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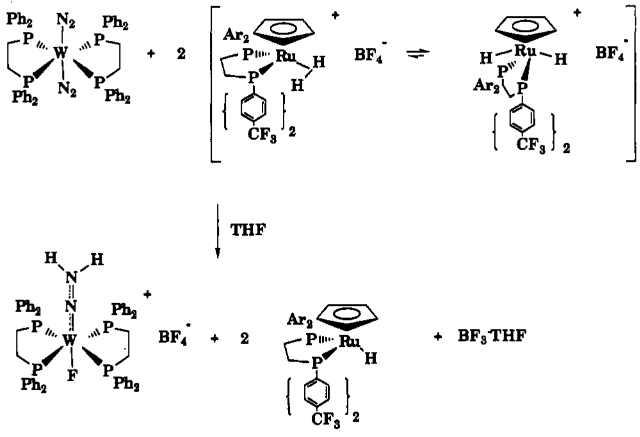
Communications

An Acidic η^2-Dihydrogen Complex Protonating Coordinated Dinitrogen

Interest in η^2-dihydrogen complexes[1,2] is turning from their structure and bonding to their modes of reactivity. An intriguing property of certain transition-metal complexes is that they can coordinate dihydrogen and turn it into a strong acid—the heterolytic cleavage of dihydrogen. Chinn and Heinekey have characterized two such acidic dihydrogen complexes, $[Re(C_5Me_5)(CO)(NO)(\eta^2\text{-}H_2)]^+$ and $[Ru(C_5Me_5)(CO)_2(\eta^2\text{-}H_2)]^+$, with pK_a values less than zero on the aqueous scale.[3] We have determined that the series of dihydrogen complexes $[Ru(C_5R_5)(\text{diphosphine})(\eta^2\text{-}H_2)]^+$ have pK_a values which range from 4.3 for complex **3** (R = H, diphosphine = $PR'_2CH_2CH_2PR'_2$, R′ = $p\text{-}CF_3C_6H_4$, dtfpe) to about 12 (R = Me, R′ = Me, dmpe) by use of equilibria with protonated tertiary phosphines of known pK_a.[4] Similarly the pK_a values for the complexes $[Ru(H)(H_2)(\text{diphosphine})_2]^+$ range from 9.0 (R′ = $p\text{-}CF_3C_6H_4$) to greater than 16 for complex **5** (R′ = Et, depe).[5] We report here that our most acidic dihydrogen complex **3** protonates coordinated dinitrogen in the complex $W(N_2)_2(\text{dppe})_2$ (**1**) (R′ = Ph, dppe) to give the hydrazido(2−) complex $[W(NNH_2)(F)(\text{dppe})_2]BF_4$ (**2**), whereas the least acidic one, complex **5**, does not. Complex **2** was originally prepared by reaction of **1** with $HBF_4{\cdot}Et_2O$ (pK_a < 0),[6] but certain very acidic carbonyl hydride complexes as the tetrafluoroborate salts also convert complex **1** to **2**.[7] Very acidic dihydrogen complexes can be prepared directly from $H_2(g)$ at 1 atm, ≤300 K,[3,5] and **1** is made by coordination of $N_2(g)$ at 1 atm, 293 K.[8] The present work demonstrates that the reaction of H_2 and N_2, when coordinated, is also possible under mild conditions.

The new, acidic dihydrogen complex **3**[9] was prepared by titrating a solution of the monohydride complex $Ru(C_5H_5)(H)(\text{dtfpe})$ (**4**)[10] in ether with HBF_4 until **3** had precipitated out quantitatively. The white solid was carefully recrystallized from CH_2Cl_2/ether to ensure complete removal of excess acid. Complex **3** exists in solution as a slowly (half-life of seconds) interconverting mixture of two tautomers, $[Ru(C_5H_5)(\text{dtfpe})(\eta^2\text{-}H_2)]^+$ (**3a**) and $[Ru(C_5H_5)(H)_2(\text{dtfpe})]^+$ (**3b**), in the ratio 1:1.6. A similar mixture of tautomers in ratio 1:2.0 has been reported for the slightly more electron-rich complex $[Ru(C_5H_5)H_2(\text{dppe})]^+$;[12] thus, the electron-withdrawing dtfpe[13] ligand shifts the equilibrium toward the dihydrogen form (relative to the "isosteric" dppe ligand), as might be expected. The complex $[Ru(C_5H_5)H_2(\text{dmpe})]^+$ has an even larger ratio of dihydrogen to dihydride forms (1:0.17), but this must be a steric effect.[14] The presence of the dihydrogen ligand in **3a** was verified by preparing the corresponding η^2-HD derivative of **3a**[15] and observing the 1:1:1 ^1H NMR resonance at −8.80 ppm with the coupling $^1J(H,D)$ = 25.3 HZ. The isotopomer $[Ru(C_5H_5)(H)(D)(\text{dtfpe})]^+$ gives a triplet at −8.67 ppm with $^2J(H,P)$ = 28.8 Hz.

Scheme I



The pK_a of **3** was estimated by observing the equilibrium of **4** and $[HP(p\text{-tol})_3]BPh_4$ by ^{31}P NMR spectroscopy (eq 1). In-

$$\mathbf{4} + [HP(p\text{-tol})_3]^+ \rightleftarrows \mathbf{3} + P(p\text{-tol})_3 \qquad (1)$$

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(9) $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 80.5 (s, $[CpRu(\eta^2\text{-}H_2)(\text{dtfpe})]^+$), 69.3 (s, $[CpRu(H)_2(\text{dtfpe})]^+$). ^1H NMR (CD_2Cl_2): δ −8.76 (br, $Ru(\eta^2\text{-}H_2)$), −8.61 (t, *J*(PH) = 28.8 Hz, RuH_2), 1.5–3.2 (m, CH_2), 4.92 (s, $CpRu(\eta^2\text{-}H_2)$), 5.58 (s, $CpRuH_2$), 7.6–8.1 (m, Ph). Anal. Calcd for $C_{35}H_{27}BF_{16}P_2Ru$: C, 45.43; H, 2.94. Found: C, 45.02; H, 2.97.

(10) **4** was prepared in a fashion similar to that for CpRuH(dppe).[11] $^{31}P\{^1H\}$ NMR (C_6H_6/C_6D_6): δ 92.6 (s). ^1H NMR (C_6D_6): δ −13.47 (t, *J*(PH) = 34.4 Hz, Ru–H), 1.6–1.8 (m, CH_2), 4.62 (s, Cp), 7.1–7.6 (m, Ph). Anal. Calcd for $C_{35}H_{26}F_{12}P_2Ru$: C, 50.19; H, 3.12. Found: C, 49.62, H, 3.14.

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(15) $[Ru(C_5H_5)(\text{dtfpe})(\eta^2\text{-}HD)]^+$ was prepared by reacting $Ru(C_5H_5)(H)(\text{dtfpe})$ (**4**) in ether with $HBF_4{\cdot}Et_2O$ in D_2O.

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tegration of the gated-{^{1}H}-decoupled ^{31}P resonances for the various species in equilibrium in CH_2Cl_2 gave equilibrium constants of 2.8 for **3a** in equilibrium with **4** and 3.9 for **3b**. Thus, the pK_a{Ru(η^2-H_2)} value for **3a** is estimated to be 4.3 on the basis of the pK_a value of 3.85 (aqueous scale)[16] for [HP(*p*-tol)$_3$]$^+$ whereas the pK_a{Ru(H)$_2$} value for **3b** is estimated to be 4.4.[17]

A 2-equiv amount of **3** reacts with 1 equiv of **1** in THF to give 2 equiv of **4** and 1 equiv of [W(NNH$_2$)(F)(dppe)$_2$]BF$_4$ (**2**)[6] according to Scheme I. The reaction occurs in less than 10 min and is quantitative as indicated by ^{31}P NMR spectroscopy. Thus, when **1** (45.5 ppm) is added to the solution of **3** in THF, resonances at 81.1 (**3a**) and 70.0 (**3b**) and 93.0 ppm (**4**, small) are replaced by just the resonance at 93.0 ppm (**4**) together with the appearance of a new resonance at 35.3 ppm (**2**, doublet with ^{183}W satellites, $^2J(P,F) = 41$ Hz, $^1J(P,W) = 288$ Hz).

No reaction occurs between **1** and 2 equiv of *trans*-[Ru(H)(η^2-H_2)($PEt_2CH_2CH_2PEt_2$)$_2$]BF$_4$ (**6**). The pK_a of the latter complex is estimated to be near 16, since its conjugate base, Ru(H)$_2$($PEt_2CH_2CH_2PEt_2$)$_2$, is protonated by neat EtOH, which has a pK_a of 15.8, to give **6** but is not protonated by ^{i}PrOH (pK_a ~16).[18] The pK_a of the related complex [Fe(H)(η^2-H_2)($PMe_2CH_2CH_2PMe_2$)$_2$]$^+$ has been estimated to be 15.8.[19]

Thus, the heterolytic cleavage of dihydrogen can lead to the protonation of coordinated dinitrogen when the dihydrogen/dihydride complex is sufficiently acidic. The dihydrogen form is expected to transfer protons more quickly than the dihydride form.[20] Methods to prepare complex **3** directly from H_2 gas are being investigated. We have recently found that a related complex, [Ru(H)(H_2)(dtfpe)$_2$]BF$_4$,[5] which can be prepared from H_2(g), also converts **1** into **2**, although in lower yield than the reaction involving **3**.

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Molecular Precursors for Indium Phosphide and Synthesis of Small III–V Semiconductor Clusters in Solution

The preparation and physical characterization of semiconductor clusters in the nanometer-size regime is currently attracting considerable attention.[1] While most studies in this area focus on II–VI semiconductors[2] (e.g. CdS, CdSe), the technological importance of III–V semiconductors (e.g. GaAs, InP)[3] makes an investigation of "quantum size effects" in these materials desirable.[4] We have previously reported the chemical conversion of the organometallic arsinogallane Cp*$_2$Ga–As(SiMe$_3$)$_2$ into small gallium arsenide clusters.[5] Herein we describe some results of related work on indium phosphide colloids.

Precursor molecules **1**–**4** containing covalently bound indium and phosphorus in a 1:1 ratio were synthesized by combining alkylindium chlorides R(R′)InCl with either P(SiMe$_3$)$_3$ or LiP(SiMe$_3$)$_2$ (see Scheme I).[6,7] Virtual coupling of the trimethylsilyl protons to two phosphorus nuclei in the ^{1}H NMR spectrum revealed the dimeric nature of the compounds in solution. The solid-state structure of the representative [Cp*(Cl)In(μ-P(SiMe$_3$)$_2$)]$_2$ (**I**)[8] was determined by X-ray diffraction (see Figure 1).[9] The molecule is a head-to-tail dimer and exhibits crystallographic inversion symmetry. Its In$_2$P$_2$ core is a nearly perfect square with an average In–P distance of 2.62 Å, slightly longer than the sum of the covalent radii (2.50 Å). The bulky Cp* ligands are situated trans to each other and are bonded to indium in a η^1-fashion. The five-membered ring shows the expected bond length alternation and angles of a localized cyclopentadiene. However, their rotation is rapid on the NMR time scale in solution and leads to observation of one and two Cp* resonances in the ^{1}H and ^{13}C spectra, respectively.

Addition of 3.0–5.0 equiv of methanol to solutions of precursors **1**–**4** in a closed vessel ultimately resulted in the precipitation of

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(9) Yellow rectangular prisms from pentane; monoclinic $\bar{P}2_1/n$; $a = 9.722$ (3) Å, $b = 18.073$ (5) Å, $c = 12.983$ (11) Å, $\beta = 97.9$ (3)°, and $Z = 4$; $R = 0.044$ and $R_w = 0.047$.

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