II) confirm the requirement of one (S,Cl)-containing ligand (at a Ni–(S,Cl) distance of 2.29 Å) in addition to approximately five (N,O)-containing ligands to simulate the first-shell Ni EXAFS of the 2-ME-bound urease derivative. Although the improvement in f' upon addition of a Ni–(S,Cl) shell to the simulation for the 2-ME-bound derivative (fit 6, Table II) is less than a factor of 2 and could result from simply the increase in the number of parameters, we have attempted other fits, the results of which suggest that the (S,Cl)-containing ligand is required to fit the data. For example, providing the same additional parameters to fit the oxidized urease data does not result in improvement in f', whether this is from a (S,Cl) shell (fit 3) or an additional (N,O) shell (fit 4). Another two-shell fit of the data for the 2-ME-bound derivative (fit 7) using different (N,O) shells does result in f' improvement (suggesting that two separate shells are required for this derivative but not for the oxidized derivative), but the resulting Ni–(N,O) distance for the second shell (2.14 Å) is chemically unreasonable.

The simplest explanation of these curve-fitting results involves the average $Ni(N,O)_5(S,Cl)$ coordination sphere discussed above. The Ni–(S,Cl) Debye–Waller factor derived from EXAFS curve-fitting is similar to that of the $[(C_6H_5)_4P]_2[Ni(SC_6H_5)_4]$ model only for a coordination number of 1 (not 0.5), supporting the binding of one 2-ME thiolate to each nickel or one thiolate simultaneously binding both. The similar intensity of the 8332-eV peak in the native and 2-ME-bound derivatives (Figure 1b) indicates the same slight distortion from octahedral symmetry, suggesting that 2-ME binding is a simple ligand-exchange reaction.

The diamagnetism observed upon 2-ME treatment of urease[4] thus correlates with direct binding of 2-ME to Ni(II) through the thiolate sulfur. Square-planar or substantially tetragonally distorted ligand fields are required for mononuclear Ni(II) compounds to adopt low-spin (diamagnetic) electronic configurations. Our edge data preclude such a large distortion from octahedral symmetry for the urease Ni(II) ions since the transition at 8336 eV, the characteristic signature of tetragonal geometries,[8] is not observed.

The alternative explanation for the diamagnetic ground state involves creation of strong antiferromagnetic coupling between the two high-spin ($S = 1$) Ni(II) ions upon 2-ME binding. Our structural results are fully consistent with the 2-ME thiolate sulfur bridging the two Ni(II) ions and mediating this antiferromagnetic exchange interaction.[13] In such a model, the competitive nature of the 2-ME inhibition would imply a substrate-binding site involving both Ni(II) ions. Future XAS studies will target identification of the Ni···Ni scattering expected from such an inhibitor-bridged binuclear site.

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(13) We cannot at this time rule out the possibility that one 2-ME molecule binds to each Ni(II) and that the strong magnetic coupling results from some indirect effect causing a large increase in the weak intrinsic magnetic interaction between the Ni(II) ions found[4] in native urease.

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Comparing the Acidity of Hydride and η^2-Dihydrogen Complexes of Transition Metals

The need for the measurement of the acidity of metal hydride complexes has been stressed, and the pK_a values for a number of carbonyl metal hydride complexes have been determined.[1] There are scattered reports that the proton of the dihydrogen ligand is acidic: for example, in $[CpRu(\eta^2\text{-}H_2)(dmpe)]^+$ (dmpe = $PMe_2CH_2CH_2PMe_2$),[2] $[IrH(\eta^2\text{-}H_2)(bq)(L)_2]^+$ (bq = 7,8-benzoquinolinate; L = PPh_3, PCy_3),[3] $[MH(\eta^2\text{-}H_2)(dppe)_2]^+$ (M = Ru, Fe; dppe = $PPh_2CH_2CH_2PPh_2$),[4] $[FeH(\eta^2\text{-}H_2)(dmpe)_2]^+$,[5] $[Cp^*Ru(CO)_2(\eta^2\text{-}H_2)]^+$,[6] and $[Cp^*Re(CO)(NO)(\eta^2\text{-}H_2)]^+$.[6] The η^2-dihydrogen ligand is known to be deprotonated in preference to the terminal hydride in the complex $[IrH(\eta^2\text{-}H_2)(bq)(L)_2]^+$ [3] and in the mixture of complexes $[CpRu(\eta^2\text{-}H_2)(dmpe)]^+$ and $[CpRu(H)_2(dmpe)]^+$.[2] We report here a simple method for the ranking of the acidity of a range of η^2-dihydrogen and dihydride compounds $[CpRu(\eta^2\text{-}H_2)(dppm)]^+$ (dppm = $PPh_2CH_2PPh_2$),[7] $[CpRuH_2(dppe)]^+$,[7,8] $[CpRu(H)_2(dppp)]^+$ (dppp = $PPh_2CH_2CH_2CH_2PPh_2$),[7] $[CpRu(H)_2(PPh_3)_2]^+$,[9] and $[MH(\eta^2\text{-}H_2)(dppe)_2]^+$ (M = Fe, Ru, Os).[10] We also describe how approximate pK_a values can be obtained.

The method involves the determination of the equilibrium constant K_{eq} for the following reaction by NMR spectroscopy:

$$MH + M'H_2^+ \rightleftarrows MH_2^+ + M'H \qquad (1)$$

We choose dichloromethane as the solvent because it is noncoordinating and it dissolves the neutral and ionic metal complexes without reaction. Although CH_3CN is the preferred solvent for hydride pK_a determinations,[1,2] it displaces H_2 from most dihydrogen complexes including the ones described in this work. In a typical experiment appropriate amounts of a neutral compound and an ionic complex were loaded into an NMR tube and then CD_2Cl_2 was added. After a period was waited to let the system reach equilibrium,[11] a ^1H NMR spectrum was recorded; a typical example is shown in Figure 1. By measuring the intensity of the hydride resonances, one can calculate the relative

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(11) The equilibrium is usually reached in less than 30 min. For example, the K values obtained 30 min or 4 h after mixing the reactants did not differ appreciably.

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Table I. Determination of pK_a Values (Aqueous Scale Extrapolated from Nonaqueous Solvent Systems) by Use of $HPCy_3^+$ as a Standard (pK_a = 9.70) (BF_4^- Counterions, Except for $HPCy_3^+$ (BPh_4^-))

reactant				
$M'H_2^+$	MH	K_{eq}[a]	MH_2^+ product	pK_a of MH_2^+
$[CpRu(H)_2(PPh_3)_2]^+$	$MH_2(dppe)_2$[b]	>50[c]	$[MH(H_2)(dppe)_2]^+$	>10
$[CpRu(H)_2(PPh_3)_2]^+$	CpRuH(dppp)	1.34	$[CpRu(H)_2(dppp)]^+$	8.4
$HPCy_3^+$[d]	$CpRuH(PPh_3)_2$	0.038	$[CpRu(H)_2(PPh_3)_2]^+$	8.3
$[CpRu(H_2)(dppm)]^+$	CpRuH(dppe)	1.71	$[CpRuH_2(dppe)]^+$	7.3[e]
$[CpRu(H)_2(PPh_3)_2]^+$	CpRuH(dppm)	0.068	$[CpRu(H_2)(dppm)]^+$	7.1

[a] ±5% error in K_{eq}, pK_a. [b] M = Fe, Ru, Os. [c] Lower-bound estimate; too large to measure. [d] See eq 4 for this pK_a determination. [e] Likely to be pK_a of $[CpRu(H_2)(dppe)]^+$ form.

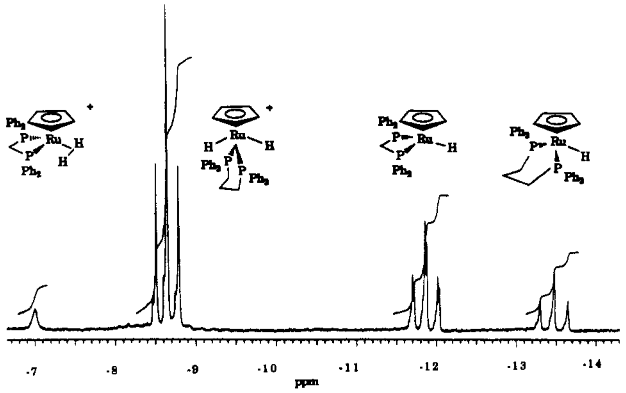

Figure 1. Hydride-region ^1H NMR spectrum (200 MHz) for the mixture of CpRuH(dppp) and $[CpRu(\eta^2\text{-}H_2)(dppm)]BF_4$ in CD_2Cl_2.

concentrations of the hydride complexes in solution and therefore the equilibrium constants (Table I).

The internal consistency of these equilibrium constants was confirmed by the fact that very similar values were obtained when the equilibrium was approached from the left or right side of eq 1. For example, for eq 2, an equilibrium constant of 18.4 was

$$[CpRu(H_2)(dppm)]^+ + CpRuH(dppp) \rightleftarrows CpRuH(dppm) + [CpRu(H)_2(dppp)]^+ \quad (2)$$

obtained if $[CpRu(\eta^2\text{-}H_2)(dppm)]BF_4$ and CpRuH(dppp) were mixed and 19.2 was obtained if CpRuH(dppm) and $[CpRu(H)_2(dppp)]PF_6$ were mixed. In addition, the equilibrium constant K_{eq3} for eq 3 is related to those of eq 2 and entry 2 of Table I:

$$[CpRu(H_2)(dppm)]^+ + CpRuH(PPh_3)_2 \rightleftarrows CpRuH(dppm) + [CpRu(H)_2(PPh_3)_2]^+ \quad (3)$$

i.e. $K_{eq3} = K_{eq2}/K_{entry2} = 18.8/1.34 = 14.0$. This is close to the experimentally determined value of 14.7 for K_{eq3}. Thus, the error in K_{eq} values by this method is less than 5%. The reaction of $[CpRu(H)_2(PPh_3)_2]^+$ with any of the complexes *cis*-$MH_2(dppe)_2$ went rapidly to completion so that only a lower bound on the pK_a of the complexes $[MH(H_2)(dppe)_2]^+$ has been obtained to date (see below). We were unable to rank the acidity of complexes $[MH(H_2)(dppe)_2]^+$ in dichloromethane by reaction with a dihydride $M'H_2(dppe)_2$ (M, M' = Fe, Ru, Os) because reaction of the dihydride with CD_2Cl_2 was faster (minutes) than the proton-transfer reaction (hours).

To estimate the pK_a values of the ionic hydride complexes, we also determined the equilibrium constants for the reactions of $[CpRu(H)_2(PPh_3)_2]^+$ with PR_3 (R = Cy, *n*-Bu) (eq 4). The

$$[CpRu(H)_2(PPh_3)_2]^+ + PR_3 \rightleftarrows CpRuH(PPh_3)_2 + HPR_3^+ \quad (4)$$

aqueous pK_a values of $HPCy_3^+$ (9.70) and $HP(n\text{-}Bu)_3^+$ (8.43) have been previously determined by nonaqueous titrimetry in CH_3NO_2 and then extrapolated to the values for aqueous solution.[12] Compared with the case for the proton-transfer reactions, these phosphorus donor bases undergo substitution reactions at a negligible rate with the complexes $[CpRu(H)_2(PPh_3)_2]^+$ and $CpRuH(PPh_3)_2$. The equilibrium constant for eq 4 when R = Cy was 26, and the pK_a value for $[CpRu(H)_2(PPh_3)_2]^+$ was therefore calculated to be 8.3; for eq 4 when R = *n*-Bu, K_{eq} = 0.65, and hence pK_a($[CpRu(H)_2(PPh_3)_2]^+$) = 8.6. Thus, the two bases give values that fall within the error of the method (errors of peak integration, extrapolation of pK_a values between solvent systems, etc.). It should be noted that the pK_a values undergo approximately equal changes in relation to the values in H_2O (provided that no leveling occurs) for groups of chemically related substances.[13]

If we use $HPCy_3^+$ as a "standard", the pK_a values of the hydride complexes in aqueous solution should be close to the values shown in Table I.

Therefore, the acidity of the ionic hydride complexes can be ordered as $[CpRu(\eta^2\text{-}H_2)(dppm)]^+ > [CpRu(\eta^2\text{-}H_2)(dppe)]^+ \gg [CpRu(H)_2(PPh_3)_2]^+ > [CpRu(H)_2(dppp)]^+ \gg [MH(\eta^2\text{-}H_2)(dppe)_2]^+$. Thus, for similar types of complexes, the proton of the η^2-dihydrogen ligand is 1 order of magnitude more acidic than that of a hydride in an analogous complex (here it is assumed that the η^2-H_2 form of the dppe complex is responsible for its acidity). Note that the pK_a of the η^2-H_2 form of $[CpRu(H_2)(dmpe)]^+$ in CH_3CN was reported to be 17.6,[2] which translates into approximately 9.8 on the aqueous scale.[14] However, the ancillary ligands play an important role in determining the electron richness and hence the relative acidity of metal hydride complexes. Thus, the complexes $[MH(\eta^2\text{-}H_2)(dppe)_2]^+$ are more electron rich and less acidic than either the η^2-H_2 or $(H)_2$ forms of the cyclopentadienyl complex $[CpRuH_2(dppe)]^+$. The determination of the relative acidities of the complexes of the type $[MH(H_2)(L)_2]^+$ (M = Fe, Ru, Os; L = diphosphine) is in progress.

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A New Ortho-Metalated Dichloro-Bridged Complex of Iridium(III) with 2,2′-Bipyridine: $[\{Ir(bpy\text{-}C^3,N')(bpy\text{-}N,N')Cl\}_2][Cl]_2$

Combination of iridium chlorides with 2,2′-bipyridine under controlled conditions results in the formation of a novel ortho-metalated dichloro-bridged dimer. The product composition of