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Highly Electrophilic, 16-Electron [Ru(P(OMe)(OH)$_2$)(dppe)$_2$]$^{2+}$ Complex Turns H$_2$(g) into a Strong Acid and Splits a Si–H Bond Heterolytically. Synthesis and Structure of the Novel Phosphorous Acid Complex [Ru(P(OH)$_3$)(dppe)$_2$]$^{2+}$

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The highly electrophilic, 16-electron, coordinatively unsaturated [Ru-(P(OMe)(OH)$_2$)(dppe)$_2$][OTf]$_2$ complex brings about the heterolytic activation of H$_2$(g) and spontaneously generates HOTf. In addition, *trans*-[Ru(H)(P(OMe)(OH)$_2$)(dppe)$_2$]$^+$ and an unprecedented example of a phosphorous acid complex, [Ru(P(OH)$_3$)(dppe)$_2$]$^{2+}$, are formed. The [Ru(P(OMe)(OH)$_2$)(dppe)$_2$][OTf]$_2$ complex also cleaves the Si–H bond in EtMe$_2$SiH in a heterolytic fashion, resulting in the *trans*-[Ru(H)(P(OMe)(OH)$_2$)(dppe)$_2$]$^+$ derivative.

The binding of molecular hydrogen to a metal center and its subsequent activation toward either homolysis or heterolysis has been intensively studied.[1] The heterolytic splitting of H$_2$ bound to electron-rich neutral metal complexes is usually brought about by strong bases. However, when H$_2$ is bound to highly electrophilic metal centers, its tendency to undergo heterolysis increases tremendously.[1] Recently, we reported the synthesis and characterization of a stable, coordinatively unsaturated, 16-electron ruthenium complex bearing the P(OMe)(OH)$_2$ moiety, [Ru(P(OMe)(OH)$_2$)(dppe)$_2$]-[OTf]$_2$, **1** (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$).[2] Complex **1** reacts with H$_2$ gas and spontaneously generates HOTf. The HOTf brings about a novel C–O bond activation in the *trans*-P(OMe)(OH)$_2$ moiety, resulting in the elimination of MeOTf and the formation of yet another air-stable, 16-electron species, [Ru(P(OH)$_3$)(dppe)$_2$]$^{2+}$, a hitherto unknown example of a P(OH)$_3$-bearing complex of ruthenium. Complex **1** also cleaves the Si–H bond of EtMe$_2$SiH in a heterolytic fashion. We present these studies in this paper.

The protonation of *trans*-[Ru(H)(P(OMe)$_3$)(dppe)$_2$][OTf] with excess HOTf under an atmosphere of Ar gave three dihydrogen complexes, *trans*-[Ru(η^2-H$_2$)(P(OMe)$_{3-x}$(OH)$_x$)-(dppe)$_2$]$^{2+}$ (x = 0, 1, 2). Eventually, all three dihydrogen complexes lose the bound H$_2$ ligand. We isolated a stable, five-coordinate species from the reaction mixture that we have been able to identify as [Ru(P(OMe)(OH)$_2$)(dppe)$_2$]$^{2+}$ on the basis of X-ray crystallography.[2] Complex **1** in CD$_2$-Cl$_2$ (saturated with Ar) reacts with 1 atm of H$_2$(g) (as head gas) at room temperature, resulting in a highly acidic dihydrogen complex, *trans*-[Ru(η^2-H$_2$)(P(OMe)(OH)$_2$)(dppe)$_2$]-[OTf]$_2$, that spontaneously generates HOTf and two other complexes. One of these species was identified as a new hydride derivative, *trans*-[Ru(H)(P(OMe)(OH)$_2$)(dppe)$_2$]$^+$ (Figure S1, Supporting Information). The ^{1}H NMR spectrum of this solution also exhibits a singlet assignable to free MeOTf (δ 3.76). This assignment was confirmed by comparison with the spectrum of an authentic sample of MeOTf. We also noted that the second species did not have P(OMe)-(OH)$_2$ as a ligand; instead, a broad feature in the ^{1}H NMR spectrum that integrated to only three hydrogens, suggesting the formation of a new phosphorus moiety of the form P(OH)$_3$, was observed. We isolated this species, and X-ray crystallography revealed without any ambiguity that the product was [Ru(P(OH)$_3$)(dppe)$_2$][OTf]$_2$.[3] The ORTEP diagram of the dication is shown in Figure 1.

The molecular structure consists of discrete [Ru(P(OH)$_3$)-(dppe)$_2$]$^{2+}$ units and two [OTf]$^-$ counterions. In addition, two water molecules were also found. The counterions and the water molecules are not shown in the figure. The structure consists of a slightly distorted square pyramid defined by the four almost coplanar dppe P atoms and the P(OH)$_3$ moiety, nearly perpendicular to this plane. The hydrogen

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(3) Crystal data for [Ru(P(OH)$_3$)(dppe)$_2$][OTf]$_2$: C$_{54}$H$_{55}$F$_6$O$_{11}$P$_5$RuS$_2$, F_w = 1314.1, orthorhombic, $P2_12_12_1$, a = 13.7747(15) Å, b = 14.3190-(15) Å, c = 29.377(3) Å, α = 90°, β = 90°, γ = 90°, V = 5794.3(11) Å^3, Z = 4, D_c = 1.504 g cm^{-3}, T = 293(2) K, 1.6° ≤ θ ≤ 24.7°, μ = 5.57 cm^{-1}, $F(000)$ = 2687, R1 = 0.03, wR2 = 0.09 for 9879 reflections with I > 2σ(I) and 736 parameters [R1(F^2) = 0.018 (all data)]. Weighting scheme: w = 1/[σ^2(F_o^2) + (0.1072P)^2 + 3.8270P], where P = (F_o^2 + 2F_c^2)/3.
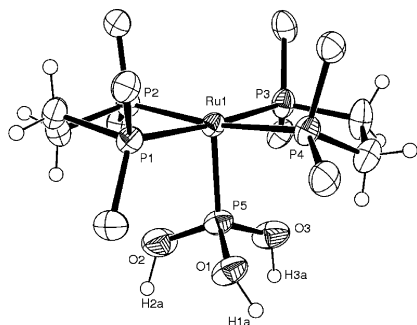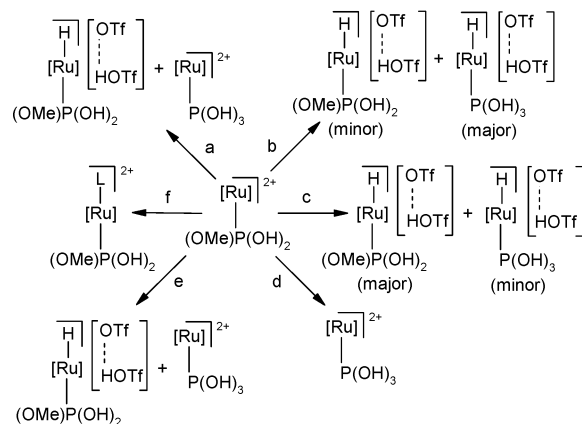
Figure 1. ORTEP view of [Ru(P(OH)$_3$)(dppe)$_2$]$^{2+}$ at the 50% probability level. The phenyl groups on the dppe P atoms have been omitted for clarity; only one carbon of each phenyl group is shown in the figure. Pertinent bond distances (Å) and angles (deg): Ru(1)−P(5) 2.2004(7), P(5)−O(1) 1.566(2), P(5)−O(2) 1.563(2), P(5)−O(3) 1.565(2); O(1)−P(5)−O(2) 105.40(14), O(1)−P(5)−O(3) 103.64(12), O(2)−P(5)−O(3) 108.83(16).

atoms of the −OH groups were located and refined for limited cycles isotropically. The Ru−P (of dppe) bond distances fall in the range 2.3591(7)−2.4454(6) Å. The dppe bite angles P(1)−Ru(1)−P(2) and P(3)−Ru(1)−P(4) are 81.63(2)° and 81.96(2)°, respectively. The significant feature is the considerable shortening of the Ru(1)−P(5) bond, which is 2.2004(7) Å, relative to Ru(1)−P (of dppe) bond distances. This distance is also quite short compared to the Ru−P distance in the somewhat analogous complex *trans*-[Ru(H)-(PF(OMe)$_2$)(dppe)$_2$]$^+$ [2.264(2) Å][4] and nearly the same as that in **1** [2.2016(9) Å].[2] This reduction in the bond distance reflects a reduction in the steric crowding, that is, the reduction of the cone angle of the P(OH)$_3$ moiety in comparison to that of the PF(OMe)$_2$ ligand. All three P−O distances are nearly the same [1.566(2), 1.563(2), and 1.565-(2) Å] and correspond to single bonds.[5] These distances are close to those found in crystalline HP(O)(OH)$_2$ (1.538−1.553 Å).[6] There is an extensive network of intra- and intermolecular hydrogen bonds involving C−H···F, O−H···F, C−H···O, O−H···S, and O−H···O. The P(OH)$_3$ group is actively hydrogen bonded to the counterion OTf$^-$ and the two lattice water molecules.

The only structurally characterized complex bearing the P(OH)$_3$ ligand is [Mo$_3$PdP(OH)$_3$S$_4$(H$_2$O)$_9$]$^{4+}$, reported by Fedin and co-workers.[7] The P(OH)$_3$ moiety in that case was obtained via the hydrolysis of PCl$_3$ in the presence of the cluster. The initial product of hydrolysis, which is HP(O)-(OH)$_2$, has to isomerize to P(OH)$_3$ during the reaction. This isomerization reaction has been postulated in several instances,[8] although it has never been directly observed. More work is needed to establish the mechanism of the reaction presented in this paper.

The reaction of **1** with H$_2$(g) (as head gas) in CD$_2$Cl$_2$ (saturated with Ar) at 273 K resulted in *trans*-[Ru(H)-

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Scheme 1. Reactivity of Complex **1**[a,b]

[a] [Ru] = [(dppe)$_2$Ru]. [b] Reaction conditions: (a) H$_2$, room temperature; (b) H$_2$, 273 K; (c) H$_2$, PPh$_3$, 273 K; (d) H$_2$, HOTf, 273 K; (e) EtMe$_2$SiH, Ar, room temperature; (f) L = CO, CH$_3$CN.

(P(OMe)(OH)$_2$)(dppe)$_2$]$^+$ (minor) and *trans*-[Ru(H)(P(OH)$_3$)-(dppe)$_2$]$^+$ (major). However, when the reaction was carried out under similar conditions with added PPh$_3$ (1 equiv with respect to the starting material), the concentrations of the two hydrides obtained were reversed (Figure S2, Supporting Information). On the other hand, when a CD$_2$Cl$_2$ solution containing **1** was purged with H$_2$(g), the sole product was *trans*-[Ru(H)(η^2-H$_2$)(dppe)$_2$]$^+$, which is a result of the substitution of the labile phosphorus ligand trans to hydride (Figure S3, Supporting Information). In an attempt to obtain [Ru(P(OH)$_3$)(dppe)$_2$]$^{2+}$ exclusively, we treated complex **1** with H$_2$(g) in the presence of HOTf. In this way, [Ru-(P(OH)$_3$)(dppe)$_2$]$^{2+}$ was obtained as the major product in ca. 70−80% yield (Figure S4, Supporting Information). This suggests that the heterolytic activation of H$_2$ to generate HOTf is suppressed when HOTf is added externally. The *trans*-[Ru(η^2-H$_2$)(P(OMe)(OH)$_2$)(dppe)$_2$]$^{2+}$ complex loses the bound H$_2$ ligand, and the added HOTf brings about the cleavage of the C−O bond of the P(OMe)(OH)$_2$ moiety, resulting in the formation of [Ru(P(OH)$_3$)(dppe)$_2$]$^{2+}$ species. In all of these experiments, small amounts of *trans*-[Ru(H)-(η^2-H$_2$)(dppe)$_2$]$^+$ are also formed as a result of substitution of the labile phosphorus ligand with H$_2$. A controlled experiment was also carried out: Treatment of **1** with HOTf under an atmosphere of Ar showed no apparent reaction. The [Ru(P(OH)$_3$)(dppe)$_2$]$^{2+}$ complex also brings about the heterolytic activation of H$_2$: When H$_2$(g) was introduced as a head gas to a CD$_2$Cl$_2$ solution (saturated with Ar) containing [Ru(P(OH)$_3$)(dppe)$_2$]$^{2+}$, HOTf formed spontaneously, along with *trans*-[Ru(H)(P(OH)$_3$)(dppe)$_2$][TfO···HOTf]. The H-bonded counterion was detected using NMR spectroscopy.[9] These reactions are summarized in Scheme 1.

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Complex **1** also activates the Si−H bond toward heterolysis. When a CD$_2$Cl$_2$ solution (saturated with Ar) of **1** was treated with 2 equiv of EtMe$_2$SiH, we obtained a mixture of *trans*-[Ru(H)(P(OMe)(OH)$_2$)(dppe)$_2$]$^+$, [Ru(H)(P(OH)$_3$)-(dppe)$_2$]$^+$, and [Ru(P(OH)$_3$)(dppe)$_2$]$^{2+}$ complexes. This reaction involves the initial heterolysis of the silane to afford the *trans*-[Ru(H)(P(OMe)(OH)$_2$)(dppe)$_2$]$^+$ complex. The *trans*-[Ru(η^2-H$_2$)(P(OMe)(OH)$_2$)(dppe)$_2$]$^{2+}$ complex is produced by the reaction of some of the starting material with H$_2$ that is generated when the silane reacts with acid (see later). This species spontaneously eliminates HOTf, which reacts with the remaining free EtMe$_2$SiH to liberate H$_2$. The H$_2$, in turn, reacts with **1** that remains unreacted in solution to generate more HOTf via heterolysis of H$_2$. We found a signal due to HOTf in the ^{1}H NMR spectrum during the course of the reaction that eventually disappears as the reaction progresses further. The [Ru(H)(P(OH)$_3$)(dppe)$_2$]$^+$ and [Ru(P(OH)$_3$)(dppe)$_2$]$^{2+}$ complexes originate as described above. A blank reaction of EtMe$_2$SiH with HOTf resulted in the evolution of H$_2$. Detailed kinetic studies of these reactions are in progress.

Complex **1** reacts with ligands such as CO and CH$_3$CN to afford the 18-electron complexes *trans*-[Ru(L)(P(OMe)-(OH)$_2$)(dppe)$_2$]$^{2+}$ (L = CO, CH$_3$CN). We have been able to characterize the *trans*-[Ru(CO)(P(OMe)(OH)$_2$)(dppe)$_2$]$^{2+}$ complex crystallographically, the details of which can be found in the Supporting Information (Figure S5, Supporting Information). The notable feature of the structure is the considerable elongation of the Ru(1)−P(5) bond, which is 2.3866(13) Å. The C(53)−O(12) bond is concomitantly shortened and was found to be 1.131(3) Å, nearly the same as that in free CO.[10] This is a result of the trans influence of the CO ligand.[11] The O(12)−C(53)−Ru(1) and the C(53)−Ru(1)−P(5) bond angles are nearly linear at 178.6(2)° and 178.39(9)°, respectively. ν(CO) of this complex is 2027 cm^{-1}.

There have been several literature reports of highly acidic dihydrogen complexes for which the pK_a's are known.[12] The heterolytic splitting of Si−H bond has also been observed by many.[13] Although the heterolytic activation of molecular hydrogen has been achieved in several systems, there have been only very few instances of generation of highly acidic η^2-H$_2$ directly from hydrogen gas and a metal fragment.[12g,12h,12i,13f,14] However, of these few, only three

systems are known to bring about the heterolytic activation of H−H and Si−H bonds in a parallel fashion.[13e,13f,13i]

In conclusion, the heterolytic activation of H−H and Si−H bonds has been achieved in a parallel fashion using complex **1**. We are currently exploring the potential of **1** in activating C−H bonds of certain alkanes heterolytically.

Supporting Information Available: Synthesis and characterization of the complexes, NMR stack plots of the reactions, X-ray data for the P(OH)$_3$ and CO complexes in CIF format, list of H-bonds, and ORTEP diagram of the CO complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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