H/D Exchange Reactions of an Iridium Dithiol Complex

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Received March 19, 1993

Intramolecular protonation of a hydride ligand by an acidic co-ligand (LH in eq 1) to give an η^2-dihydrogen ligand is a reaction with very few examples.[1] This reaction and the reverse are

$$M(LH)(H)L_n \rightleftarrows M(\eta^2\text{-}H_2)L_{n+1} \quad (1)$$

important to the mechanisms of hydrogenation,[2,3] hydrogenolysis,[4-7] hydroformylation[8] and (Fe,Ni) hydrogenase[9,10] reactions. Such reactions have been postulated to explain intramolecular H/D exchange reactions in $[IrH(Cl)(NH_3)_2(PEt_3)_2]PF_6$[11] and $[IrH(H_2O)(bq)(PCy_3)_2]^+$ (bqH = 7,8-benzoquinoline).[12] We report a new exchange reaction involving an unprecedented chelating 1,3-propanedithiol ligand[13] in the complex $[Ir(H)_2(HS(CH_2)_3SH)(PCy_3)_2]BF_4$ (**1**, Cy = C_6H_{11}).[14] The acidic thiol protons of **1** ($pK_a \approx 9$) exchange much more rapidly than the hydride ligands with deuterium from MeOD. This allows a unique opportunity to measure the rate constant for intramolecular H/D transfer between thiol and hydride, a process which likely proceeds via an unobserved η^2-HD complex.

Complex **1** was prepared by the action of 1,3-propanedithiol and $HBF_4{\cdot}Et_2O$ on $IrH_5(PCy_3)_2$,[15,16] probably via the known complex $[Ir(H)_2(\eta^2\text{-}H_2)_2(PCy_3)_2]BF_4$.[12]

$$Ir(H)_5(PCy_3)_2 + HBF_4 + HS(CH_2)_3SH \rightarrow [Ir(H)_2(HS(CH_2)_3SH)(PCy_3)_2]BF_4 + 2H_2 \quad (2)$$

The formulation of **1** was determined by NMR spectroscopy and confirmed by FAB/MS and X-ray crystallography.[17] The virtual triplet for the α-carbons of the Cy groups shows that the PCy_3 ligands are trans.[18] The presence of a proton on each sulfur atom was established by the observation of (a) a ν(S-H) vibration in the IR spectrum and (b) a pseudoquintet in the ^1H NMR spectrum at 3.21 ppm (integral of 2) which disappears after addition of D_2O or CD_3OD. The pseudoquintet results from the thiol hydrogen coupling to two equivalent P atoms ($^3J_{HP}$ = 8.1 Hz, observed with homonuclear decoupling of the $SCH_2CH_2CH_2S$ protons) and two equivalent α-methylene protons on the dithiol ($^3J_{HH}$ = 7.4 Hz, observed with decoupling of the central methylene protons).

The pK_a of **1** is believed to be approximately 9 on the aqueous scale because **1** is deprotonated by PCy_3 (pK_a of conjugate acid is 9.7[19]), only slightly (2%) by CpRuH(dape) (pK_a 8.1[20,21]), and not at all by CpRuH(dppm) (pK_a 7.1[20,21]).[22] This represents a decrease of less than one unit from that of the free thiol.[23] The very little data in the literature concerning the reduction in pK_a of thiols upon coordination suggest that metal-to-ligand back-bonding, if present, prevents a large pK_a drop.[24]

Addition of excess CD_3OD to a CD_2Cl_2 solution of **1** results in **1**-d_2, (80% D at thiol, 2% D at hydride) after 4 min. H/D exchange reactions between MeOD and hydrosulfide complexes have been reported,[25,26] but this is the first example of such exchange with a bound thiol proton. Prolonged exposure to CD_3OD results in the deuteration of the hydride ligands, giving **1**-d_4. No exchange occurs between **1** and $CDCl_3$ or CD_2Cl_2. The chemical shift of the hydride proton of $[Ir(H)(D)(L)(PCy_3)_2]BF_4$ (L = 1,3-propanedithiol) is upfield of that of $[Ir(H)_2(L)(PCy_3)_2]BF_4$ by 0.022 ppm in CD_2Cl_2, because of an isotopic chemical shift.

The rate constant, k_1, of eq 3 for the intramolecular transfer of deuterons from the thiol to the hydride site of **1**-d_2 in CD_2Cl_2 (or the k_1 for the reverse reaction) was determined at 22°C to be $3 \pm 1 \times 10^{-4}$ s^{-1} for three different starting concentrations of **1**-d_2.[27] The most likely mechanism for this process is the reversible

$$[Ir(H)(DSR)]^+ \underset{k_1}{\overset{k_1}{\rightleftarrows}} [Ir(D)(HSR)]^+ \quad (3)$$

intramolecular protonation of a cis hydride by the thiol, forming

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(16) A suspension of $IrH_5(PCy_3)_2$ (270 mg, 0.35 mmol) in CH_2Cl_2 (40 mL) reacted with 1,3-propanedithiol (45 μL, 0.45 mmol) and $HBF_4{\cdot}Et_2O$ (120 μL, 0.41 mmol) to give a yellow solution. This was reduced in volume by vacuum evaporation to 4 mL after 10 min. Addition of Et_2O (20 mL), filtration, and reprecipitation from CH_2Cl_2/Et_2O produces white flakes of **1** (73%). IR (cm^{-1}, Nujol): 2227 (m, Ir–H), 2552 (m, S–H). ^1H NMR (200 MHz, CD_2Cl_2, δ): −18.45 (t, J = 16.5 Hz, 2H, Ir*H*), 1.53–2.07 (multi, 66H, C_6H_{11}), 2.48 (multi, 2H, $HSCH_2CH_2CH_2SH$), 2.86 (multi, 4H, $HSCH_2CH_2CH_2SH$), 3.21 (qn, J = 8.3 Hz, 2H, S*H*). ^{13}C NMR (CD_2Cl_2, δ): 24.45 (s, $HSCH_2CH_2CH_2SH$), 26.84 (s, Cδ of PCy_3), 27.69 (t, J(PC) = 4.8 Hz, Cγ), 30.13 (s, Cβ), 31.86 (s, $HSCH_2CH_2CH_2SH$), 37.35 (t, J(PC) = 13.7 Hz, Cα). ^{31}P NMR (CD_2Cl_2, δ vs H_3PO_4): 9.6. FAB/MS: calcd for $C_{39}H_{76}{}^{193}IrP_2S_2$, 863; observed, 863 ($M^+$), 584 ($M^+ - PCy_3$); Anal. Calcd for $C_{39}H_{76}BF_4IrP_2S_2$: C, 49.3; H, 8.1; S, 6.8. Found: C, 48.7; H, 8.0; S, 7.5.
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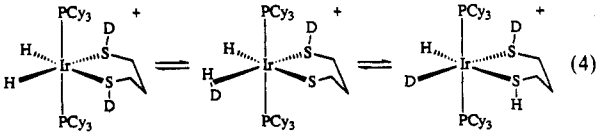
an η^2-HD complex (eq 4).[28] The rate constant for this reaction



(4)

would be independent of the concentration of **1**, which is consistent with our observations.

Evidence for such an intermediate is the observation of H/D exchange between **1**-d_4 and H_2 gas. Exposure of a CD_2Cl_2 solution of **1**-d_4 to H_2 gas results in equal increases in the intensity of the thiol proton and hydride peaks in the ^1H NMR spectrum, reaching 55% conversion after 3 h. The reverse reaction, the preparation of **1**-d_4 by reaction of D_2 gas with **1**, was also observed. The η^2-H_2 intermediate would be relatively stable with respect to H_2 loss because the estimated[29] electrochemical half-wave potential, $E_{1/2}$(Ir(IV)/Ir(III)), of the corresponding dinitrogen complex is 1.8, within the range for stable η^2-H_2 complexes. However its pK_a value must be less than that of **1**, i.e., pK_a <9; its predicted value is <11.[29] Related complexes, $[IrH(\eta^2\text{-}H_2)L(PCy_3)_2]^+$ (L = 2-mercaptopyridine[17] or bq[12]) have been observed.

We are still searching for a system in which the M(H)(HL) and M(η^2-H_2)(L) forms are observed simultaneously.

Note Added in Proof. Recently the existence of an equilibrium [Rh(H)(HSR)] ⇌ [Rh(H_2)(SR)] has been proposed to explain D_2/H^+ exchange catalyzed by [Rh(H)(CO)($^{bu}S_4$)]. Sellmann, D.; Käppler, J.; Moll, M. *J. Am. Chem. Soc.* **1993**, *115*, 1830.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council for funding this work.

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(27) The concentrations of SH and IrH protons were determined as a function of time by integration of their resonances in the ^1H NMR spectra. Concentrations calculated from an integrated rate expression for the first order reactions of eq 3 were fit to the data by an iterative procedure. This treatment neglects any kinetic isotope effects; these appear to be small because the equilibrium isotope effect for eq 3 is close to 1.

(28) A reviewer wondered whether the exchange could proceed via deprotonation of **1** by free PCy_3 to give a thiolate hydride complex which would then reductively eliminate, undergo H/D exchange and then oxidatively re-add. There is no evidence in the ^{31}P NMR spectrum for free PCy_3. There is no evidence in the ^1H NMR spectrum for the dissociation of PCy_3 from **1** considering that J_{HP} couplings to hydride and SH protons are observed.

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