_3$), along with smaller, less dense white needles of $RuH_2(CO)(PPh_3)_3$ (7)[9] (~10% yield). The solution and white needles were decanted from the heavier crystals of 3 (which remained attached to the sides of the flask); 3 was washed with EtOH and stored under Ar. The complex is soluble in benzene, toluene, and THF, decomposes in acetone, and is insoluble in alkanes.

(b) Ar was bubbled slowly through a benzene-d_6 solution of 1 for 16 h, resulting in a slow color change to red-orange. The products were identified as yellow $RuH_2(PPh_3)_4$ (4)[6,12] and red 3 by NMR spectroscopy.

(c) A sealed THF-d_8 solution of 1 was heated at 50 °C for 4 h, resulting in a slow color change to red-orange. The products were identified as a mixture of 4 and 3 by NMR spectroscopy.

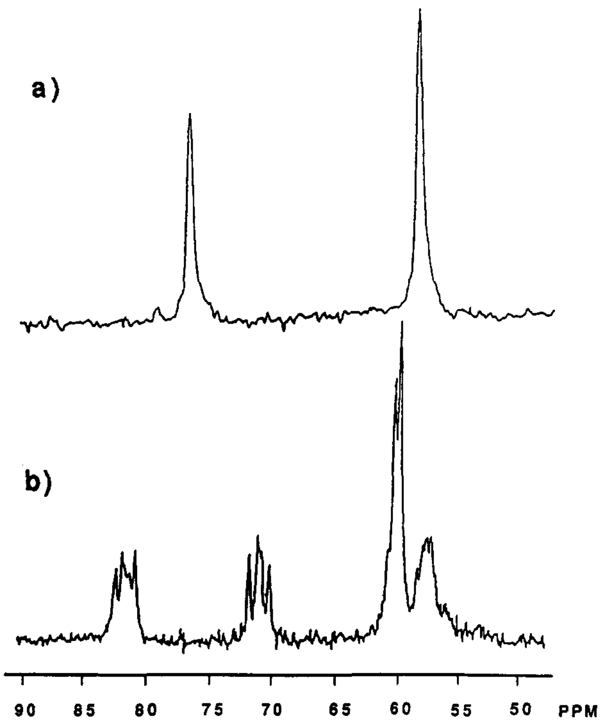

Figure 1. $^{31}P\{^1H\}$ NMR spectra of 3 (THF-d_8): (a) 25 °C; (b) −90 °C.

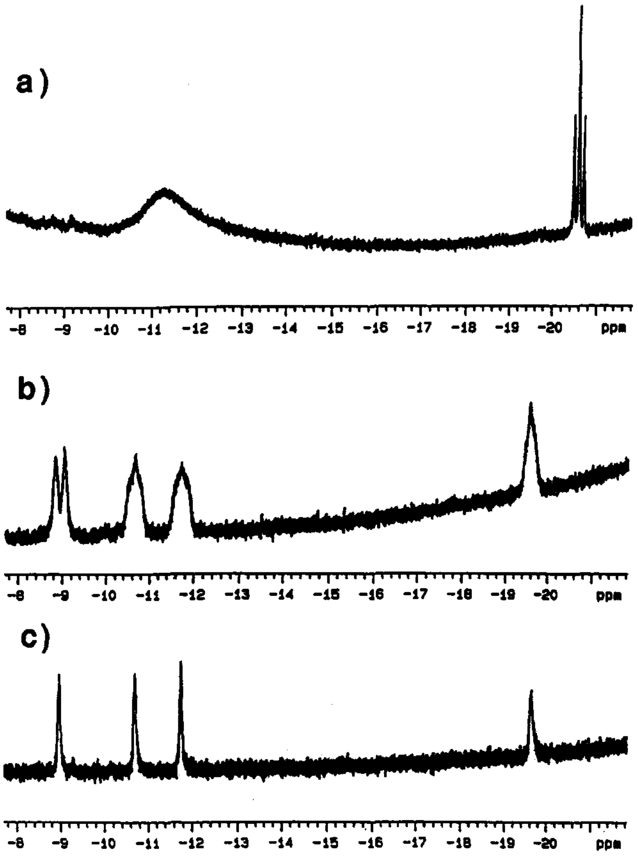

Figure 2. ^1H NMR spectra in the hydride region of 3 (THF-d_8): (a) 25 °C; (b) −90 °C; (c) $^1H\{^{31}P\}$, −90 °C.

^1H NMR of pure 3 (25 °C, benzene-d_6): δ −20.2 (t, 1 H, J_{HP} = 34 Hz), −11.1 (br, 3 H), 6.7 (m), 6.8 (m), 6.9 (m), 8.0 (br). ^1H NMR (−90 °C, THF-d_8): −19.6 (br t, 1 H), −11.7 (br t, 1 H), −10.7 (br t, 1 H), −9.0 (br d, J_{HP} = 63 Hz, 1 H), $^{31}P\{^1H\}$ NMR (25 °C, benzene-d_6): δ 75.0 (s, 2 P), 58.8 (s, 3 P). $^{31}P\{^1H\}$ NMR (−90 °C, THF-d_8): δ 81.3 (m, 1 P), 70.8 (m, 1 P), 60.2 (s, 1 P), 59.8 (s, 1 P), 57.3 (m, 1 P). $^{31}P\{^1H\}$ NMR (25 °C, benzene-d_6, *selective*

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(7) Ashworth, T. V.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1976**, 706.

(8) (a) Crabtree, R. H.; Hamilton, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 3124. (b) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126.

(9) (a) Knoth, W. H. *J. Am. Chem. Soc.* **1972**, *94*, 104. (b) Chaudret, B. M.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546. (c) Cole-Hamilton, D. J.; Wilkinson, G. *Nouv. J. Chim.* **1977**, *1*, 133.

(10) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 945.

(11) (a) Knoth, W. H. *J. Am. Chem. Soc.* **1968**, *90*, 7172. (b) Ito, T.; Kitazume, S.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1970**, *92*, 3011. (c) Eliades, T. I.; Harris, R. O.; Zia, M. C. *J. Chem. Soc., Chem. Commun.* **1970**, 1709. (d) Knoth, W. H. *Inorg. Synth.* **1974**, *15*, 31.

(12) Yamamoto, A.; Kitazume, S.; Ikeda, S. *J. Am. Chem. Soc.* **1968**, *90*, 1089.

hydride coupling): δ 75.0 (br d, J_{HP} = 30 Hz), 58.8 (br d, J_{HP} = 34 Hz). Low-temperature results in THF-d_8 are shown in Figures 1 and 2. IR (25 °C, mineral oil, cm^{-1}): terminal ν(M–H) = 1818; bridging ν(M–H) = 1618; phenyl ν(C–C) = 1581, 1566; δ(C–H) = 1479, 1429. Anal. Calcd for $C_{90}H_{79}P_5Ru_2$: C, 71.22; H, 5.26. Found: C, 72.00; H, 5.57. Mp: 216–222 °C. Mass spectral data (analyzed by using fast atom bombardment in the positive-ion mode under an inert atmosphere, sulfolane matrix; m/z): molecular ion peak (M), 1518 (calcd M_r 1517.68); M – PPh_3 – $2H_2$, 1253; M – PPh_3 – $^3/_2H_2$ – 2Ph, 1095; M – $2PPh_3$ – $2H_2$, 989; M – $2PPh_3$ – $3H_2$, 910; largest intensity peak M – $3PPh_3$ – $2H_2$, 727.

Decarbonylation of Ethanol: Formation of $RuH_2(CO)(PPh_3)_3$ (7). (a) The EtOH/benzene filtrate saved from the isolation of 1 was allowed to sit at room temperature under Ar for a period of 2 weeks. Fine white needles of the product were formed (~10% yield based on $RuCl_2(PPh_3)_3$), along with heavier red crystals of 3 (~10% yield). The solution and white needles of 7 were decanted from the red crystals attached to the sides of the flask, the needles were isolated by filtration, and the product was dried in vacuo.

(b) An EtOH suspension of 1 was stirred at room temperature for 7 days, and the solvent was removed in vacuo. The product was identified by IR, ^1H NMR, and $^{31}P\{^1H\}$ NMR data.[6,7,11]

(c) Heating of a sealed benzene-d_6 solution of 1 containing trace amounts of EtOH for 24 h at 60 °C resulted in a product mixture of 3, 4, and 7 as identified by ^1H and ^{31}P NMR data.[6,7,11,12]

Decarbonylation of Methanol: Formation of 7. Heating of a benzene-d_6 solution of 1 containing 10 equiv of MeOH for 8 h at 60 °C resulted in production of 7 as identified by ^1H NMR data.[6,7,11] A small peak due to an unidentified product was also observed at –8.6 ppm (br t) in the ^1H NMR spectrum.

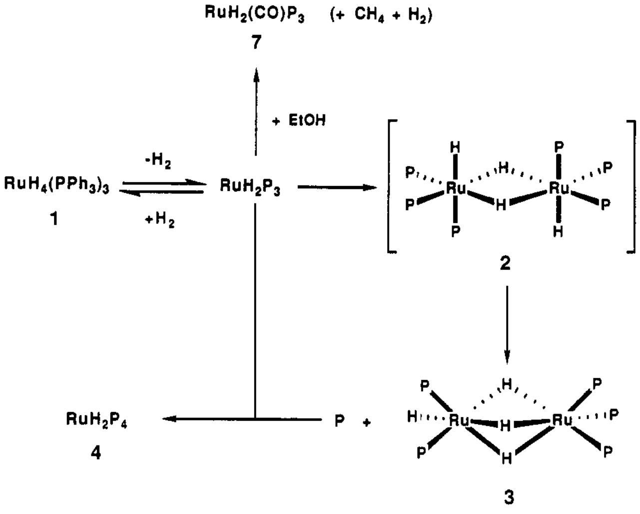
Decarbonylation of 1-Propanol: Formation of 7. Heating of a benzene-d_6 solution of 1 containing 10 equiv of n-PrOH for 5 h at 60 °C resulted in a product mixture of 3 and 7 as identified by ^1H NMR data.[6,7,11] A small peak due to an unidentified product was also observed at –8.6 ppm (br t) in the ^1H NMR spectrum.

Decarbonylation of Benzyl Alcohol: Formation of 7. Heating of a toluene-d_8 solution of 1 containing 10 equiv of $PhCH_2OH$ for 5 h at 60 °C resulted in a product mixture of 3, 4, 7, and C_6H_6 as identified by ^1H NMR data.[6,7,11,12] Also observed in the ^1H NMR spectrum were a peak due to a small amount of unreacted 1 and a small peak due to an unidentified product at –12.7 ppm (t, J_{PH} = 30 Hz).

Results and Discussion

Synthesis and Characterization of $(PPh_3)_2(H)Ru(\mu\text{-}H)_3Ru(PPh_3)_3$ (3). We have found that the phosphine ligands of $RuH_4(PPh_3)_3$ (1) are bound in a meridional configuration; the $^{31}P\{^1H\}$ NMR spectrum consists of a doublet of ratio 2 (60.6 ppm, J_{PP} = 18.4 Hz) and a triplet of ratio 1 (49.3 ppm) at –95 °C in THF-d_8. Thus, the metal–phosphine substructure of 1 and its tendency toward reversible loss of H_2 parallel that of the iron analogue $Fe(\eta^2\text{-}H_2)(H)_2(PPh_2Et)_3$, which has been structurally characterized.[13] 1 has been shown to react with a number of Lewis bases, always resulting in substitution of H_2 rather than the naively predicted substitution of a bulky phosphine ligand.[6,7,9,11,12,14,15] Even the weak Lewis base N_2 will reversibly coordinate to the Ru center, forming $RuH_2(N_2)(PPh_3)_3$.[11] In the presence of D_2, deuteration of the ortho positions of the phosphine phenyl rings of 1 takes place, indicating that the $RuH_2(PPh_3)_3$ intermediate is reactive enough to activate aromatic C–H bonds.[16] Other studies have focused on the ability of 1 to catalytically hydrogenate alkenes through the intermediacy of Ru–alkene complexes and orthometalated species.[15,16]

Scheme I



In our efforts to isolate $RuH_2(PPh_3)_3$ by encouraging loss of H_2, we observed that bubbling Ar through a benzene-d_6 solution of 1 resulted in a color change from colorless to bright red over a period of 16 h. The $^{31}P\{^1H\}$ NMR spectrum of this solution revealed signals for the known complex $RuH_2(PPh_3)_4$ (4)[6,12] and free PPh_3 and two broad resonances (δ 75.0 and 58.8 ppm in a ratio of 2:3) assigned to a new compound 3. Selective decoupling of only the aromatic protons in the $^{31}P\{^1H\}$ NMR spectrum allows both peaks to be resolved into broad doublets (J_{PH} = 30, 34 Hz). The low-temperature $^{31}P\{^1H\}$ NMR spectrum in THF-d_8 resulted in coalescence of the signal at 58.8 ppm at –30 °C and resulted in five signals at –90 °C (see Figure 1).

The corresponding ^1H NMR spectrum (toluene-d_8 or THF-d_8) of the above solution confirmed the presence of 4 and exhibited hydride resonances due to 3 at –20.2 (t, J_{PH} = 34 Hz) and –11.1 ppm (br; see Figure 2). Cooling to –90 °C (THF-d_8) resulted in a broadening of the resonance at –20.2 ppm and a splitting of the broad resonance at –11.1 ppm into three peaks: one broad doublet at –9.0 ppm (J_{PH} = 63 Hz) and two broad triplets. The fact that the fine structure in all four signals is due to J_{PH} was established when complete phosphorus decoupling collapsed all hydride signals to broad singlets.

The red product 3 can best be isolated in crystalline form from the EtOH/benzene filtrate obtained in the synthesis and isolation of 1. In this synthesis,[6] $RuCl_2(PPh_3)_3$ is reacted with $NaBH_4$ in an EtOH/benzene solution under H_2, and colorless 1 precipitates. Isolation of 1 by filtration leaves a red filtrate that produces red needles (invariably twinned) of 3 after sitting at 25 °C for 1 week under Ar; white crystals, which we have identified as $RuH_2(CO)(PPh_3)_3$ (7),[6,9,11c] are also formed along with the red crystals of 3. Use of i-PrOH as the solvent prevents formation of 7 but still results in formation of 3.

An elemental analysis of 3 is consistent with the formula $Ru_2H_4(PPh_3)_5$ and, along with the NMR data, suggests the dinuclear structure $(PPh_3)_2(H)Ru(\mu\text{-}H)_3Ru(PPh_3)_3$ as shown in I and Scheme I. The complex is an unsymmetrical d^6–d^6 dinuclear compound, one ruthenium center (Ru_1) being coordinated by two phosphines and a terminal

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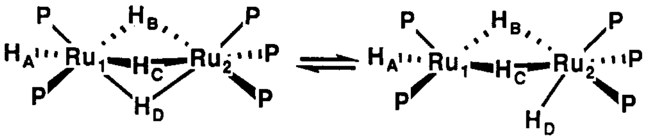
(13) Van Der Sluys, L. S.; Eckert, J.; Eisenstein, O.; Hall, J. H.; Huffman, J. C.; Jackson, S. A.; Koetzle, T. F.; Kubas, G. J.; Vergamini, P. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 4831.

(14) (a) Komiya, S.; Yamamoto, A.; Ikeda, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 101. (b) Chaudret, B. M.; Poilblanc, R. *Inorg. Chim. Acta* **1979**, *34*, 1209. (c) Kolomnikov, I. S.; Gusev, A. I.; Aleksandrov, G. G.; Lobeeva, T. X.; Struchkov, Y.; Vol'pin, M. E. *J. Organomet. Chem.* **1973**, *59*, 349. (d) Komiya, S.; Yamamoto, A. *J. Organomet. Chem.* **1972**, *46*, C58.

(15) (a) Komiya, S.; Yamamoto, A.; Ikeda, S. *J. Organomet. Chem.* **1972**, *42*, C65. (b) Cole-Hamilton, D. J.; Wilkinson, G. *Nouv. J. Chim.* **1977**, *1*, 133.

(16) Linn, D. E.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 2969.



I II

hydride and the second ruthenium (Ru_2) being coordinated by three phosphines; the two ruthenium centers are bridged by three hydrides. A metal–hydride stretch assigned to the bridging hydrides is observed at 1618 cm^{-1} in the IR spectrum, and a terminal metal–hydride stretch is observed at 1818 cm^{-1}.

This formulation for **3** is supported by fast atom bombardment mass spectral data, in which a molecular ion peak was observed at m/z 1518 (calculated $M_r = 1517.7$). Fragments due to sequential loss of phosphines, phenyl rings, and H_2 were observed; the largest intensity peak at m/z 727 corresponded to loss of three phosphines and one H_2 molecule. The isotopic pattern of the molecular ion peak was very close to the calculated pattern.

The NMR data for **3** can be easily interpreted with respect to this dinuclear formula. In the ^1H NMR spectrum, the broad signal at −11.1 ppm is due to the three bridging hydrides H_B, H_C, and H_D (which are equivalent at room temperature), while the triplet at −20.2 ppm is due to the terminal hydride H_A. The coupling constant of 34 Hz is consistent with cis coupling of H_A to the two phosphines on Ru_1, and selective decoupling of the ratio 2 ^{31}P signal at δ 75.0 ppm collapses this triplet to a singlet. The equivalence of the bridging hydrides can be explained by a fluxional process whereby one bridging hydride becomes a terminal hybride as shown in II (e.g., H_D becomes terminal on Ru_2), and the resultant five-coordinate ruthenium center (Ru_1) becomes fluxional and undergoes pseudorotation; this is followed by reattachment of H_D to again become a bridging hydride. Since the hydride signals do not coalesce at 25 °C, exchange between the bridging hydrides and the terminal hydride H_A is not taking place at this temperature. Therefore, conversion from a bridging hydride to terminal must always take place at Ru_2, with preferential breakage of a Ru_1–(μ-H) bond.

At low temperatures, four separate hydride signals are observed in the ^1H NMR spectrum, indicating inequivalence caused by the complete absence of molecular symmetry. Two of the bridging hydrides (H_B and H_D) couple to two trans phosphines (thus the broad triplet patterns), while one bridging hydride (H_C) couples to only one trans phosphine (this is the hydride trans to the terminal hydride H_A, and selective decoupling of the low-temperature ratio 1 ^{31}P signal at δ 57.3 ppm collapses this doublet to a singlet).

Likewise, the ^{31}P NMR spectrum of **3** shows that each phosphine is strongly coupled to one hydride (the respective trans hydride in each case) and that all five are inequivalent at low temperature. The fact that two signals are observed in the ^{31}P NMR spectrum at room temperature in a ratio of 2:3 indicates that no phosphine migration across the Ru–Ru bond takes place. To account for the inequivalence of all of the phosphines and hydrides at low temperature, we propose that the lowered symmetry results from either asymmetrical bridging of the three hydrides or restricted rotation of the bulky phosphine ligands. We prefer the former explanation, since asymmetrical bridging is more consistent with the fluxional process described above, in which a Ru–(μ-H) bond is preferentially broken at Ru_1.

3 was also formed when a sealed THF solution of **1** was heated for 4 h under vacuum or when a benzene solution of **1** was allowed to sit for several days under Ar. The $P(p\text{-}MeC_6H_5)_3$ analogue of **3** was similarly formed from a benzene solution of $RuH_4(P(p\text{-}MeC_6H_5)_3)_3$ after sitting 10 days under Ar.[17]

As shown in Scheme I, we propose that the first step in formation of this dimer is loss of H_2 from **1** to form $RuH_2(PPh_3)_3$, consistent with the known reactivity of **1**. $RuH_2(PPh_3)_3$ may dimerize to satisfy its electronic requirements, resulting in the intermediate "$(PPh_3)_3(H)Ru(\mu\text{-}H)_2Ru(H)(PPh_3)_3$" (**2**). Formation of **3** would then require loss of a phosphine (favorable because steric hindrance is reduced) and formation of a third hydride bridge (to satisfy the coordination requirements of the Ru from which the phosphine was lost). The eliminated phosphine would react easily with the $RuH_2(PPh_3)_3$ present (or replace H_2 in **1**), forming the observed byproduct **4**.

Addition of PPh_3 to benzene-d_6 solutions of **3** does not result in isolation of the proposed intermediate **2**; no reaction occurs after 12 h. This is probably due to the steric bulk of PPh_3; addition of 1 equiv of PPh_2Et produces what we believe to be $(PPh_3)_2(PPh_2Et)(H)Ru(\mu\text{-}H)_2Ru(H)(PPh_3)_3$ from NMR data.[18] A related molecule, $(PMe_3)_3(H)Ru(\mu\text{-}H)_2Ru(H)(PMe_3)_3$, has been synthesized by reaction of H_2 with $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ and has been structurally characterized in the literature.[19]

A similar reaction pathway has been proposed for *photolytic* dissociation of H_2 in an Os analogue of **1**, $Os(H)_4(PMe_2Ph)_3$.[20,21] However, in this system the Os analogue of **2** was isolable and the structure was found by X-ray diffraction to be $(PMe_2Ph)_3(H)Os(\mu\text{-}H)_2Os(H)(PMe_2Ph)_3$. Reversible phosphine dissociation from this dimer resulted in formation of small amounts of the Os analogue of **3**, $Os_2H_4(PMe_2Ph)_5$; the $PMePh_2$ analogue of this molecule has been structurally characterized by X-ray crystallography and shown to contain a metal–metal triple bond, three bridging hydrides, and one terminal hydride. The NMR data for $Os_2H_4(PMePh_2)_5$ are almost identical with those for **3**,[20,22] lending support to our proposed structure.

These data support the reaction scheme that we have proposed for ruthenium, the differences between Os and Ru being the tendency toward H_2 elimination and the size and basicity of the phosphines. The stability of the 4+ oxidation state of Os and the basicity of PMe_2Ph result in a tetrahydride ground state, rather than a dihydrogen complex. However, H_2 loss can be induced photolytically, producing the same intermediates as in the ruthenium case and forming similar products. The smaller bulk of PMe_2Ph as compared to PPh_3 is reflected in the reversibility of the conversion from $Os_2H_4(PMe_2Ph)_6$ to $Os_2H_4(PMe_2Ph)_5$. In the ruthenium case, the bulky phosphine renders **2** unstable and favors formation of **3**.

These results can also be compared to the work of Chaudret et al.,[23] in which the complexes RuH_4L_3 (**5**)

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(17) ^1H NMR (benzene-d_6, hydride region, 25 °C): δ −10.0 (br), −21.5 (m). $^{31}P\{^1H\}$ NMR (benzene-d_6, 25 °C): δ 72.7 (br, 2 P), 54.6 (br, 3 P).

(18) ^1H NMR (toluene-d_8, hydride region, 25 °C): δ −11.5 (br), −19.0 (br), −20.0 (br). $^{31}P\{^1H\}$ NMR (toluene-d_8, 25 °C); δ 76.0 (m, 2 P), 60.0 (s, 1 P), 59.5 (s, 1 P), 51.4 (br, 1 P), 48.6 (m, 1 P).

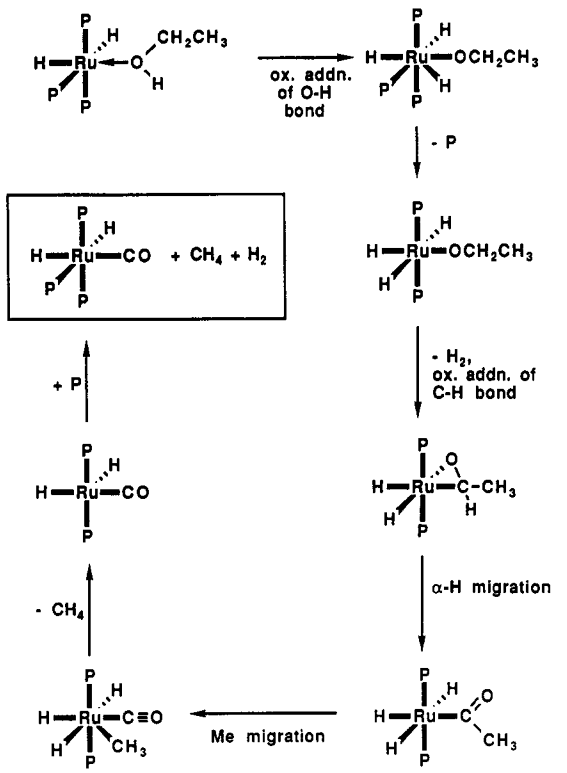
(19) Jones, R. A.; Wilkinson, G.; Colquohoun, I. J.; McFarlane, W.; Galas, A M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1980**, 2480.

(20) (a) Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1983**, *243*, C78. (b) Bruno, J. W.; Huffman, J. C.; Green, M. A.; Zubkowski, J. D.; Hatfield, W. E.; Caulton, K. G. *Organometallics*, in press.

(21) Decarbonylation of EtOH has not been observed for $OsH_4(PMe_2Ph)_3$.

(22) NMR data for $Os_2H_4(PMePh_2)_5$[20b] (25 °C, benzene-d_6): δ −20.1 (terminal hydride, t, $J_{HP} = 26$ Hz, 1 H), −8.9 (br d, $J_{HP} = 46$ Hz, 3 H). $^{31}P\{^1H\}$ NMR (25 °C, benzene-d_6): δ 6.2 (q, $J = 6$, 2 P), −1.9 (t, $J = 6$, 3 P).

Scheme II



(where L = P-*i*-Pr_3, PCy_3, or $P(NEt_2)_3$) reversibly dissociate a *phosphine* ligand in solution to give "RuH_4L_2". These complexes activate aromatic solvents through arene coordination and catalyze H–D exchange of benzene-d_6.[24] Alternatively, the intermediate "RuH_4L_2" complexes can dimerize with elimination of 1 mol of H_2/2 Ru atoms, giving the dimer $Ru_2H_6L_4$ (6). The structure of the N_2 analogue $Ru_2H_4(N_2)L_4$ (L = PCy_3) was found in an X-ray study to be the triply hybride-bridged complex $L_2(H)Ru(\mu\text{-}H)_3RuL_2(N_2)$,[23] and it was postulated that the structure of 6 is similar. The NMR data for this dinitrogen complex are strikingly similar to our data for 3[25] and again lend support to our proposed structure.

The striking contrast between the RuH_4P_3 complexes studied by Chaudret et al. and those described in this paper must be due to the difference in phosphine. Although PPh_3 is bulky, the cone angle is not as large as that of P-*i*-Pr_3, PCy_3, or $P(NEt_2)_3$. Thus, elimination of a second phosphine from 3 is not required for stability. The basicity of PPh_3 is also different from that of the very basic ligands in 5, and perhaps its π-acidity stabilizes the complex in this case. Consequently, dissociation of H_2 from 1 is the dominant method of reactivity resulting in formation of 3, while dissociation of L from 5 is dominant and results in formation of a very different dimer 6.

Decarbonylation of Alcohols. The isolation of $RuH_2(CO)(PPh_3)_3$ (7)[9] reveals that 1 is able to decarbonylate EtOH under remarkably mild conditions. 7 can be isolated either from the EtOH filtrate solution of the synthesis of 1 or from stirring of pure, isolated 1 in EtOH for 7 days. The reaction is quantitative and irreversible, and again we propose that $RuH_2(PPh_3)_3$ is the reactive intermediate in this case. A possible mechanism for this process is shown in Scheme II.[26] Similar mechanisms have been proposed for the decarbonylation of alcohols by various Ru complexes,[27] and the first step of oxidative addition of an alcohol O–H bond is well precedented.[28,29]

The conditions under which 1 decarbonylates EtOH are milder than in a similar system, namely that of the complex $RuH(BH_4)(PMe_2Ph)_3$.[30] In this system, synthesis of the RuH_4P_3 analogue was not successful; only the BH_4 adduct was isolated. The greater basicity and smaller size of PMe_2Ph as compared to the PPh_3 ligand in 1 most probably accounts for this difference. The reaction of the BH_4 complex with EtOH, which takes place at reflux in 1 h to form $RuH_2(CO)(PMe_2Ph)_3$, is considered to represent mild conditions compared to other well-documented cases.[27] It was proposed that the mild conditions for this reaction were due to a reaction of EtOH with the intact ruthenium–borohydride linkage or another boron hydride species. However, in comparison to our data, a mechanism similar to Scheme II is possible. In most documented cases,[27] basic conditions are required for decarbonylation of EtOH, and the reaction is initiated via coordinated ethoxide; in our system, the decarbonylation takes place in neutral EtOH solutions.

We have also studied the ability of 1 to effect the decarbonylation of other alcohols at 60 °C. In the case of methanol, the reaction proceeds smoothly to produce exclusively 7 (the byproducts 3 and 4 are absent). This reflects the ability of the *methanol* decarbonylation reaction to actively compete with the dimerization and ligand redistribution reactions as shown in Scheme I. The decarbonylation of 1-propanol is comparable to that of ethanol (in which small amounts of 3 and 4 are produced), but the reaction with benzyl alcohol is less facile; this is shown by the presence of unreacted 1 after identical reaction times. Benzene is produced in this case, as well as greater amounts of 3 and 4. Production of benzene lends support to the mechanism illustrated in Scheme II, suggesting that corresponding organic products are produced in each of the reactions of 1 with alcohols (e.g. methane production in the decarbonylation of ethanol).

Conclusion

We have established tht H_2 dissociation from RuH_4P_3 yields the reactive species $RuH_2(PPh_3)_3$. This transient has the ability to dimerize with loss of a phosphine to form $(PPh_3)_2(H)Ru(\mu\text{-}H)_3Ru(PPh_3)_3$ and decarbonylate EtOH under mild conditions in nonbasic solutions at 25 °C. The reactivity of the new Ru dinuclear complex is currently under investigation.

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[23] (a) Chaudret, B. M.; Devillers, J.; Poilblanc, R. *J. Chem. Soc., Chem. Commun.* **1983**, 641. (b) Chaudret, B. M.; Poilblanc, R. *Organometallics* **1985**, *4*, 1722. (c) Chaudret, B. M.; Devillers, J.; Poilblanc, R. *Organometallics* **1985**, *4*, 1727. (d) Arliguie, T.; Chaudret, B.; Morris, R. H.; Sella, A. *Inorg. Chem.* **1988**, *27*, 599.

[24] Chaudret, B. M. *J. Organomet. Chem.* **1984**, *268*, C33.

[25] NMR data for $(PCy_3)_2(H)Ru(\mu\text{-}H)_3Ru(PCy_3)_2(N_2)$[23c] (25 °C, benzene-$d_6$): δ −18.2 (terminal hydride, t, J_{HP} = 35 Hz, 1 H), −15.0 (quin, J_{HP} = 13 Hz, 1 H), −8.0 (d, J_{HP} = 64 Hz, 2 H). $^{31}P\{^1H\}$ NMR (25 °C, benzene-d_6): δ 87.1 (br, 2 P), 78.05 (br, 3 P).

[26] An alternate pathway may involve dissociation of aldehyde from the Ru(η^2-RCHO) intermediate, oxidative addition of the aldehyde C–H bond, and subsequent reaction to form products.

[27] (a) Bennett, M. A.; Bruce, M. I.; Matheson, T. W. In *Comprehensive Organometalic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K. 1982; Vol. 4, pp 721–723. (b) Benedetti, E.; Braca, G.; Sbrana, G.; Salvetti, F.; Grassi, B. *J. Organomet. Chem.* 1972, *37*, 361. (c) Chatt, J.; Shaw, B. L.; Field, A. E. *J. Chem. Soc.* 1964, 3466. (d) Chaudret, B. M.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* 1977, 1546.

[28] (a) Milstein, D.; Calabrese, J. C.; Williams, I. C. *J. Am. Chem. Soc.* 1986, *108*, 6387. (b) Monaghan, P. K.; Puddephatt, R. J. *Organometallics* 1984, *3*, 444.

[29] An alternate first step is transfer of a proton from coordinated alcohol to a hydride ligand, with loss of H_2.

[30] Bruno, J. W.; Huffman, J. C.; Caulton, K. G. *Inorg. Chim. Acta* 1984, *89*, 167.

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Coordinated Water/Anion Hydrogen Bonds and Pd–H Bond Acidity in Cationic Palladium(II) Aquo Hydrides and the X-ray Crystal and Molecular Structures of *trans*-$[(Cy_3P)_2Pd(H)(H_2O)]BF_4$

Piero Leoni,*,[1a,b] Milena Sommovigo,[1b] Marco Pasquali,*,[1b] Stefano Midollini,[1c] Dario Braga,†,[1d]
and Piera Sabatino[1d]

Scuola Normale Superiore, Piazza dei Cavalieri 7, 56100 Pisa, Italy,
Dipartimento di Chimica e Chimica Industriale, Via Risorgimento 35, 56100 Pisa, Italy,
Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione ISSECC CNR,
Via J. Nardi 39, 50132 Firenze, Italy, and Dipartimento di Chimica "G. Ciamician",
Via Selmi 2, 40126 Bologna, Italy

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Palladium(II) bis(tricyclohexylphosphine) cationic hydrides have been obtained by oxidative addition of the strong acids $[H_3O^+][BF_3OH^-]$ or $[H_3O^+][BF_4^-]$ to $(PCy_3)_2Pd$, 1; by this route, the compounds *trans*-$[(Cy_3P)_2Pd(H)(H_2O)]X$ ($X = BF_3OH$, 2; $X = BF_4$, 4) have been isolated and characterized. A strong dependence of the stability of *trans*-$[(Cy_3P)_2Pd(H)(L)]X$ complexes upon the L–X combinations was observed. When $L = H_2O$, stable cationic hydrides are obtainable only with fluorine-containing anions (BF_3OH^-, BF_4^-, or PF_6^-), while immediate decomposition to 1 was observed when the metathesis of X^- with BPh_4^- or $B(n\text{-}Bu)_4^-$ was attempted. Stable complexes with $X = BPh_4$ could be isolated when L = MeCN. No reaction was observed when 1 was reacted with $[Et_2OH^+][BF_4^-]$. These findings can be explained in principle by two hypotheses: (i) when the strength of the M–L bond is not sufficient to stabilize the $[(R_3P)_2Pd(H)(L)]X$ complexes, further thermodynamic assistance is furnished by hydrogen-bond formation between the metal-bonded ligand L and the X counteranion, and/or (ii) depending upon the nature of L, the cationic hydrides are sufficiently acidic to decompose reactive anions such as BPh_4^- or $B(n\text{-}Bu)_4^-$. IR and crystallographic data on *trans*-$[(Cy_3P)_2Pd(H)(H_2O)]BF_4$ show the existence, *in the solid state*, of strong hydrogen bonds between the Pd-bound water molecule and the BF_4^- anion. A conductivity study on 4 and on the related hydride *trans*-$[(Cy_3P)_2Pd(H)(MeCN)]BF_4$, 5, shows the existence of large concentrations of ions both in 4 and 5 *solutions*, though the values of Λ_M (10–20% lower for 4 as compared to 5) could account for the presence in 4 of appreciable amounts of the hydrogen-bonded species. The aquohydride 4 has evidenced its acidic behavior by protonating strong and weak bases (Ph_3C^-, OH^-, Et_3N, and PCy_3), and further information on its acid–base behavior has been obtained through the study of exchange reactions with D_2O. The aquodeuteride *trans*-$[(Cy_3P)_2Pd(D)(H_2O)]BF_4$, **9**, can in fact be obtained by reacting for a few minutes a solution of complex 4 with D_2O while the d_3 derivative *trans*-$[(Cy_3P)_2Pd(D)(D_2O)]BF_4$, **10**, can only be obtained after prolonged reaction times. Complex 2 behaves similarly, and *trans*-$[(Cy_3P)_2Pd(D)(H_2O)]BF_3OD$, 11, or *trans*-$[(Cy_3P)_2Pd(D)(D_2O)]BF_3OD$, 12, can be prepared by controlling the reaction times with D_2O. These data suggest that the acidity of the hydridic hydrogen is higher than the acidity of the hydrogens of the $PdOH_2$ moiety. The last hypothesis is further confirmed by the reaction of *trans*-$[(Cy_3P)_2Pd(D)(H_2O)]BF_4$ with Ph_3CLi, which yields a 70/30 Ph_3C-*d*/Ph_3C-*h* mixture. Crystals of 4 are monoclinic, $C2/c$, $a = 30.587$ (6) Å, $b = 13.408$ (4) Å, $c = 19.121$ (5) Å, $\beta = 99.23$ (3)°, $V = 7740.2$ Å^3, $Z = 8$, $R = 0.040$ for 3077 reflections with $F_o > 4\sigma(F_o)$.

Introduction

A rapidly growing interest in the reactivity of the O–H bond toward late transition metals (LTMs) can be perceived in the recent literature. This is not surprising if one thinks that relevant reactions catalyzed by LTM complexes need a LTM/OH bond interaction; representative examples are the Wacker oxidation reaction,[2] the water gas shift (WGS) reaction,[3] olefin hydrocarbonylations,[4] olefin, alkyl halide and alcohol carboalkoxylations,[2,5] carbonyl compound hydrogenations[2] and alcohol dehydrogenations,[2] and nitrile[2,6] and olefin[2,7] hy-

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* To whom correspondence should be addressed.

† To whom correspondence dealing with the crystal structure should be addressed.

(1) (a) Scuola Normale Superiore. (b) Dipartimento di Chimica e Chimica Industriale. (c) ISSECC. (d) Dipartimento "G. Ciamician".

(2) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163 and references therein.

(3) (a) Choudhury, D.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1982**, 1885. (b) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941.

(4) Zudin, V. N.; Chinakov, V. D.; Nekipelov, V. M.; Rogov, V. A.; Likhobolov, V. A.; Ermankov, Yu. I. *J. Mol. Catal.* **1989**, *52*, 27.

(5) (a) Komiya, S.; Akai, Y.; Tanaka, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 1130. (b) Milstein, D. *J. Chem. Soc., Chem. Commun.* **1986**, 817. (c) Zahalka, H. A.; Alper, H.; Sasson, Y. *Organometallics* **1986**, *5*, 2497.

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