complexes and the similarity of the electronic spectra[10,11] between diastereomers provide firm evidence for a head-to-head orientation of ligands in all the complexes studied.

We are aware of only one other study that compares rate data for technetium and rhenium complexes. The Tc(IV) complex $TcCl_6^{2-}$ exchanges chloride 50 times faster than its rhenium congener, and $TcBr_6^{2-}$ exchanges bromide 20 times faster than $ReBr_6^{2-}$.[12] Our data show the technetium complex **2a** racemizing 50 times faster than **2b** at 25 °C. Very few direct comparisons exist between the chemistry of technetium and rhenium,[13] and our data demonstrate structural similarities and kinetic differences between the two metals. The ability to make such comparisons should prove helpful in the development of new ^{99m}Tc imaging agents as well as in the design of radiotherapeutic agents based on ^{186}Re or ^{188}Re. In addition, pharmacokinetic studies on the ^{99m}Tc penicillamine complexes show that stereoisomerism can be a significant concern in the development of new radiopharmaceuticals.[14]

Acknowledgment. This work was supported by Department of Energy Contracts DE-AC02-82ER60048 and DE-AC02-83ER60140 to A.R.F. and by National Science Foundation Grant No. CHE 820-8821 to the Colorado State University Regional NMR Center.

Registry No. **1a**, 92844-14-9; **1b**, 92998-63-5; **2a**, 92998-49-7; **2b**, 92844-15-0; $NH_4^+TcO_4^-$, 13598-66-8; $NH_4^+ReO_4^-$, 13598-65-7.

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(10) The UV–vis spectrum of **1a** is in good qualitative agreement with the previously published spectrum; however, the extinction coefficient we calculate is substantially less. For **1a**, λ_{max} = 424 nm (ϵ 4890 M^{-1} L^{-1}); for **2a**, λ_{max} = 421 nm (ϵ = 5050 M^{-1} L^{-1}). For **1b**, λ_{max} = 345 nm (ϵ = 5020 M^{-1} L^{-1}); for **2b**, λ_{max} = 342 nm (ϵ = 4390 M^{-1} L^{-1}). The reaction of $TcCl_6^{2-}$ with penicillamine has been reported to give a product with λ_{max} = 420 nm (ϵ = 4800 M^{-1} L^{-1}), assigned as Tc(IV) because of its precursor.[4a] The stereochemistry of the penicillamine was not reported, but this product is almost certainly **1a** or a mixture of **1a** and **2a**.

(11) A reviewer has suggested the possibility that the relative stereochemistry of penicillamine ligands could be mutually trans rather than mutually cis. If this were the case, the mixed complexes would show static NMR spectra and the stereochemically pure complexes would show fluxational behavior. Since **1a** is chromatographically identical with the complex characterized crystallographically as mutually cis by Lock, the mixed complex **2a** must also be mutually cis to account for its fluxional behavior. The same argument rigorously proves the rhenium complexes to also be mutually cis. An alternative structure for the mixed complexes would have neither carboxylate coordinated, but this structure would not be expected to be fluxional and would not fit our chromatographic data.

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Molecular A-Frames. Identification and Characterization of the Rhodium A-Frame Precursor Complex Bis(μ-hydrido)dicarbonylbis(bis(diphenylphosphino)methane)dirhodium, $Rh_2(\mu-H)_2(CO)_2(dppm)_2$

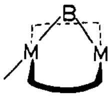
CARRIE WOODCOCK and RICHARD EISENBERG*

Received February 2, 1984

The product of the borohydride reduction of $Rh_2Cl_2(CO)_2(dppm)_2$ has been reinvestigated and characterized as the dihydrido species $Rh_2(\mu-H)_2(CO)_2(dppm)_2$. Under vacuum or N_2, the complex rapidly loses H_2 as it undergoes a first-order decomposition. The decomposition is inhibited by H_2, and solutions of the complex under H_2 are somewhat stabilized. Under D_2 the rapid formation of HD is observed. Solutions of the complex under H_2 react cleanly with various substrates. With HCl, the quantitative conversion to $Rh_2Cl_2(CO)_2(dppm)_2$ is observed. The complex reacts with HBr to form $Rh_2Br_2(CO)_2(dppm)_2$ and the new complex $[Rh_2(\mu-H)(\mu-CO)Br_2(dppm)_2]Br$. Methyl iodide reacts with the complex to form 1 equiv of CH_4 and the new complex $Rh_2(\mu-H)(\mu-I)(CO)_2(dppm)_2$.

Introduction

Molecular A-frames are binuclear complexes of general structure I in which two d^8 metal ions are maintained in close, fixed proximity for the binding and activation of simple substrate molecules.[1,2] The structural integrity of A-frame complexes is maintained through the use of difunctional bridging ligands such as bis(diphenylphosphino)methane (dppm) and a bridgehead ligand, B, which generally consists of a small molecule or ion such as CO, H^+, CNR, SO_2, Cl^-, S^{2-}, and CH_2.[1-9] Adducts of A-frame complexes have been reported in which the addend molecule is bound in the "pocket" or endo site of the A-frame structure,[10-12] and examples of



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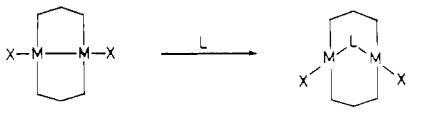
these compounds have been described as catalysts for homogeneous hydrogenation,[12,13] hydroformylation,[12] and the water gas shift reaction.[12] The synthesis, chemistry, and structure of these binuclear complexes dating from their initial reports in 1977 have recently been reviewed.[14]

One of the most successful approaches to the synthesis of A-frame complexes has involved the insertion of small molecules into the metal–metal bond of bis(bis(phosphine))-bridged systems such as $M_2X_2(dppm)_2$ (M = Pd, Pt; X = Cl, Br), eq 1, as reported by Balch,[2] Puddephatt,[4] and others.[15] In this context, we reported in 1980 the BH_4^- reduction of the binuclear complex $Rh_2Cl_2(CO)_2(dppm)_2$ (II) to yield the metal–metal-bonded species III as shown in eq 2. This complex was observed to react readily with CO and H^+ to produce the A-frame complexes IV and V, eq 3, and appeared to be a convenient precursor for the formation of A-frame systems.[3]



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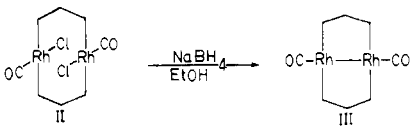

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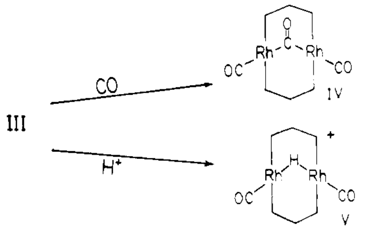

(3)

In this paper, we describe further studies on the spectroscopic and chemical characterization of the complex produced in eq 2. These studies reveal that the complex initially isolated is actually a dihydride species that decomposes readily under N_2 or vacuum. An investigation into the decomposition reaction of this species shows that it can be stabilized for up to several hours under H_2. We also describe the reaction chemistry of this dihydride complex with protic substrates and with CH_3I.

Experimental Section

Reagents. Rhodium trichloride hydrate (Johnson-Matthey), bis(diphenylphosphino)methane (Strem), sodium borohydride (J. T. Baker), tetrafluoroboric acid–diethyl ether complex (Aldrich), and gases H_2, D_2, CO, and HBr (Matheson CP) were used as purchased. Tetrahydrofuran and benzene were dried by distilling from sodium/benzophenone. Toluene was distilled from sodium. Ethanol was distilled from magnesium turnings. Me_2SO-d_6 was dried by storing over molecular sieves in a drybox.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 467 grating spectrophotometer calibrated with polystyrene film and cyclohexane solution. Samples were either solutions prepared under N_2 or Nujol mulls on NaCl plates. ^1H and ^{31}P NMR spectra were recorded on a Bruker WH-400 spectrometer at 400 and 162 MHz, respectively. Chemical shifts are reported in ppm downfield of internal Me_4Si for ^1H NMR and external 85% H_3PO_4 for ^{31}P NMR. Samples were prepared on a high-vacuum line and flame sealed under vacuum, except where stated. Gases were analyzed on a Hewlett-Packard 5700A gas chromatograph with a thermal conductivity detector and helium carrier gas (40 mL/min). Gas samples (0.5 mL) were withdrawn from the reaction flask through septa by using a gas-tight Pressure-Lok syringe. The following columns were used: H_2, CO, 2 ft × $^1/_4$ in. 5A molecular sieves and 12 ft × $^1/_4$ in. Porapak Q; CH_4, CO_2, 12 ft × $^1/_4$ in. Porapak Q. Conductance measurements were made on DMF solutions of the complexes under inert atmosphere by utilizing a Barnstead DM-70CB conductivity bridge equipped with a Barnstead B-10 1.0-cm cell. A working cell constant was determined from the ratio of the observed specific conductance of 0.02 N aqueous KCl with the literature value of 0.002 768 Ω^{-1} cm^{-1} at 25 °C.[16] Typically, equivalent conductances for the complexes in solution were determined at five concentrations ranging from ca. 5 to 0.1 mM. The equivalent conductances at 1 mM were then determined from an Onsager plot of equivalent conductance vs. $(concentration)^{1/2}$. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Hydrogen Evolution Studies. The amount of H_2 produced in the reaction of VI with various substrates was measured as follows. Complex VI was partially dissolved/suspended in a minimum amount of dry ethanol under N_2. The reacting substrate was quickly added through a septum. GC measurements were made until a constant value was obtained for H_2 pressure. The volume of the gas phase above the reaction mixture was greater than 100 mL. Therefore, the withdrawal of 0.5-mL aliquots for sampling did not significantly affect the amount of H_2 present.

Preparation of Complexes. All syntheses were routinely performed under an atmosphere of dry nitrogen with modified Schlenk techniques. $Rh_2(CO)_3(dppm)_2$ (IV), $Rh_2Cl_2(CO)_2(dppm)_2$ (II), $Rh_2Br_2(CO)_2(dppm)_2$ (IX), and $Rh_2(\mu\text{-}CO)Br_2(dppm)_2$ (dppm = bis(diphenylphosphino)methane) were prepared by published procedures.[12,17]

$Rh_2H_2(CO)_2(dppm)_2$ (VI). Sodium borohydride, 0.025 g (0.66 mmol), is dissolved in 15 mL of dry, N_2-purged EtOH and syringed into a flask containing $Rh_2Cl_2(CO)_2(dppm)_2$, 0.10 g (0.091 mmol), under N_2. A purple precipitate is formed over a period of 1 h and then collected under N_2. The complex is washed with water followed by dry ethanol and then dried under a stream of N_2; yield 0.083 g (88%). The air sensitivity and thermal instability of this complex precluded accurate elemental analysis. IR (Nujol): 1920 cm^{-1}. ^1H NMR (C_6D_6): 7.6 (s, 16 H), 6.9 (s, 24 H), 3.6 (s, 4 H), −7.9 (br t, J = 20 Hz, 2 H) ppm. $^{31}P\{^1H\}$ NMR ($(CD_3)_2SO$): 39.3 (symmetric multiplet) ppm.

$Rh_2D_2(CO)_2(dppm)_2$ (VI-d_2). $Rh_2H_2(CO)_2(dppm)_2$ (VI) is dissolved in THF under a D_2 atmosphere. After the solution is stirred at room temperature for 15 min VI-d_2 is precipitated by the addition of an equal volume of ether. IR (Nujol): 1920 cm^{-1}. ^1H NMR (C_6D_6): 7.6 (s, 16 H), 6.9 (s, 24 H), 3.6 (s, 4 H), ppm.

$[Rh_2(\mu\text{-}H)(\mu\text{-}CO)Br_2(dppm)_2]Br$ (VII). Complex VI, 0.10 g (0.097 mmol), is partially dissolved in 10 mL of THF under H_2. A stream of gaseous HBr is passed over the reaction, causing an immediate clearing and color change to orange-brown. The solution is stirred under HBr for 30 min. The solution volume is reduced to ca. 5 mL under vacuum followed by the addition of 15 mL of ether. A yellow-orange precipitate forms, which is collected and washed with ether, resulting in 0.11 g (90%) of the product. Equivalent conductance (DMF): 92 Ω^{-1} cm^2 mol^{-1} [lit.[18] (DMF) 65–90 for 1:1 electrolyte]. IR (Nujol): 1810 cm^{-1}. ^1H NMR (C_6D_6): 7.8 (s, 8 H), 7.7 (m, 8 H), 6.9 (m, 12 H), 6.7 (m, 4 H), 6.6 (m, 8 H), 4.0 (m, 2 H), 3.1 (m, 2 H), −16.3 (m, 1 H) ppm. $^{31}P\{^1H\}$ NMR ($(CD_3)_2SO$): 19.8 (symmetric multiplet) ppm.

$Rh_2(\mu\text{-}H)(\mu\text{-}I)(CO)_2(dppm)_2$ (VIII). Complex VI, 0.10 g (0.097 mmol), is partially dissolved in THF, 10 mL, under H_2. CH_3I, 7 μL (0.112 mmol), is added with a microliter syringe. After 2 h, the reaction mixture becomes a clear yellow-brown solution. GC analysis of the gases over the reaction mixture indicates the presence of 1 equiv of methane (0.097 mmol). The solvent is removed with a N_2 stream, and the resulting brown residue is recrystallized from THF/Et_2O; yield 0.10 g (90%). Anal. Calcd for $C_{52}H_{45}P_4O_2Rh_2I$: C, 53.13; H, 3.87; I, 12.16. Found: C, 52.71; H, 4.08; I, 12.34. Equivalent

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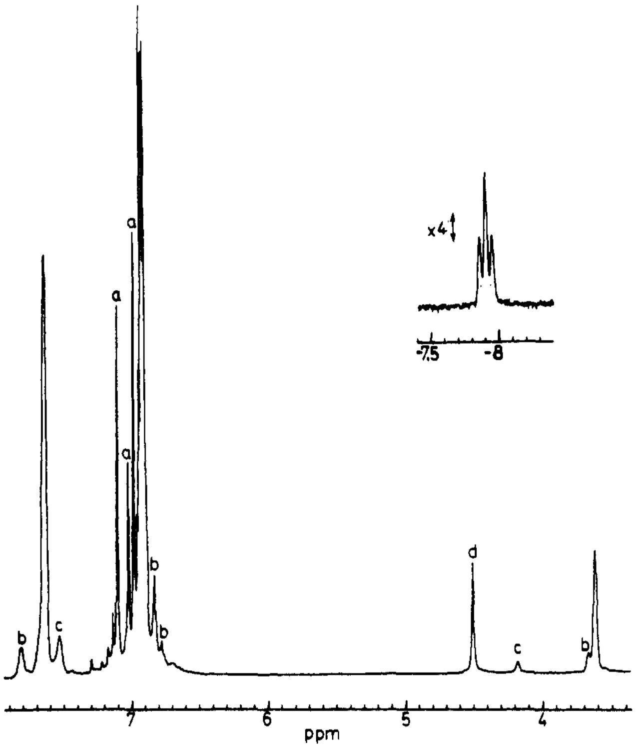


Figure 1. ^1H NMR spectrum of $Rh_2(\mu\text{-}H)_2(CO)_2(dppm)_2$ (VI): a = residual toluene; b = unknown decomposition product(s); c = $Rh_2(CO)_3(dppm)_2$ (IV); d = dissolved H_2.

conductance (DMF): 30 Ω^{-1} cm^2 mol^{-1}. IR (Nujol): 1965, 1940 cm^{-1}. ^1H NMR (C_6D_6): 7.8 (m, 16 H), 6.9, 6.8 (m, 24 H), 4.6 (m, 2 H), 3.8 (m, 2 H), −11.5 (t of q, J_{RhH} = 24 Hz, J_{PH} = 12 Hz, 1 H) ppm. $^{31}P\{^1H\}$ NMR ($(CD_3)_2SO$): 24.2 (symmetric multiplet) ppm.

Results and Discussion

Reduction of $Rh_2Cl_2(CO)_2(dppm)_2$ by Borohydride. The sodium borohydride reduction of $Rh_2Cl_2(CO)_2(dppm)_2$ (II) in dry ethanol results in the precipitation of a deep purple solid originally postulated[3] to be complex III. The IR spectrum of this solid shows a single ν(CO) band at 1920 cm^{-1} which is unchanged when the reduction is carried out with $NaBD_4$ or after a solution of the complex has been placed under a D_2 atmosphere. In the initial characterization of this complex, we reported that no hydride resonances were observed in its ^1H NMR spectrum. However, the spectrum showed very broad resonances in the aromatic region uncharacteristic of other dppm complexes, suggesting that significant solution decomposition of the purple product had occurred. This proposal was supported by an observed color change of the complex solution from purple to brown over the period of 1 h and by the fact that the complex did not react quantitatively with substrates under N_2, especially after solutions of the complex had been allowed to stand for short periods (15–30 min). In these reactions, evidence for the formation of significant amounts of $Rh_2(CO)_3(dppm)_2$ (IV) was obtained.

More extensive characterization of the purple product of eq 2 thus appeared to be in order. The ^1H NMR spectrum of the complex recorded immediately after dissolution under H_2 is shown in Figure 1. This spectrum reveals a cleaner aromatic region consisting of two resonances at 7.6 and 6.9 ppm corresponding to ortho and meta + para phenyl protons, respectively, a resonance at 3.6 ppm assignable to the dppm methylene group, and a previously unseen resonance in the hydride region of the spectrum at −7.9 ppm. The hydride resonance is a broadened triplet (J_{RhH} = 20 Hz, J_{PH} < 2 Hz) and integrates to 1 H/dppm ligand. The triplet is unchanged down to −80 °C in toluene solution. On phosphorus decoupling, the triplet remains intact and does not appear to sharpen, indicating that the P–H coupling is small. The remaining resonances in the spectrum are due to decomposition products including $Rh_2(CO)_3(dppm)_2$ (IV), which appears at 7.56 and 4.20 ppm.

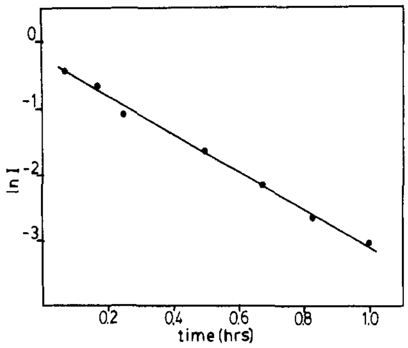
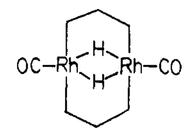


Figure 2. Concentration of VI vs. time plotted as ln (hydride integral/calibration standard integral) vs. time (h).

When 1 equiv of CO is added via a gas-tight syringe to a freshly prepared ethanolic suspension of the purple product, the formation of $Rh_2(CO)_3(dppm)_2$ (IV) is observed. Analysis of the gases above the suspension shows an amount of H_2 corresponding to 1 mol of H_2/mol of complex, assuming a binuclear formulation. Similarly, the reaction of a freshly prepared ethanolic suspension with HBF_4 leads to the evolution of 1 equiv of H_2 with concomitant production of $Rh_2(\mu\text{-}H)(CO)_2(dppm)_2^+$ (V), while reaction with excess HCl leads to the production of 2 equiv of H_2 and quantitative recovery of the dichloride complex, $Rh_2Cl_2(CO)_2(dppm)_2$ (II). A freshly prepared ethanolic suspension of the purple product is also observed to react with CH_3I to yield 1 equiv of CH_4 and a monohydride complex as described below. These results indicate that the purple complex initially isolated from the BH_4^- reduction of $Rh_2Cl_2(CO)_2(dppm)_2$ is a previously unrecognized binuclear dihydride species. On the basis of its IR and ^1H NMR spectra, we assign this complex to have structure VI.



VI

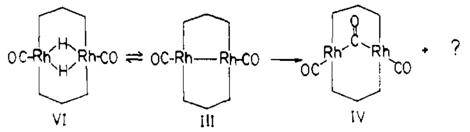
The evolution of H_2 in the reactions of VI with different substrates suggested that solutions of VI might be stabilized by placement under H_2. This is indeed the case. When dissolved in THF under H_2, VI reacts with protic substrates and with CH_3I to give higher yields of complex products, making most of the reactions nearly quantitative in metal complex. However, even under H_2, decomposition is still seen to occur, as discussed below.

Decomposition of $Rh_2(\mu\text{-}H)_2(CO)_2(dppm)_2$ (VI). The decomposition of VI in toluene-d_8 under vacuum was examined by using ^1H NMR spectroscopy. The disappearance of the hydride resonance follows first-order kinetics as shown in Figure 2 and yields a k_1 of 7.8 × 10^{-4} s^{-1}. Similar results are obtained when the sample is prepared in the absence of ambient light. The rate of decomposition of VI is significantly reduced at lower temperatures. For example, under vacuum at −50 °C the intensity of the hydride resonance after 1 h corresponds to only 20% decomposition compared with 96% decomposition after the same time at ambient temperature.

One of the products of the decomposition of VI is $Rh_2(CO)_3(dppm)_2$ (IV), which, on the basis of ^1H NMR integration, forms to the extent of 0.5 mol of IV/mol of VI. The remainder of VI is converted into several species that have not been definitively characterized but that exhibit broadened resonances in the ^{1}H NMR spectrum and a broad ν(CO) at 1950 cm^{-1}.

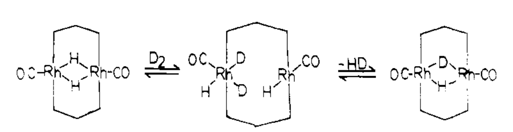
The degree of stabilization of VI when dissolved in toluene-d_8 under H_2 relates directly to the pressure of the H_2 atmosphere. This was examined over the range of 0.2–0.9 atm. The observed decomposition under H_2 shows an inverse dependence on H_2 pressure and follows approximately first-order kinetics during the intermediate stage of the reaction with $k_{obsd} = 1.2 \times 10^{-4}$ s^{-1} at 0.21 atm of H_2, $k_{obsd} = 9 \times 10^{-5}$ s^{-1} at 0.40 atm of H_2, and $k_{obsd} = 6 \times 10^{-5}$ s^{-1} at 0.76 atm of H_2. However, the reaction deviates from first-order behavior during both its early and latter stages. Initially, VI decomposes more rapidly than predicted by a first-order decay and is 50% depleted after ca. 30 min. After long periods of time (>4 h), the decomposition rate is slower than first order with traces of VI still observed after 2 weeks under 1 atm of H_2. The decomposition mixture formed under H_2 is similar to that formed under vacuum except that smaller amounts of IV are produced (0.15–0.25 equiv compared with 0.5 equiv under vacuum). The ^{31}P NMR spectrum of VI after 2 weeks shows resonances at 34 ppm (a four-line pattern but not a quartet with ~23-Hz coupling), 28 and 24 ppm (broad and unresolved), 19.4 ppm (symmetric pattern due to $Rh_2(CO)_3(dppm)_2$), and 10 and −9 ppm (poorly resolved triplets with ~70-Hz coupling).

The inverse dependence on H_2 pressure for the decomposition of VI is consistent with a mechanism involving an equilibrium between VI and the metal–metal-bonded species III, which then decomposes irreversibly as shown in eq 4. The rate law for this mechanism predicts an inverse first-order dependence on H_2 pressure with which the data are consistent. The formation of a metal–metal-bonded species by the elimination of H_2 from two metal hydrides has ample precedent, such as in the formation of the Rh(0) dimer $Rh_2(CO)_4(PPh_3)_4$ from $RhH(CO)_2(PPh_3)_2$ under a stream of N_2.[19] The ligand donor set in this example is essentially the same as that in VI. The formation of IV in the decomposition presumably arises by the reaction of III with other species to obtain an additional CO ligand.



(4)

H/D Exchange. Under D_2, complex VI undergoes facile H/D exchange as evidenced by rapid loss of the hydride resonance while all other resonances in the ^{1}H NMR spectrum are maintained. Concomitant with the loss of the hydride resonance are the appearance and growth of both a 1:1:1 triplet at 4.42 ppm (C_6D_6, J = 42 Hz), which is due to HD,[20] and a singlet at 4.46 ppm, which is due to H_2.[20] The formation of HD cannot be achieved by a simple intramolecular reductive elimination of H_2 from VI and reversible oxidative addition of D_2 to III and thus indicates that equilibria in addition to that shown in eq 4 must exist between binuclear species and H_2. While no species other than VI and the decomposition products is observed directly, HD formation can be envisioned via two possible pathways. The first involves an *inter*molecular reductive elimination of HD from VI and VI-d_2. The second is shown in eq 5 and involves oxidative addition of D_2 to VI to yield a Rh(I)–Rh(III) intermediate that can then reductively eliminate HD while deuterating the hydride position. Equation 5 thus corresponds to a *intra*molecular H/D exchange.



(5)

Reactions of $Rh_2(\mu\text{-}H)_2(CO)_2(dppm)_2$ (VI) with Substrates. Essentially two sets of reaction conditions were employed. Reactions that were done to quantify the amount of H_2 produced were performed on suspensions of the complex in absolute ethanol under N_2. Reactions that were nearly quantitative in metal complex conversion were performed by using solutions of VI in THF under H_2.

As noted above, ethanolic suspensions of VI react instantly with HBF_4 to yield 1 equiv of H_2 and V as its BF_4^- salt and with excess HCl to yield 2 equiv of H_2 and the chloro complex II. Similarly, an ethanolic suspension of VI reacts with gaseous HBr to yield 2 equiv of H_2 and $Rh_2Br_2(CO)_2(dppm)_2$ (IX) as identified by comparison of the IR and ^{1}H NMR spectra with literature values.[21] In this case, the new complex $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)Br_2(dppm)_2]Br$ (VII) is also produced, giving a combined metal complex yield of 95% (IX:VII ≈ 1:1). The identity of complex VII is based on comparison of its IR and ^{1}H NMR spectra with those of similar complexes. The IR stretch for the bridging carbonyl ligand occurs at 1810 cm^{-1}, which is identical with that reported for $[Rh_2(\mu\text{-}CO)I(CO)(dppm)_2]I$[22a] and lies well within the range of values reported for other μ-CO–dppm bridged binuclear complexes (1755 cm^{-1} for $Rh_2I_2(\mu\text{-}CO)(dppm)_2$,[22b] 1868 cm^{-1} for $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(dppm)_2]BPh_4$,[22c] and 1870 cm^{-1} for $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(dppm)_2]PF_6$[12]). The ^{1}H NMR spectra of VII exhibits typical phenyl and methylene resonances for the dppm ligands of A-frame type molecules,[12] and the hydride resonance located at −16.3 ppm is a multiplet that is similar in appearance to the hydride resonance of $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(dppm)_2]PF_6$ located at −9.6 ppm. The upfield shift of the hydride resonance on going from a trans-CO to a trans-Br ligand is well documented for terminal hydrides and may be similarly valid for bridging hydride ligands.

The ionic nature of VII is evident from conductivity measurements. When VII is further reacted with HBr and CO, IX is formed quantitatively. Complex IX is also formed when the known complex $Rh_2(\mu\text{-}CO)Br_2(dppm)_2$[22a] is reacted with gaseous HBr. In these reactions with HX the presence of highly coordinating X^- drives the removal of both hydride ligands from VI whereas reaction of VI with the noncoordinating acid HBF_4 results in the removal of just one hydride ligand.

Complex VI in THF solution under H_2 is also observed to react with CH_3I. GC measurements on the gas phase above the reaction mixture reveal the presence of 1 equiv of CH_4 based on metal complex. Methane presumably arises from the coupling of the methyl group of CH_3I with one of the hydride ligands of VI. The metal complex product is $Rh_2(\mu\text{-}H)(\mu\text{-}I)(CO)_2(dppm)_2$ (VIII), which exhibits a hydride resonance at −11.5 ppm. This resonance is a triplet of quintets with J_{RhH} = 24 Hz and J_{PH} = 12 Hz as shown by collapse of the resonance to a triplet, J = 24 Hz, on phosphorus decoupling. In addition, the ^{1}H NMR spectrum exhibits dppm phenyl resonances at 7.8, 6.9, and 6.8 ppm as well as dppm methylene resonances at 4.6 and 3.8 ppm typical of A-frame type molecules. The complex also exhibits terminal CO stretches in the IR spectrum at 1965 and 1940 cm^{-1}, similar to the known complex $Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(dppm)_2^+$[12] in

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which ν(CO) bands are observed at 1970 and 1955 cm^{-1}.

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Dinuclear Uranium Alkoxides. Preparation and Structures of $KU_2(OCMe_3)_9$, $U_2(OCMe_3)_9$, and $U_2(OCHMe_2)_{10}$, Containing [U(IV),U(IV)], [U(IV),U(V)], and [U(V),U(V)], Respectively

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The structural results by X-ray crystallography are reported for three uranium alkoxides, two of which are new compounds. All three are dinuclear in the solid state, and they contain the following combinations of oxidation states: [U(IV),U(IV)], [U(V),U(IV)] and [U(V),U(V)]. $K[U_2(OCMe_3)_9]\cdot C_6H_{14}$: monoclinic, $P2_1/c$, a = 10.713 (3) Å, b = 25.990 (8) Å, c = 19.480 (6) Å, β = 91.13 (5)°, Z = 4. $U_2(OCMe_3)_9$: orthorhombic, $Pbcm$, a = 13.749 (7) Å, b = 19.977 (7) Å, c = 16.923 (8) Å, Z = 4. $U_2(OCHMe_2)_{10}$: triclinic, $P\bar{1}$, a = 10.974 (3) Å, b = 12.226 (3) Å, c = 10.002 (2) Å, α = 111.56 (2)°, β = 110.09 (2)°, γ = 67.87 (2)°, Z = 1. The first two contain confacial bioctahedra with U···U distances of 3.631 (2) and 3.549 (1) Å, respectively. The $U_2(OCHMe_2)_{10}$ molecule consists of edge-sharing octahedra with a U···U distance of 3.789 (1) Å. The terminal alkoxide groups in all three compounds display nearly linear U–O–C arrangements, with U–O–C bond angles between 160 and 176°. This appears to be a general feature of uranium alkoxides and suggests a high degree of O $\pi \rightarrow$ U contribution to the metal–oxygen bonds.

Introduction

It is now well established that the group 6 transition elements chromium, molybdenum, and tungsten, and especially the last two, have a pronounced tendency to form metal–metal bonds.[1] In particular, molybdenum and tungsten in their oxidation states III–V regularly exhibit bonds of orders 3, 2, or 1 in the presence of alkoxide ligands. We therefore reasoned that if uranium, formally a group 6 element, were to have any tendency to resemble molybdenum and tungsten in forming metal–metal bonds, this tendency might well manifest itself in the structures of uranium alkoxides. We recognized, of course, that for uranium the nature of the valence shell is somewhat different because of the participation of the 5f orbitals. It is known that the radial extent of these wave functions brings them significantly into or beyond the same spacial region as the 6s and 7p shell[2] and there is evidence from photoelectron spectroscopy and electronic absorption spectra that 5f orbitals participate in some forms of bonding to the actinide elements.[3]

By following the procedure of Gilman[4] for the preparation of $[U(OCMe_3)_4]_n$, we obtained a previously unreported type of U^{IV} compound, $K[U_2(O_2CMe_3)_9]$ (**1**). Though it is formally an ionic compound, **1** is soluble in hexane where, at 5 °C, it is slowly and spontaneously transformed into the U^{IV}/U^{V} compound $U_2(O_2CMe_3)_9$ (**2**). We have also obtained the previously known U^{V}/U^{V} compound $U_2(OCHMe_2)_{10}$ (**3**). The crystal and molecular structures of all three of these compounds have been determined and are reported here.

Experimental Section

Standard high-vacuum, Schlenk, and inert-atmosphere glovebox procedures were used throughout this study. Solvents were dried over Na/K alloy and distilled under argon. The alcohols were dried over activated molecular sieves and degassed by pump–freeze procedures. Commercial UCl_4, purified by the procedure of Marks,[5] was used.

Preparation of the Compounds. $U_2(O\text{-}i\text{-}Pr)_{10}$ (**3**) was prepared by alcohol exchange from $[U(OC_2H_5)_5]_n$ following published procedures.[6] Single crystals of suitable size were grown by slow sublimation as well as by slowly cooling a saturated solution in 2-propanol to 5 °C. We did not notice a significant difference in crystal habit or diffraction quality between the two batches.

Uranium(IV) *tert*-butoxide, in our hands, was obtained as green $K[U_2(O\text{-}t\text{-}Bu)_9]\cdot C_6H_{14}$, when following Gilman's procedures.[4,7] It has been noted before[8] that the preparation is not always reproducible and that U(V) alkoxides may be obtained instead of the expected U(IV) compounds. We attribute these difficulties to the relative instability of the U(IV) compound in solution. Only after we established dry and anaerobic conditions very carefully and did not allow

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