5404 *Inorg. Chem.* **2000,** *39,* 5404−5406

Observation of a Large Coupling of a Bound Dihydrogen Ligand to Phosphorus Ligands in *trans*-$[(dppe)_2Ru(\eta^2\text{-}H_2)(PF(OMe)_2)][BF_4]_2$ Complex[†]

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Received April 13, 2000

Introduction

Ever since the discovery by Kubas and co-workers of the first transition metal dihydrogen complex $(P^iPr_3)_2W(\eta^2\text{-}H_2)(CO)_3$,[1] a plethora of H_2 complexes have been prepared and characterized. A large number of different coligands have been employed in such studies.[2] ^1H NMR spectroscopy has proven to be a valuable tool for the characterization of an intact H−H bond in these derivatives.[3] In general, the observation of rapid relaxation of the H_2 ligand (short spin−lattice relaxation time, T_1) and a large H−D coupling constant in the partially deuterated complex has been considered conclusive evidence for a bound dihydrogen ligand. Earlier, it has been shown both experimentally and theoretically[4] that the ability of dihydrogen to coordinate in an η^2-manner or to oxidatively add to a metal center depends to a great extent on the electronic factors of the metal and the ancillary ligands.[2c]

A large number of dihydrogen complexes that have been prepared to date possess phosphorus coligands. It was earlier reported that coupling constants of bound H_2 with adjacent phosphorus nuclei in the complex are generally much smaller than those observed in comparable hydride complexes.[2c,d]

Bianchini and co-workers reported cationic rhodium and cobalt complexes $[(PP_3)Rh(H_2)]^+$ and $[(PP_3)Co(H_2)]^+$ ($PP_3 = P(CH_2CH_2PPh_2)_3$) in refs 5 and 6, respectively. Both of these species have been formulated as complexes possessing intact H−H bonds based on the observation of relatively short spin−lattice relaxation times, T_1 minima for the hydride ligands (170 ms for the rhodium complex (THF-d_8, 303 K, 80 MHz) and 19 ms for the cobalt complex (THF-d_8, 203 K, 300 MHz)), and H−D coupling constants ($J(H,D) = 18$ and 28 Hz for the rhodium and the cobalt complexes, respectively). In addition, they also reported coupling constants $J(H,P)$ of 67 Hz for rhodium and 27−31 Hz for the cobalt derivative. In fact those two reports were the first claims of substantial coupling of a bound dihydrogen ligand with a phosphorus nucleus.

Heinekey and co-workers[7] reinvestigated the NMR spectra of these two complexes, and on the basis of their results, they concluded that the dihydrogen was actually oxidatively added and not "side-on" bound. There have been few other reports in the literature of substantial coupling of a bound dihydrogen (H_2 or HD) ligand to phosphorus coligands.[8]

During the course of an investigation that we recently initiated on the heterolytic activation of dihydrogen using certain ruthenium complexes, we prepared and characterized dihydrogen complexes wherein the ancillary ligands are exclusively phosphorus-based ones. The complexes that we prepared are of the type *trans*-$[(dppe)_2Ru(\eta^2\text{-}H_2)(L)][BF_4]_2$ (dppe = $Ph_2CH_2CH_2PPh_2$; L = phosphite or phosphine). The objective was to study how sensitive the properties of the dihydrogen complexes would be to the changes in the steric as well as the electronic properties of the *trans*-phosphorus ligand. We have observed for the first time a large coupling of about 50 Hz between a bound dihydrogen and a *trans*-phosphorus ligand.

Experimental Section

General Procedures. All the reactions were carried out under Ar at room temperature using standard Schlenk and inert atmosphere techniques unless otherwise specified. Solvents for the reaction that involved the preparation of dihydrogen complex were thoroughly saturated with either Ar or H_2 just before use. The ^1H and ^{31}P NMR spectral data were obtained using AMX Bruker 400 MHz instrument. Variable temperature proton T_1 measurements were carried out at 400 MHz in the temperature range 298−203 K in CD_2Cl_2 using the inversion recovery method (180°−τ−90° pulse sequence at each temperature).[3] ^{31}P NMR chemical shifts have been measured relative to 85% H_3PO_4, while ^{19}F NMR spectra were recorded with respect to $CFCl_3$.

Preparation of *trans*-$[(dppe)_2Ru(\eta^2\text{-}H_2)(PF(OMe)_2)][BF_4]_2$ (2). A 5 mm NMR tube with a septum was charged with 25 mg of *trans*-$[(dppe)_2Ru(H)(PF(OMe)_2)][BF_4]$[9] (**1**) and was dissolved in CD_2Cl_2 (0.7 mL). It was then subjected to three freeze−pump−thaw cycles, after which time argon gas was introduced. Upon addition of excess (ca. 20 equiv) 54% $HBF_4{\cdot}OEt_2$, an orange solution consisting of the dihydrogen complex (**2**) along with a small amount of the starting hydride complex (**1**) was obtained. Complete conversion of the hydride to the dihydrogen complex required ca. 30 equiv of $HBF_4{\cdot}OEt_2$. The sample was analyzed by NMR spectroscopy. ^1H NMR (CD_2Cl_2, 298 K): δ −5.12 (d, 2H, η^2-H_2, $J(H{-}P_{trans}) = 50$ Hz), 2.75 (br m, 4H, $Ph_2PCH_2CH_2PPh_2$), 3.04 (br m, 4H, $Ph_2PCH_2CH_2PPh_2$), 3.23 (d, 6H, $PF(OMe)_2$, $J(H,P) = 11.6$ Hz), 6.27−7.31 (m, 40H, $Ph_2PCH_2CH_2PPh_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 48.56 (d, 4P, *dppe*, $J(P,P) = 43.3$ Hz), 125.29 (d qnt, 1P,

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[†] Dedicated to our beloved colleague, Prof. S. S. Krishnamurthy on the occasion of his 60th birthday.

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10.1021/ic000419q CCC: $19.00

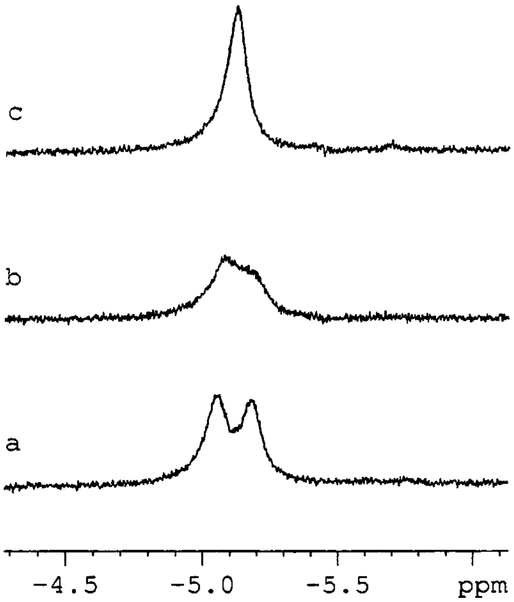

Figure 1. (a) ^{1}H NMR spectrum (hydride region) of *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(PF(OMe)$_2$)][BF$_4$]$_2$ complex (400 MHz, 298 K) in CD$_2$Cl$_2$. (b) ^{1}H{selective ^{31}P, dppe} spectrum (hydride region). (c) ^{1}H{selective ^{31}P, PF(OMe)$_2$} spectrum (hydride region).

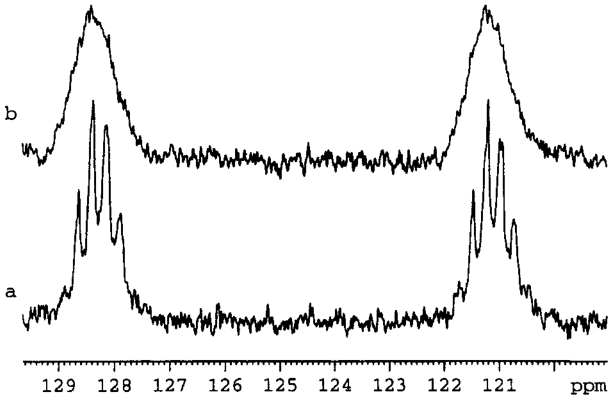

Figure 2. (a) ^{31}P{^{1}H} spectrum (PF(OMe)$_2$ region shown only). (b) ^{31}P spectrum showing ^{1}H coupling (PF(OMe)$_2$ region shown only).

*P*F(OMe)$_2$, J(P,F) = 1158.2 Hz). ^{19}F{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ 73.97 (d, 1F, P*F*(OMe)$_2$), −29.67(br s, 8F, 2B*F*$_4^-$).

Observation of *trans*-[(dppe)$_2$Ru(η^2-HD)(PF(OMe)$_2$)][BF$_4$]$_2$ (3). A CD$_2$Cl$_2$ solution of *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(PF(OMe)$_2$)][BF$_4$]$_2$ (**2**) in a 5 mm NMR tube was purged with D$_2$ gas at a steady rate for ca. 10 min. The HD isotopomer formed was observed by ^{1}H NMR spectroscopy. The H−D coupling constant was found to be 29 Hz.

Results and Discussion

The protonation of *trans*-[(dppe)$_2$Ru(H)(PF(OMe)$_2$)][BF$_4$] (**1**) using excess HBF$_4$·OEt$_2$ in CD$_2$Cl$_2$ results in the dihydrogen complex *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(PF(OMe)$_2$)][BF$_4$]$_2$ (**2**) along with a small amount of the unreacted starting hydride complex. The ^{1}H NMR spectrum shows a broad doublet in the hydride region at δ −5.12 ppm (see Figure 1). The separation between the two peaks of this doublet corresponds to 50 Hz. We believe that the splitting of the broad signal of the dihydrogen ligand could be due to coupling with the *trans*-phosphorus ligand. The ^{31}P{^{1}H} NMR spectrum gave a doublet of quintets centered at 125.29 ppm (see Figure 2) corresponding to the phosphite phoshorus in addition to the doublet at 48.56 ppm for the dppe phosphorus. The separation between the two quintets (J(P,F)) is equal to 1158.2 Hz. From the ^{31}P NMR spectral data it is clear that all four dppe phosphorus atoms are equivalent and that they are in a plane, whereas the phosphite and the dihydrogen ligands occupy the fifth and the sixth coordination sites, respectively, in an idealized octahedral geometry.

To establish that an intact H−H bond is present in the complex, we carried out variable temperature T_1 measurements. We obtained a T_1 (minimum) of 16.6 ms (400 MHz) at 268 K. By fitting the equations that describe the dominant dipolar relaxation mechanism to the variable temperature T_1 data as described earlier,[10] we obtained a calculated T_1 (minimum) of 16.94 ms, an excellent agreement with the experimental value. The H−H distances have been calculated from the T_1 data by the method of Halpern and co-workers[11] and found to be 1.08 and 0.86 Å for slow and fast rotation regimes, respectively. Further evidence for the bound dihydrogen ligand was provided by the H/D partial exchange experiments and the measurement of the J(H,D). The η^2-HD ligand of *trans*-[(dppe)$_2$Ru(η^2-HD)(L)][BF$_4$]$_2$ has been observed in the ^{1}H NMR spectrum, which is quite complex because of the coupling of the proton (of η^2-HD) with the phosphorus and in turn with the deuterium. The spectrum was obtained without nullifying the η^2-H$_2$ resonance, adding to the complexity of the signal. The J(H,D) has been found to be 29 Hz. The *doublet* that was obtained for the η^2-H$_2$ ligand is now further split into a doublet of triplets because of H−D coupling. Gusev et al.[12] brought out a correlation of the H−H distances calculated from J(H,D) and T_1 (minima) and $\Delta G^\ddagger$ for the loss of H$_2$ ligand from the metal center. The H−H bond length that has been calculated in our complex from J(H,D)[13] was found to be 0.95 Å. This distance could be interpreted as though it is consistent with the longer distance calculated from the T_1 data or is a value between the distances calculated using fast and slow spinning regimes of the H$_2$ ligand. Thus, this complex differs from several other earlier complexes (of the general formula [(P−P)$_2$M(H)(η^2- H$_2$)]$^+$) studied by Morris and co-workers.[10,14] In those cases, the H−H distances were found to be consistent only with the distances obtained using the fast-spinning approximation of H$_2$ (0.86−0.90 Å). Morris and Wittebort[15] suggested that the H−H distances calculated from J(H,D) values that fall between the values obtained from T_1 (min) slow and fast data indicate that either torsional libration or fast hopping significantly influences the relaxation process. There are several complexes reported in the literature where such a situation has been observed.[15]

To show that the *doublet* obtained for the dihydrogen ligand in the ^{1}H NMR spectrum is due to coupling with the *trans*-phosphorus, we recorded the ^{1}H NMR spectrum of the sample in CD$_2$Cl$_2$, selectively decoupling the *cis*-phosphorus atoms (dppe phosphorus atoms) using the globally optimized alternating phase rectangular pulses (GARP) decoupling sequence.

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Although the splitting pattern of the *doublet* was not lost, slight broadening of the signal took place with the coupling constant remaining the same (50 Hz) (see Figure 1). Upon selective decoupling of the *trans*-phosphite phosphorus nucleus, a singlet was obtained whose line width at half-maximum ($\Delta\nu_{1/2}$) is 33 Hz (see Figure 1). We have also examined the ^{31}P NMR spectral details. The proton-coupled ^{31}P NMR spectrum shows broadening of the resonances due to the phosphite phosphorus, and the multiplicity is lost (see Figure 2). This is due to the introduction of the coupling of the dihydrogen with the phosphite phosphorus (J(H,P$_{\text{trans}}$) = 50 Hz) that is already split by the dppe phosphorus atoms (J(P,P) = 43.2 Hz), resulting in overlapping of the signals. However, the signal due to the dppe phosphorus nuclei that appears as a doublet in the ^{31}P{^{1}H} NMR spectrum remains intact as a doublet although slight broadening takes place. This slight broadening could be a result of the coupling of the dppe phosphorus nuclei with the dihydrogen ligand that is perhaps less than 5−7 Hz to be distinctly observable.

It has been found earlier that phosphites exhibit larger couplings to other nuclei than phosphines in metal complexes.[16] This has been attributed to an increased “s” character in the bonding orbitals of phosphite complexes compared to those in phosphines. The presence of the most electronegative F substituent on the phosphorus in our complex results in further enhancement of the “s” character of the bonding orbitals if it is assumed that the coupling is dominated by the Fermi contact term.[16a] This accounts for the large J(H,P$_{\text{trans}}$) observed in this work compared to previously observed J(H,P) for phosphine complexes.

Conclusion

The short T_1 value combined with a J(H,D) of 29 Hz in the η^2-HD isotopomer of *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(PF(OMe)$_2$)][BF$_4$]$_2$ complex establishes the H−H intact bond without any ambiguity. We have observed significant coupling of the dihydrogen ligand with the *trans*-phosphorus ligand of J(H,P) = 50 Hz.

Acknowledgment. Financial support from the Council of Scientific and Industrial Research, India is gratefully acknowledged. We thank the Sophisticated Instruments Facility, Indian Institute of Science for the NMR spectra.

Supporting Information Available: The variable temperature T_1 data (observed and calculated) of the dihydrogen ligand of *trans*-[(dppe)$_2$Ru(η^2-H$_2$)(PF(OMe)$_2$)][BF$_4$]$_2$ complex and the hydride region of the ^{1}H NMR spectrum of *trans*-[(dppe)$_2$Ru(η^2-HD)(PF(OMe)$_2$)][BF$_4$]$_2$ and the ^{31}P{^{1}H} and proton-coupled ^{31}P NMR spectra (dppe phosphorus) of the dihydrogen complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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