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Structure and H_2-Loss Energies of $OsHX(H_2)(CO)L_2$ Complexes (L = P(*t*-Bu)$_2$Me, P(*i*-Pr)$_3$; X = Cl, I, H): Attempted Correlation of ^1J(H−D), T_{1min}, and $\Delta G^{\ddagger}$

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^1J(H−D), T_{1min} and k_1 for H_2 dissociation from $OsHX(H_2)(CO)L_2$ have been measured for X = Cl, I, H (L = P(*t*-Bu)$_2$Me or P(*i*-Pr)$_3$), as well as for $OsCl_2(H_2)(CO)(P(i\text{-}Pr)_3)_2$. For comparison, new data (including previously unobserved coupling constants) have been reported for $W(HD)(CO)_3(P(i\text{-}Pr)_3)_2$. A comprehensive consideration of T_{1min} data for over 20 dihydrogen complexes containing only 1−2 phosphines *cis* to H_2, together with a consideration of the shortest "conceivable" H−H distance for H_2 bound to a d^4 or d^6 metal, is used to argue that the "fast spinning" model is not appropriate for determining *r*(H−H) in such complexes. Regarding $OsHX(H_2)(CO)L_2$, the stronger electron-donor (lighter) halide, when *cis* to H_2, facilitates loss of H_2. The complete absence of π-donor ability when X = H renders H_2 loss most difficult. However, a π-donor *trans* to H_2 also makes H_2 loss unobservable. Within the series of isoelectronic, structurally analogous Os complexes, a longer H−H bond shows a larger $\Delta G^{\ddagger}$ for H_2 loss. However, this correlation does not continue to $W(H_2)(CO)_3(P(i\text{-}Pr)_3)_2$, which has *r*(H−H) comparable to that of OsH(halide)$(H_2)(CO)(P(i\text{-}Pr)_3)_2$, but a significantly higher $\Delta G^{\ddagger}$. This may originate from lack of a π-donor ligand to compensate as H_2 leaves W.

Introduction

Many molecules $OsH_4L(PR_3)_2$ have properties consistent with classical $Os^{IV}(H)_4$ structures.[1] $Os(H)_4(PMe_2Ph)_3$[2] has been shown by neutron crystallography to contain no dihydrogen ligand. The molecule of formula $OsH_4(CO)L_2$, described[3] as a "tetrahydride" and as containing Os(IV), is of interest since the presence of a π-acid CO ligand is expected to favor η^2-H_2 ligation. $OsH_4(CO)L_2$ (L = P(*i*-Pr)$_3$ or P(*t*-Bu)$_2$Me) has been widely used as a hydrogen transfer catalyst,[4] and it has been postulated to lose H_2 to give transient $OsH_2(CO)L_2$.[5] We report here new evidence that $OsH_4(CO)L_2$ is in fact a dihydrogen complex, along with kinetic parameters on its loss of H_2.

In order to attempt some general correlation of T_{1min}, ^1J(H−D), and $\Delta G^{\ddagger}$ for *loss* of H_2 with the identity of the ligand X in $OsHX(H_2)(CO)L_2$, we have measured all of these parameters for a series of molecules of this type. These molecules have the advantage that H_2 is *trans* to H, and thus intramolecular H/H_2 site exchange is slow (except X = H) on the ^1H NMR time scale below 25 °C. Consequently, dynamic (fluxional) averaging of spectroscopic parameters does not impede direct determination of T_{1min} and ^1J(H−D). This has led us into an evaluation of both the T_1 and T_2 relaxation data for these complexes and of the entire matter of attempting to derive the H/H distance within a dihydrogen ligand from the T_{1min} value. This, in turn, has led us to do a more thorough study of these NMR parameters for $W(H_2)(CO)_3(P(i\text{-}Pr)_3)_2$. This molecule, the earliest example of a dihydrogen complex, contains one of the shortest and most reliably established H/H distances. As will be seen, this is a situation which has special significance for deciding the suitability of currently competing methods for extracting *r*(H−H) from T_{1min}. This point is of critical importance since the field of H_2 complexes suffers from the reporting of H/H distances both with and without a "spinning correction". Without an ability to select which data processing model is correct, the resulting H/H distances, which differ by ∼0.2 Å, are at best of limited value.

Results

Synthesis and Characterization of $OsH_4(CO)L_2$ Species. We have synthesized $OsH_4(CO)L_2$ (L = P(*t*-Bu)$_2$Me) by the literature method (eq 1).[4] We have also synthesized it by two

$$OsH(BH_4)(CO)L_2 \xrightarrow[\Delta]{i\text{-PrOH}} OsH_4(CO)L_2 + ... \tag{1}$$

other methods, which involve hydrogenolysis of the Os−C bonds of either of the two unsaturated molecules[6] shown in eq 2. These reactions are complete in the time of mixing in pentane or benzene solvent and 1 atm of H_2.

$$OsH(R)(CO)L_2 + 2H_2 \rightarrow OsH_4(CO)L_2 + RH \tag{2}$$

$$R = Me, Ph$$

The 300 MHz ^1H NMR spectrum of $OsH_4(CO)(P(t\text{-}Bu)_2Me)_2$ shows a hydride triplet (J_{HP} = 10.8 Hz) at 20 °C. The P*Me* signal is a virtual triplet, consistent with *trans* phosphines. Only one *t*-Bu virtual triplet is seen, indicating a molecular plane of symmetry containing the POsP axis, either real or time-averaged;

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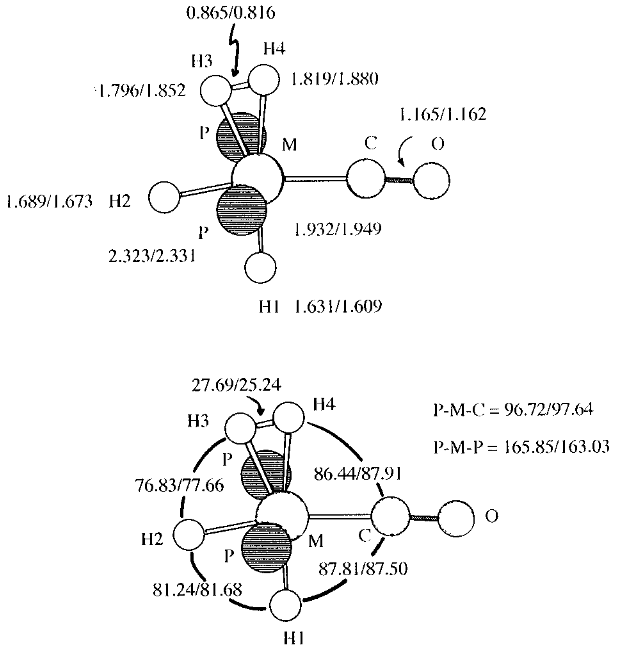
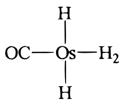
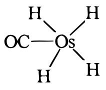


Figure 1. Optimized structures for ground state MH$_4$(CO)(PH$_3$)$_2$ (M = Os, Ru). Distances are in Å, top drawing; angles are in degrees, bottom drawing. All distances are from M to indicated atom, unless otherwise noted. The first value in any pair is for Os, the second for Ru.

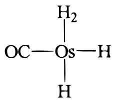
this mirror plane causes the two potentially diastereotopic *t*-Bu groups on a single phosphorus to be equivalent by ^{1}H NMR at 20 °C. Attempts to decoalesce the hydride resonance in a mixed CDFCl$_2$/CDF$_2$Cl solvent show only broadening of the −8 ppm hydride signal down to −140 °C. At −140 °C, this resonance has a half-width of 500 Hz, but decoalescence was not achieved. A T_1(min) value of 24 ± 1 ms (300 MHz) was measured at −75 °C, which is sufficient to rule out classical structure **B** (*trans* phosphine ligands lie out of the page in **A**−**C**, and are not drawn). The structure of RuH$_4$(CO)(P(*i*-Pr)$_3$)$_2$ is established with certainty to be as in **C**.[7]



A



B



C

Since the ^{1}H NMR spectrum could not be decoalesced, the choice between **A** and **C** for Os and for Ru was pursued through *ab initio* DFT calculations. Optimization was done with the Becke 3LYP method and showed a ground state for MH$_4$(CO)(PH$_3$)$_2$ (M = Ru and Os) in which an H$_2$ ligand (r(H−H) is calculated to be 0.87 Å for Os and 0.82 Å for Ru) lies *trans* to a hydride (**C**). As shown in Figure 1, M−H *trans* to H$_2$ is shorter than M−H *trans* to CO and the M−H (of H$_2$) distances are longer for Ru than for Os. On the basis of separate optimization of the 16-electron M(H)$_2$(CO)(PH$_3$)$_2$ species and H$_2$, the M−(H$_2$) bond dissociation energy (without zero point energy correction) is larger for Os (18.9 kcal/mol) than for Ru (14.0 kcal/mol), in agreement with the less stretched H−H distance in the latter. The preferred conformation of H$_2$ is found to be when the H−H vector eclipses the Os−H bond (i.e., lies in the *xz* plane). However, the barrier to rotation is calculated to be very small (0.54 kcal/mol for Os and 0.93 kcal/mol for Ru).

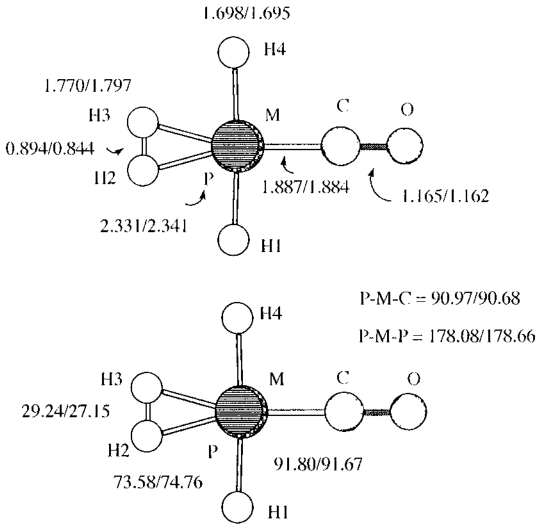
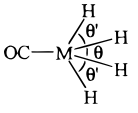


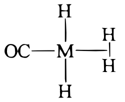
Figure 2. Optimized transition states for hydride exchange in MH$_4$(CO)(PH$_3$)$_2$. Distances are in Å, top drawing; angles are in degrees, bottom drawing. All distances are from M to indicated atom, unless otherwise noted. The first value in any pair is for Os, the second for Ru.

This comes from the fact that back-bonding is better in the plane containing the phosphines since π^{X}_{CO} in the orthogonal plane stabilizes the d$_{xz}$ orbital. However, the interaction with the *cis*-hydride (*cis*-effect) compensates for the loss of back-bonding in the plane of CO and favors the conformation with the lesser back-donation. It is interesting to notice that the cis interaction is sufficient to overcome the loss of back-bonding associated with one CO. The observed H$_2$ alignment is also sterically favored, especially when considering the additional bulk of the phosphines used experimentally. The higher rotational barrier for Ru may be a stronger *cis*-interaction (≈hydrogen bonding) involving the less stretched (and thus more acidic) H$_2$. The H$_2$ bends slightly toward the *cis* hydride as a manifestation of the *cis* effect.

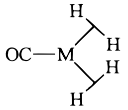
We have probed the mechanism for the observed H/H$_2$ site exchange of **C** by optimizing a C_{2v} structure **D**, which minimizes to structure **E** (Figure 2) in preference to structure **F**. The barrier heights are 6.1 kcal/mol for M = Os and 7.9 kcal/mol when M = Ru. The latter is in agreement with the experimental value (8.0(2) kcal/mol).[7b] This lower barrier could account for the lack of hydride decoalescence in the ^{1}H NMR of M = Os at −140 °C. The origin of this difference can be traced to the relative energies of **G** and **H**. **G** lies 11.7 kcal/mol above the ground state for Os and 14.5 kcal/mol above for Ru because of the larger *trans* influence of hydride.



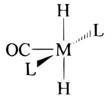
D



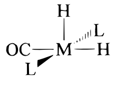
E



F



G



H

This M(H)$_2$(H$_2$) fluxionality bears a *formal* similarity to that in Ir(H)$_2$Cl(H$_2$)(P(*i*-Pr)$_3$)$_2$,[8] **I**. The mechanism of the latter has

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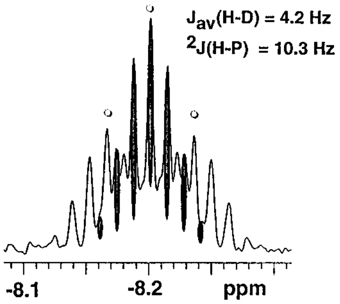
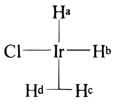
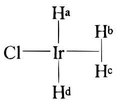


Figure 3. Room-temperature ^1H NMR spectrum of $Os(HD_3)(CO)P(t\text{-}Bu)_2Me)_2$ in the hydride region, showing a triplet of septets $OsHD_3$ resonance. The couplings to two phosphorus (triplet; open circles) and four deuteriums (septet; one shown darkly shaded) are shown.

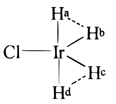
been well studied by NMR spectroscopy in a single crystal, with the conclusion that the transition state is not **J**, but is instead **K**. The difference between the IrCl and OsCO cases is likely determined by the carbonyl ligand (which favors a dihydrogen form **E**) and the chloride ligand (whose π-donation favors rupture of the H^b-H^c bond of **J**).



I



J



K

We have measured the H/D coupling constant in $OsHD_3(CO)(P(t\text{-}Bu)_2Me)_2$. This isotopomer is readily formed by stirring $OsH_4(CO)(P(t\text{-}Bu)_2Me)_2$ under a 9:1 mixture of D_2-H_2 at 1 atm in CD_2Cl_2 at 25 °C for 2 h. That exchange occurred this readily is consistent with (but does not prove) the presence of H_2 as a ligand in $OsH_4(CO)L_2$. Indeed, this exchange could likely be mediated by the equilibrium shown in eq 3. However,

$$Os(H)_2(H_2)(CO)L_2 \rightleftharpoons Os(H)_2(CO)L_2 + H_2 \tag{3}$$

our attempts to produce detectable quantities of putative $Os(H)_2(CO)(P(t\text{-}Bu)_2Me)_2$ by three freeze/pump/thaw cycles of a toluene solution gave no change in the $^{31}P\{^1H\}$ NMR spectrum. Similarly, solid $OsH_4(CO)(P(t\text{-}Bu)_2Me)_2$ is unchanged by dynamic vacuum for 12 h. With either of these treatments, $Ru(H)_2(H_2)(CO)(P(i\text{-}Pr)_3)_2$ loses H_2.[7a]

The ^1H NMR spectrum of the hydride signal of $OsHD_3(CO)(P(t\text{-}Bu)_2Me)_2$ produced as described above is a triplet of seven-line H−D coupled patterns shown in Figure 3, and permits determination of the average value of J(HD) of 4.2 Hz.

H_2 Loss Kinetics. We have sought evidence for eq 3 by recording the ^1H NMR spectra of $OsH_4(CO)(P(t\text{-}Bu)_2Me)_2$ in the presence of free H_2 over 10 °C increments between 60 and 100 °C in toluene-d_8. The lines for both free H_2 and OsH_4 are sharp at 25 °C but show increased broadening in the 60−100 °C range. By 90 °C, the OsH_4 signal is too broad to resolve the triplet structure. These observations clearly indicate that exchange is already taking place, on a lifetime of seconds, at 60 °C. Quantitative evaluation of $k_1(T)$ from the line widths of free H_2 followed by an Eyring plot of these data yields $\Delta S^\ddagger = -15(2)$ cal/(mol K) and $\Delta H^\ddagger = 12.0(5)$ kcal/mol; $\Delta G^\ddagger(95\ °C) = 17.8(5)$ kcal/mol.

For $OsH_4(CO)(P(t\text{-}Bu)_2Me)_2$, we have also established that the line width of free (added) H_2 is first-order in $[OsH_4(CO)(P(t\text{-}Bu)_2Me)_2]$, with $[OsH_4(CO)(P(t\text{-}Bu)_2Me)_2]$ in the range $(1.14-2.28) \times 10^{-2}$ M and using added H_2 to establish $[OsH_4(CO)(P(t\text{-}Bu)_2Me)_2]/[H_2]$ ratios of 1.14−2.25. Similarly, the line width of the hydride $^1H\{^{31}P\}$ NMR signal of $OsH_4(CO)(P(t\text{-}Bu)_2Me)_2$ at 80 °C in the concentration range $(1.84-5.31) \times 10^{-3}$ M is *constant* within experimental error. This confirms the dissociative mechanism (eq 3) for line broadening.

We have also made the corresponding measurements on $OsH_4(CO)(P(i\text{-}Pr)_3)_2$. This molecule has a T_{1min} of 32 ms at −67 °C, which is consistent with it having an $Os(H)_2(H_2)(CO)(P(i\text{-}Pr)_3)_2$ structure with longer H/H contacts than for the $P(t\text{-}Bu)_2Me$ analog. ^1H NMR measurement on $OsD_3H(CO)(P(i\text{-}Pr)_3)_2$ yields an average J(H−D) value of 3.1 Hz. We find that line broadening of both the ^1H NMR signal of the metal bound protons of $OsH_4(CO)(P(i\text{-}Pr)_3)_2$ and of added free H_2 is diminished compared to a corresponding sample of $OsH_4(CO)(P(t\text{-}Bu)_2Me)_2$ at the same temperature. Consistent with this, exchange of D_2 with $OsH_4(CO)L_2$ is qualitatively slower for L $= P(i\text{-}Pr)_3$ than for L $= P(t\text{-}Bu)_2Me$. The $\Delta G^\ddagger(95\ °C)$ for the $P(i\text{-}Pr)_3$ complex (19.6(5)) kcal/mol) is nearly 2 kcal/mol higher than that for $P(t\text{-}Bu)_2Me$. In summary, a comparison of the $P(i\text{-}Pr)_3$ and $P(t\text{-}Bu)_2Me$ cases shows the former to have smaller ^{av}J(H−D), longer T_{1min} and higher $\Delta G^\ddagger$ for H_2 loss. Consistent with this ranking of these phosphines, we report elsewhere that MeNC binds more strongly to $Ru(CO)_2L_2$ when L $= P(i\text{-}Pr)_3$ than when L $= P(t\text{-}Bu)_2Me$.[9]

Statement of the Problem. Spectroscopic characterization of $OsH_4(CO)L_2$ as a dihydrogen complex, $Os(H_2)(H)_2(CO)L_2$, is firmly supported by NMR in this work. However, this example shows that the assignment of classical vs nonclassical bonding in polyhydrides (more than two H ligands) from *experimental* data is more troublesome than in dihydrides. Only a few nonclassical polyhydrides show decoalesced metal hydride and dihydrogen resonances, so structural conclusions cannot be based on direct observation of distinct chemical shifts and spin−spin couplings. Thus, structural assignments of polyhydrides very often require analysis of *exchange-averaged* spectroscopic parameters, such as T_{1min} and ^{av}J(H−D). The following simplifying assumptions are usually made: (a) H···D coupling between non-mutually-bonded hydrogens is negligible;[10c,11,12] (b) there is a negligible thermodynamic isotope effect in eq 4.

$$L_nMH(HD) \rightleftharpoons L_nMD(H_2) \tag{4}$$

The additional assumption is made that dihydrogen spinning is fast relative to molecular tumbling when $^1J(H-D) \gtrsim 24$ Hz.[11,12] Implicit in this assumption is a correlation of J_{HD} with H_2 ligand rotation rate, for which there is only intuitive and empirical (not quantitative) evidence.

We therefore now combine and compare newly measured NMR data for $Os(H_2)(H)_2(CO)(P(t\text{-}Bu)_2Me)_2$ and some related molecules in order to (i) comment on the validity of the above assumptions, (ii) make the existing interpretation scheme more rigorous, and (iii) investigate a correlation among T_{1min}, ^1J(H−D), and the kinetic stability of dihydrogen complexes. We would also like to learn accurately what is the H−H distance

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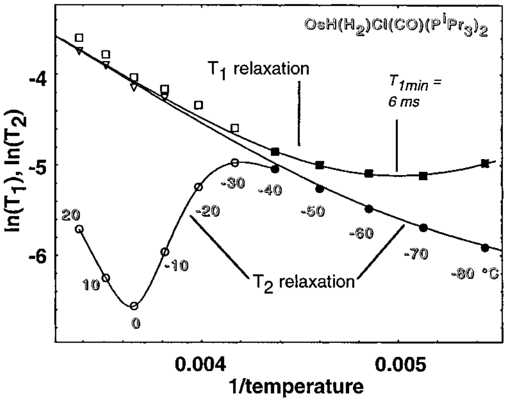

Figure 4. T_1 and T_2 relaxation of coordinated H_2 in $OsH(H_2)(Cl)(CO)P(i\text{-}Pr)_3)_2$. Filled squares and circles show slow exchange data and fit theoretical dependences (solid lines); see Discussion. Open squares and circles are the experimental data affected by the H_2 loss—the circles are connected only for demonstration. The triangles represent T_1 calculated from the exchange averaged points (squares) based on the H_2(free)/H_2(bound) ratio in this solution and T_1 for free H_2. $\tau_0 = 4 \times 10^{-13}$ s; $E_A = 2.6$ kcal/mol.

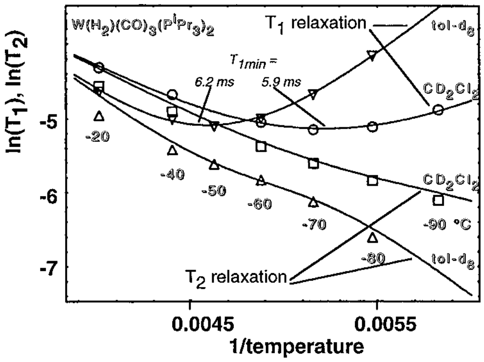

Figure 5. T_1 and T_2 relaxation of H_2 in $W(H_2)(CO)P(i\text{-}Pr)_3)_2$ in CD_2Cl_2 and toluene-d_8. τ_0 (10^{-13} s); E_A (kcal/mol) = (4; 2.6) in CD_2Cl_2 and (0.5, 3.8) in toluene-d_8.

in $Os(H_2)(H)_2(CO)L_2$, and where it lies on the continuum between classical hydride and dihydrogen complexes.

General Comments on the Relaxation Behavior of Coordinated H_2. Although apparently abundant in the literature, relatively little relaxation data has been reported for hydride and dihydrogen complexes. Generally, only $T_{1\min}$ values are reported, or sometimes only a single T_1 value at "low" temperature. Very little attention is traditionally paid to the line width of the hydride/dihydrogen resonances. The information available from Figures 4 and 5 may invite and encourage more detailed spectroscopic research, which can sometimes provide useful structural/dynamic information beyond that available from $T_{1\min}$.

Figures 4 and 5 show variable-temperature T_1 and T_2 values in $Os(H_2)HCl(CO)(P(i\text{-}Pr)_3)_2$ and $W(H_2)(CO)_3(P(i\text{-}Pr)_3)_2$. The transverse relaxation is measured as $T_2 = 1/(\pi\Delta)$, where Δ is the H_2 line width. The magnitude of T_2 is expected to be determined by proton-proton dipole-dipole interactions (also a dominant contributor in T_1 relaxation) as long as the line width does not conceal unresolved couplings and is not affected by any exchange. The complexes under discussion are characterized by very short $T_{1\min}$ values and strong H••H dipole−dipole interactions and, hence, reveal quite broad lines (80−90 Hz at the temperature of $T_{1\min}$) for the coordinated H_2. Below −40 °C, the experimental T_2 points for both complexes nicely fit the theoretical curves calculated using the H−H distances, correlation times τ_0, and activation energies E_A for the molecular reorientations determined from analysis of the T_1 data. The T_1 data were fit with a temperature-dependent correlation time, $\tau_c = \tau_0\exp(E_A/RT)$. From a practical point of view, it means that most of the other H_2 complexes must show $\Delta \leq$ ca. 80 Hz above the temperature at which T_1 is a minimum. The "excess" line widths (above −40 °C) indicate some spectroscopic (coupling) and/or dynamic contribution beyond the H•••H dipole broadening. In Figure 5, the higher viscosity of toluene increases the barrier for tumbling and also the temperature where $T_{1\min}$ occurs.

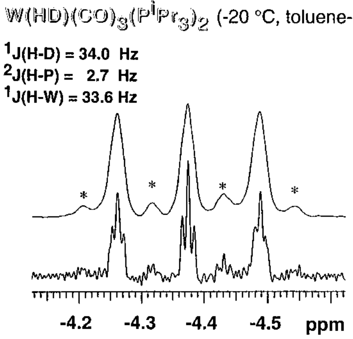

Figure 6. W(HD) resonance of $W(HD)(CO)_3P(i\text{-}Pr)_3)_2$ coupled to deuterium, phosphorus, and tungsten nuclei. The tungsten satellites are marked with stars.

Figures 4 and 5 demonstrate significant deviation from the expected T_1-T_2 relationship (i.e., similar slope) when the temperature increases above −40 °C. Most clearly, Figure 4 shows how T_2 shortens and reaches a "minimum" at 0 °C for the H_2 relaxation in $Os(H_2)HCl(CO)(P(i\text{-}Pr)_3)_2$. This spectroscopic behavior is due to site exchange between coordinated and free (dissolved) hydrogen. As the temperature increases, the lifetime of coordinated H_2 (τ) decreases, which broadens the resonance according to $\Delta = 1/(\pi T_2) + 1/(\pi\tau)$. Eventually (at 0 °C), the signals for free and coordinated H_2 coalesce.

These T_2 data permit selection of the optimum temperature for measurement of ^1J(H−D). In $Os(HD)DCl(CO)(P(i\text{-}Pr)_3)_2$, for instance, an exchange-averaged (i.e., overestimated when dissolved HD is present) coupling is observed at room temperature in a rather broad H−D pattern. It is not resolved between 10 and −20 °C. The best resolution is achieved at −40 to −50 °C, in agreement with the data in Figure 4. Even more drastic changes are seen when one compares spectra of $W(HD)(CO)_3(P(i\text{-}Pr)_3)_2$ at 25−35 °C (reported elsewhere[13]) and −20 °C (Figure 6). A resolution-enhanced H−D spectrum in Figure 6 (lower spectrum) clearly reveals proton-phosphorus coupling. Tungsten "satellites" give evidence of tungsten-dihydrogen proton spin−spin interaction in the moderately line-broadened (*S*/*N* ratio improved) spectrum. Only a poorly-resolved H−D triplet could be observed at 30 °C, at which temperature exchange destroys the other couplings.

One final comment should be made about interpretation of T_1 relaxation data. Obviously, the ^{1}H T_1 relaxation in H−D is less efficient than that in H−H. Theoretically, $T_{1\min}$(H−D)/$T_{1\min}$(H−H) ≈ 14.6 (see Experimental Section), and $T_{1\min}$(H−D) values of 90.5 and 87.6 ms are expected for W(HD) and Os(HD) based on $T_{1\min}$(H−H) values of 6.2 and 6.0 ms, respectively. Finding this experimentally should prove that the fast relaxation in $W(H_2)(CO)_3(P(i\text{-}Pr)_3)_2$ and $Os(H_2)HCl(CO)(P(i\text{-}Pr)_3)_2$ does originate from a close H−H interaction. The $T_{1\min}$(H−D) values observed here are 69 and 66 ms, respectively, which gives an experimental $T_{1\min}$(H−D)/$T_{1\min}$(H−H) ≈ 11. The disparity in the relaxation rates (1/0.069 − 1/0.0905 and 1/0.066 − 1/0.0876) amounts to 3.4−3.7 s^{-1}, which is attributed to

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Table 1. ^1H NMR (300 MHz) Spectroscopic Characteristics of the Dihydrogen Ligands and Kinetic Data for the H_2 Loss

complex	$T_{1\text{min, ms}}$	J(H−D), Hz	r(H−H),[a] Å	k_1,[b] s^{-1}	$\Delta G^{\ddagger}$,[b] kcal/mol
$W(H_2)(CO)_3(P^iPr_3)_2$	5.9−6.2[c]	34.0	0.96−0.97/0.76−0.77[c]	8	14.8
$Os(H_2)HCl(CO)(P^tBu_2Me)_2$	5.5	*d*	0.95/0.75	20000	10.6
$Os(H_2)HCl(CO)(P^iPr_3)_2$	6.0	30.9	0.96/0.76	950	12.2
$Os(H_2)HI(CO)(P^iPr_3)_2$	6.5	29.9	0.97/0.77	70	13.6
$Os(H_2)(H)_2(CO)(P^tBu_2Me)_2$	>12.6[e]	≈22.6[f]	>1.09/0.87	0.6	17.8[h]
$Os(H_2)(H)_2(CO)(P^iPr_3)_2$	>17.1	≈16.0	>1.15/0.92	0.002	19.6[h]
$Os(H_2)Cl_2(CO)(P^iPr_3)_2$	15.0	19.5	1.13/0.90	*g*	*g*

[a] Assuming slow/fast H_2 spinning, respectively. [b] At 273 K. [c] In CD_2Cl_2 and toluene-d_8, respectively. [d] Could not be measured. [e] Calculated from averaged $T_{1\text{min}} = 24$ ms; $T_{1\text{min}} = 0.5/(1/\text{av } T_{1\text{min}} - 3.9/2)$. [f] Calculated from average J(H−D); see Discussion. [g] Not measurable. [h] At 368 K.

dipole interactions with the phosphine protons. The hydride in the osmium complex $Os(H_2)HCl(CO)(P(i\text{-}Pr)_3)_2$ provides an opportunity to get an independent measure of this relaxation contribution since its only dipole interactions are with phosphine hydrogens. $T_{1\text{min}}$ of that hydride resonance is measured to be 255 ms ($1/T_{1\text{min}} = 3.9\ s^{-1}$), in close agreement to the expected value ($3.7\ s^{-1}$). In all distance calculations in this work (Table 1) we used a correction of $3.9\ s^{-1}$ to yield a relaxation contribution due only to the relaxation contribution *within* the H_2 ligands.[14]

H−H Distances: Slow Spinning vs Fast Spinning of the H_2 Ligands. Since the "T_1 criterion" was introduced a decade ago,[15] it has been questioned, heavily criticized, amended, and checked in a number of publications.[14] The current understanding is simple: if the relaxation of proton A from dipole interaction with nucleus B can be determined, then the A−B distance can be accurately calculated *when both A and B are relatively immobile* in the molecule (i.e., low vibrational amplitude). There is convincing evidence in the literature that this works well for hydride−hydride and metal−hydride distance determination in classical complexes.[15] However, dihydrogen complexes have the unfortunate complication of a significant probability of fast internal rotation of the H−H ligand.

Dihydrogen ligand rotation can be treated like another very common intramolecular reorientation−rotation of CH_3, for which the H−H distance calculated from $T_{1\text{min}}$ is corrected by a factor of 0.794.[16] This idea, suggested by Morris and coworkers in 1988, was strongly supported by the structural and spectroscopic data obtained in that research group for a family of complexes of general formula $M(H_2)H(P\text{-}P)_2^+$.[10a,b] These molecules all have a distorted octahedral structure with hydride *trans* to H_2. For M = Fe and Ru, they show large ^1J(H−D) couplings (29.5 to 32.8 Hz) apparently consistent only with the fast-spinning result (0.86−0.90 Å); the slow-spinning approximation gave unreasonably long H−H distances (1.09−1.15 Å).[10b] In the solid state, the distance was determined as 0.82 Å by neutron diffraction[17] (it is now recognized[18] that it should be a few hundredths of an angstrom longer).

For further discussion, we would like to define what might be the shortest H−H distance in coordinated hydrogen. Free H_2 has r(H−H) = 0.74 Å. Coordinated H_2 should show some elongation. The most unstable dihydrogen complexes isolated and characterized so far (i.e., those with lowest ΔH for loss of H_2) are $Mo(H_2)(CO)(dppe)_2$, $Cr(H_2)(CO)_3(P(i\text{-}Pr)_3)_2$, and $Ir(H_2)(H)_2I(P(i\text{-}Pr)_3)_2$.[18] The first shows an uncorrected H−H distance of 0.736 Å from neutron diffraction, which has been corrected for librational motion to the range 0.80−0.88 Å, and (considered more accurate) a solid-state NMR distance[19] of 0.88 Å. The distance 0.86(1) Å is found by solid-state NMR in $Cr(H_2)(CO)_3(P(i\text{-}Pr)_3)_2$.[18c] The iridium complex has an uncorrected H−H separation of 0.856(9) Å determined by neutron diffraction.[18b] All these complexes are characterized by low barriers for the H_2 rotation (by inelastic neutron scattering): *ca.* 0.7, 1.17, and 0.98 kcal/mol, respectively.[18b] We suggest 0.86(1) Å to be accepted as the most reliable presently-known, shortest distance in dihydrogen complexes, at least as applied to isolable species. This minimum r(H−H) yields a calculated lower limit for $T_{1\text{min}}$ of rapidly spinning H_2 ligand of 12 ms at 300 MHz, when the relaxation is determined by proton−proton dipole interactions. In the same way, slow-spinning H_2 will not have a $T_{1\text{min}}$ shorter than 3 ms at 300 MHz.

Among the complexes we measured in this work (see $T_{1\text{min}}$ and r(H−H) in Table 1), none shows data which are reasonably interpreted in the fast-spinning approximation. The most prominent example is Kubas' complex, $W(H_2)(CO)_3(P(i\text{-}Pr)_3)_2$. We feel that the distance of 0.76−0.77 Å which results from the fast-spinning correction is so close to that in free H_2 (0.74 Å) that it is incorrect. It is also far too short when compared to the neutron diffraction result, 0.82 Å (not corrected),[20] and the solid-state NMR distance of 0.89(1) Å.[21] We conclude that the fast-spinning model is inappropriate for this molecule.

As shown unambiguously above, the relaxation in $W(H_2)(CO)_3(P(i\text{-}Pr)_3)_2$ is >97% governed by dipole interactions of the two close protons. When no "fast-spinning correction" is made, the H−H distance is 0.96−0.97 Å in solution, or 0.07−0.08 Å longer than in the solid state. This disparity certainly stems from the solid-state NMR distance being derived from a unique temperature-independent (i.e., effectively static) component of the dipolar tensor.[19] An averaged tensor, however, determines the T_1 relaxation of coordinated H_2 in liquids, which must be affected by high-amplitude torsional and vibrational motions in the $M-(H_2)$ fragment. This should lead to overestimation of the H−H distance by $T_{1\text{min}}$.[22]

Solid-state ^1H NMR spectra of $W(H_2)(CO)_3(P(i\text{-}Pr)_3)_2$ (Figure 3 in ref 20) show that the dihydrogen ligand is confined to

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Table 2. $T_{1\mathrm{min}}$ and ^1J(H−D) for a Number of Dihydrogen Complexes with ^1J(H−D) > 25 Hz

complex	^1J(H−D), Hz	$T_{1\mathrm{min}}$, ms (ν, MHz)	r(H−H),[a] Å
$\mathrm{ReCp^*(CO)(NO)(H_2)^+}$	27	5 (500)	0.86/0.68
$\mathrm{Re(CO)_3(PCy_3)_2(H_2)^+}$	32	3 (300)	0.86/0.68
$\mathrm{Re(CO)_3(P^iPr_3)_2(H_2)^+}$	33	4 (300)	0.90/0.71
$\mathrm{RuCp(CO)(PCy_3)(H_2)^+}$	28.5	4 (250)	0.93/0.74 (0.97)[d]
$\mathrm{FeH(tetraphos)(H_2)^+}$	28.5	6 (300)	0.96/0.76
$\mathrm{RuH(tetraphos)(H_2)^+}$	29.7	6 (300)	0.96/0.76
$\mathrm{RuH(CO)(triphos)(H_2)^+}$	5.5[b] (250)	0.98/0.78	
$\mathrm{Re(CO)_3(PMe_3)_2(H_2)^+}$	33	6.7 (300)	0.98/0.78
$\mathrm{FeCp^*(dppe)(H_2)^+}$	27	7 (300)	0.98/0.78
$\mathrm{Re(CO)_2(PMe_2Ph)_3(H_2)^+}$	31	7 (250)	1.02/0.81
$\mathrm{Re(CO)_2(PMe_3)_3(H_2)^+}$	33.7	8.2 (300)	1.02/0.81
$\mathrm{Re(H)_2(CO)(PMe_3)_3(H_2)^+}$	33.6	8.3[c] (300)	1.02/0.81[c]
$\mathrm{Re(CO)_2(triphos)(H_2)^+}$	30.8	8.6 (300)	1.04/0.82
$\mathrm{Re(CO)(PMe_3)_4(H_2)^+}$	27.7	9.0 (300)	1.04/0.82
$\mathrm{Re(H)_2(CO)(PMe_2Ph)_3(H_2)^+}$	34	8[c] (250)	1.05/0.82[c]
$\mathrm{IrH(bq)(PPh_3)_2(H_2)^+}$	29.5	8[c] (250)	1.05/0.83[c] (0.94)[d]
$\mathrm{RuCl(dppb)(\mu\text{-}Cl)_3Ru(dppb)(H_2)}$	29.4	12 (300)	1.08/0.86

[a] Assuming slow/fast H_2 spinning, respectively. All distances calculated with $1/T_{1\mathrm{min}}$ corrected by 3.5 $\mathrm{s^{-1}}$ for the phosphine protons contribution and 3.5 $\mathrm{s^{-1}}$ for that of metal in the rhenium complexes.[16b] More accurate determination of these contributions does not significantly change the r(H−H) distances. [b] Calculated from average $T_{1\mathrm{min}}$. [c] These relaxation times and distances can be slightly overestimated by H/H_2 scrambling at the $T_{1\mathrm{min}}$ temperature. [d] Determined by solid-state NMR.[20]

torsions (librations) in a plane perpendicular to the coordination axis, which cause eventual reorientation of H_2. This is the zero-point libration below 100 K. At higher temperature, the H_2 oscillator occupies higher energy levels and the observed (motionally-affected) dipolar tensor is then averaged (Boltzmann population-weighted) between the accessible states. Zilm and Millar have already indicated[19] that, in this case, any refinement of the treatment of the dipolar relaxation (T_1) in solution is problematic, since the internal reorientation of H_2 is not a simple rotational diffusion.

How Should One Distinguish "Fast" and "Slow" Spinning $\mathbf{H_2}$? The slow-spinning approximation in the calculations of r(H−H) from $T_{1\mathrm{min}}$ is advocated here for $\mathrm{OsHX(H_2)(CO)L_2}$ and $\mathrm{W(H_2)(CO)_3L_2}$ complexes. This may appear confusing, at least in the case of $\mathrm{W(H_2)(CO)_3(P(\mathit{i}\text{-}Pr)_3)_2}$, because it does have a *rapidly* reorienting H_2. As required, the rotational barrier is lower (1.9−2.2 kcal/mol in the solid state,[18c] determined by inelastic neutron scattering spectroscopy) than that for the molecular tumbling, 2.6−3.8 kcal/mol (see Figure 5). There is no experimental data on this for the osmium complexes in Table 1, but all $\mathrm{Os(H_2)HX(CO)L_2}$ complexes are expected to have low (<3 kcal/mol) rotational barriers.

To this point, our choice to not apply any fast spinning correction in the distance calculation has been very much dictated by the experimental data. Contrary to this, a number of complexes *trans*-$\mathrm{M(H_2)H(P\text{-}P)_2^+}$ seem to require the spinning correction to arrive at reasonable H−H distances. In this challenging situation, it is useful to consider more examples, either *pro* or *con*, in the literature. From a recent review[23] of 134 dihydrogen complexes (Table 2 in ref 23), we have selected examples (excluding the *trans*-$\mathrm{M(H_2)H(P\text{-}P)_2}$ structural type) with ^1J(H−D) > 25 Hz, i.e., values considered indicative of short and (for the d^4 or d^6 electronic configuration) easily rotating H_2. For simplicity, we have excluded fluxional polyhydrides where evaluation of ^1J(H−D) and $T_{1\mathrm{min}}(H_2)$ is model-dependent. The data are collected in Table 2. This table also lists some recently reported rhenium complexes.[24]

The majority of the distances calculated assuming fast H_2 spinning are very short, much shorter than 0.86(1) Å—the shortest known H−H distance in coordinated dihydrogen. This, determined experimentally *in the solid state*, suggests that values longer than 0.9 Å can be found *in solution*. Table 2 clearly encourages, for these molecules, direct interpretation of $T_{1\mathrm{min}}$ *without introducing any corrections*, in preference to assuming fast H_2 spinning.

Table 2 shows no simple correlation between $T_{1\mathrm{min}}$ and ^1J(H−D). Moreover, the H−D coupling is between 27 and 34 Hz, while the distance is calculated between 0.86 and 1.08 Å.

To rationalize why some H_2 complexes (e.g., those *not* shown in Table 2) may need a fast-spinning correction and some not, we suggest that this depends on the character of H_2 reorientation in the molecules. Inelastic neutron scattering (INS) provides some information, since determination of a barrier height from measurements of the transitions of a hindered H_2 rotor requires an energy profile for this rotation. The simplest model that satisfies the INS data assumes that H_2 rotation: (a) is constrained to a plane perpendicular to the M−H_2 axis, and (b) is subject to a double-minimum potential given by the equilibrium orientation of the ligand.[18a] A smaller 4-fold term has been added to the potential in order to achieve better agreement with the measurements of the rotational transitions. It is suspected, however, that "the reason for this is simply that the potential is, in fact, not exactly sinusoidal, so the 4-fold term primarily changes the shape of the well rather than giving an indication of a second equilibrium orientation (90° away) of the H_2 at some higher energy."[18a]

The question of whether a 90° rotation of H_2 in $\mathrm{Os(H)_2(H_2)(CO)(PH_3)_2}$ from the ground state conformation is a minimum or a transition structure was investigated by further DFT calculations by rotating H_2 5 and 10° from the structure with the H−H parallel to the M-P vector. The energy increases from 5 and 10° rotation (55 and 68 cal/mol) are small relative to available thermal energy. We consider it quite likely that this very small energy rise will be compensated by steric relief in the experimental system, making the structure with H−H aligned with P−Os−P a true transition state.

For NMR relaxation, the principal difference between a 2-fold and any n-fold reorientation is that the former *does not* change orientation of the H−H dipole with respect to the molecular system of coordinates and the external magnetic field and *cannot* influence T_1 (the H_2 torsions do influence T_1, as mentioned above). Many dihydrogen complexes are expected to show simple 180° H_2 reorientation which, either slow or fast, is of no consequence for T_1 relaxation. This 180° separation of

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energy minima is applicable for all osmium complexes in this work and many of the examples in Table 2. Other examples would certainly require the fast-spinning correction if the ligands are appropriately arranged to create more than two steric and/or electronic barriers for the 360° H_2 reorientation. In this category fall complexes with chelating ligands, $M(H_2)X(P\text{-}P)_2$, which have four *identical* ligands *cis* to H_2.

We propose that this consideration should replace the current criterion (when $J_{HD} > 26$ Hz) for use of the fast-spinning correction. Additional accounting for the H−H librations is, unfortunately, an unrealistic task, since they must differ greatly in structurally different H_2 complexes. Apparently, solution H−H distances can be overestimated by some hundredths of an angstrom (≤0.07−0.08 Å), if they are not corrected. (Note that, for the same reason, neutron-diffraction H−H distances can be underestimated by this amount.) This empirical correction can be used for comparative purposes, but *the disparity becomes smaller for elongated and less vibrationally active H_2.* For example, the same (1.1 Å) distance could be determined for $Ru(H_2)(C_5Me_5)(dppm)^+$ both in solid state (neutron diffraction) and solution.[12] A good related example is determination of C−H bond length from the dipolar $^{13}C-^{1}H$ NMR relaxation, which is affected by C−H stretching and bending vibrations. Two molecules analyzed, propane and octane, have shown 2.3 and 5.6% increases in the effective bond length, i.e., overestimated by 0.022 and 0.061 Å, respectively. The difference in r_{eff} was almost exclusively due to the fact that octane is more torsionally flexible and characterized by larger amplitude of the torsional vibrations.[22]

H−H Distance in $Os(H_2)(H)_2(CO)(P(t\text{-}Bu)_2Me)_2$ and How It Compares to Those of the Other Osmium Complexes. From the exchange-averaged $T_{1\mathrm{min}}$ of 24 ms, we can estimate $T_{1\mathrm{min}}$ of the dihydrogen ligand to be about 12.6 ms in $Os(H_2)(H)_2(CO)(P(t\text{-}Bu)_2Me)_2$ (calculated as $0.5/(1/0.024 - 3.9/2)$, which still includes the interaction of the H_2 with phosphine protons, i.e., as if it had been measured under conditions of slow H/H_2 exchange). The value of 1.09 Å in Table 1 was calculated from 12.6 ms using *no H_2 spinning correction.* In fact, $T_{1\mathrm{min}}$ is probably longer than 12.6 ms because contributions of two additional interactions were not considered so far: one between the two *cis*-hydrides, and a second between one H_2 proton and the hydride *cis* to H_2. The first is about 1 s^{-1}, assuming two hydrides are 2 Å apart. The second should be larger, about 3.5 s^{-1} if the protons are separated by a shorter distance, 1.6 Å. Under these assumptions, $T_{1\mathrm{min}}$ is calculated to be 14.2 s^{-1}, which gives a distance of 1.12 Å. Probably no chemical reasoning will be fundamentally altered by such inaccuracy, although we are left with an H−H range of 1.09−1.12 Å.

Calculations of $^{1}J_{HD}$ from $^{av}J_{HD}$ above the coalescence temperature should also be treated with caution. The HD coupling observed in a complex with n hydrogens at the metal is the following for an HD_{n-1} isotopomer: $^{av}J(H-D) = n^{-1}\sum_i\chi_i[\sum_j(J_{ij}/(n-1))]$, where $i \neq j$. Here, χ_i is the likelihood that the proton occupies site *i*, and $\sum_i\chi_i = 1$. J_{ij} is the coupling between a proton in site *i* and a deuteron in site *j*. For a mono(dihydrogen) complex, this gives $^{av}J(H-D) = 2\,^{1}J(H-D)/(n^2 - n)$ *only* if all $^{2}J_{ij}$ are negligible besides the one-bond coupling and all χ_i are equal. For an HD ligand in $OsHD_3(CO)(P(t\text{-}Bu)_2Me)_2$, the derived $^{1}J(H-D) = 25.2$ Hz is six times $^{av}J(H-D) = 4.2$ Hz only if the hydrides have neither mutual coupling nor coupling to the H_2 ligand. This assumption is almost certainly not true. *Regular* geminal H···H couplings in classical hydrides are often about 6 Hz, and the H···D coupling then should be about 1 Hz (based on the ratio in gyromagnetic ratios of ^{1}H and ^{2}H isotopes). Accounting for this in $OsHD_3(CO)(P(t\text{-}Bu)_2Me)_2$ changes the "extracted" $^{1}J(H-D)$ to 24.2 Hz. Additionally, in the experiments with deuterated $Os(H,D)_3Cl(CO)(P(i\text{-}Pr)_3)_2$, we clearly observe a 5.2 Hz $^{2}J(H-H)$ coupling in the isotopomer $Os(HD)HCl(CO)(P(i\text{-}Pr)_3)_2$. If this *trans* hydride-dihydrogen spin-spin coupling should also be present in $Os(H_2)(H)_2(CO)(P(t\text{-}Bu)_2Me)_2$, a calculated $^{1}J(H-D)$ would decrease further to 22.6 Hz. The assumption that all χ_i are equal is quite likely correct in the present case, since both "OsH_4" and "$OsHD_3$" isotopomers show the same averaged $^{2}J(H-P)$.[25]

The analysis of average H−D couplings is especially troubling given the increasing number of *classical* hydrides demonstrating *two-bond* $^{2}J(H-D)$ couplings large enough to be mistaken for an *averaged one-bond* H−D coupling. The known examples include 2.8 Hz in $(P(i\text{-}Pr)_3)_2Os(MeCN)_2(H)_3^+$,[26] 3.7 Hz in $CpIr(H)_3(AsPh_3)^+$, 2.4 Hz in $[(dippp)Pd]_2(\mu\text{-}H)_2$, 3.3 Hz in Tp^*IrH_4, and 3.8 Hz in $Os(H)_3(PMe_3)_4^+$ (the first and the two latter examples are averaged couplings, indicating some of the two-bond H−D couplings are even larger in the molecules).[27] All these molecules have structurally proximate (<1.7 Å) hydrides. It seems very probable that $^{2}J(H\cdots D)$ (also H···H) coupling increases gradually when the H−M−D(H) angle decreases. This would mean the existence of a family of hydrides with intermediate H···H distances (1.45 ± 0.15 Å) *not distinguishable* from alternatively-formulated "dihydrogen" complexes by consideration of only $^{av}J(H-D)$. Any interpretation in this class of molecules can be additionally endangered by inappropriate application of the "spinning correction" (0.794) in the distance calculations from $T_{1\mathrm{min}}$.

From this discussion, it becomes clear that the result of calculations of $^{2}J(H-D)$ from $^{av}J(H-D)$ is extremely dependent on the assumptions made about other couplings and the structural model used, and neglecting two-bond H−D couplings is a potential source of significant error. Equally clear, then, is the impropriety of seeking correlations of such derived J(H−D) values to other observables like $r(H-H)$ or $\Delta G^{\ddagger}$ for H_2 release from the metal.

Caveat: An Example. A good example which demonstrates the problem is our earlier studied[28] *cis*-$IrH_3Cl_2(P(i\text{-}Pr)_3)_2$ (J. Eckert; private communication). After the complex had been shown to have an elongated H_2 by neutron diffraction ($r(H-H) = 1.10(3)$ Å)[28] with the barrier for H_2 rotation (2.1 kcal/mol), the same as in $W(H_2)(CO)_3(P(i\text{-}Pr)_3)_2$, the solution data appeared to be also interpreted by this structure. Indeed, an H−H distance of 1.07 Å and $^{1}J(H-D)$ of *ca.* 12 Hz could be calculated from the exchange-averaged $T_{1\mathrm{min}} = 57$ ms (300 MHz) and $^{av}J(H-D) = 4 \pm 1$ Hz, *assuming the complex was cis-$IrH(H_2)Cl_2(P(i\text{-}Pr)_3)_2$ in solution and the H_2 was spinning rapidly*. Our present knowledge suggests the latter assumption is unreasonable and the first is not necessarily true, when one

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(25) A thermodynamic preference has been reported for deuterium to occupy the nonclassical site in $(PMe_2Ph)_3ReHD_3(CO)^+$:

$$L_3Re(CO)HD(D_2) \xrightleftharpoons{K = 0.77} L_3Re(CO)D_2(HD)$$

An equilibrium isotope effect of 0.77 was measured. See: Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 6912.

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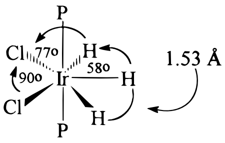
compares solid-state and solution structures. We cannot now exclude that, *in solution*, the molecule is the C_{2v} iridium(V) trihydride, $Ir(H)_3Cl_2(P(i\text{-}Pr)_3)_2$, **L**, with close metal-bound



L

hydrides (r(H···H) = 1.53 Å; *the angles* involving P and Cl in **L** are taken from the neutron diffraction data).[28] A distance of 1.53 Å is not unprecedented: a pair of hydrides in $OsH_5(PMe_2Ph)_3^+$ are separated by 1.49(4) Å.[29] The H···D coupling of 4 Hz is comparable to that observed in the trihydrides $CpIr(H)_3(AsPh_3)^+$ and $Os(H)_3(PMe_3)_4^+$.[27a,d]

$IrH_3Cl_2(P(i\text{-}Pr)_3)_2$ is a typical example of a highly fluxional hydride complex where no solution technique can provide a unique structural conclusion. Any interpretation of the data must be fair to all structural possibilities, free from prejudices, and even leave room for further modifications, should the existing understanding be subsequently improved.

Returning to the characterization of $Os(H_2)(H)_2(CO)(P(t\text{-}Bu)_2Me)_2$, we prefer the structural model leading to r(H−H) = 1.12 Å and ^1J(H−D) = 22.6 Hz. It represents a dihydrogen complex with elongated H_2 that is reminiscent of that in $Ru(H_2)(C_5Me_5)(dppm)^+$, r(H−H) = 1.09(1) Å and ^1J(H−D) = 21.1−22.3 Hz.[12]

Conclusions

The present series of isoelectronic, isostructural complexes *trans*-$Os(H_2)HX(CO)L_2$ shows increasing resistance to H_2 loss and a longer H−H bond when X (a group *cis* to the H_2) is a better σ-donor and L is less bulky (less repulsive): r(H−H)/$\Delta G^\ddagger$ (kcal/mol) (X/L) = 0.95/10.6 (Cl/P(t-Bu)$_2$Me) < 0.96/12.2 (Cl/P(i-Pr)$_3$) < 0.97/13.6 (I/P(i-Pr)$_3$) < 1.09 Å/17.8 (H/P(t-Bu)$_2$Me) < 1.15/19.6 (H/P(i-Pr)$_3$) (Table 1). The π-donating property of a ligand X *cis* to H_2 is clearly a minor factor, with the σ donicity dominating. The former, however, becomes enormously influential when a π-donor is located *trans* to a π-acidic H_2 ligand: when the hydride in $Os(H_2)HCl(CO)(P(i\text{-}Pr)_3)_2$ is replaced by a π-donor halide, the resulting $Os(H_2)Cl_2(CO)(P(i\text{-}Pr)_3)_2$ has a stability that approaches that of $Os(H_2)(H)_2(CO)(P(i\text{-}Pr)_3)_2$. While this might seem counterintuitive, the overwhelming effect here must be the stereochemistry of the $H_2{-}Os^{II}{-}X$ unit: When these are *trans*, "push/pull" π-donation[30] from X to $\sigma^*(H_2)$ is much more effective than when these are *cis*. This is due in part to the shorter Os/H_2 distance when X is not the *trans* labilizing ligand hydride, since X has less *trans* influence than hydride.

The trend shown by the osmium complexes in this work parallels that in related iridium systems. Both $Ir(H_2)(H)_2Cl(P(i\text{-}Pr)_3)_2$ and $Ir(H_2)HCl_2(P(i\text{-}Pr)_3)_2$ with *cis* halide and H_2 ligands (H_2 *trans* to H) are unstable and lose H_2 easily.[31] The isomer *cis* $Ir(H_2)HCl_2(P(i\text{-}Pr)_3)_2$ (H_2 *trans* to Cl) is a stable dihydrogen complex in the solid state, and it cannot be excluded that it is a trihydride in solution. Other examples include higher stability and longer H_2 in *trans*-$Ru(H_2)Cl(diphos)_2^+$ vs *trans*-$Ru(H_2)H(diphos)_2^+$.[32] A definite trend in this direction is shown by *trans*-$Os(H_2)X(en)_2^{2+}$ complexes.[33]

All comparisons above seem reasonably safe when made within a closely related series of isostructural complexes. Table 1 shows this may not be true for complexes of different metals. The H_2 is more strongly bound to tungsten in $W(H_2)(CO)_3(P(i\text{-}Pr)_3)_2$ than to osmium in $Os(H_2)HX(CO)(P(i\text{-}Pr)_3)_2$ ($\Delta G^\ddagger$ = 14.8 vs 12.2−13.6 kcal/mol). This is not apparent from the $T_{1\min}$ and ^1J(H−D) data; ^1J(H−H) definitely decreases from 34.0 in the tungsten complex to 30.9 (X = Cl) and 29.9 Hz (X = I). If interpreted as indicative of a more stretched and reduced H_2 in $Os(H_2)HX(CO)(P(i\text{-}Pr)_3)_2$, the constants might erroneously imply a weaker metal dihydrogen interaction (also a shorter H−H distance) in $W(H_2)(CO)_3(P(i\text{-}Pr)_3)_2$. A reliable comparison for M−(H_2) bond strength, i.e., stability against H_2 loss, should rely on the kinetic, not spectroscopic, data. In the tungsten case, the higher $\Delta G^\ddagger$ may result from lack of early internal compensation, for H_2 loss, by the halide π-donation available in the $Os(H_2)HX(CO)L_2$ series. The ultimate agostic cyclohexyl or i-Pr stabilization[34] in $W(CO)_3(PR_3)_2$ apparently must await more complete loss of H_2.

Experimental Section

Unless otherwise noted, all manipulations were done in an N_2 or H_2 atmosphere by use of Schlenk and drybox techniques. All solvents were dried over appropriate reagents. PhLi was purchased from the Aldrich Chemical Co. and used without further purification. The ^{31}P NMR was recorded on a Nicolet 360 spectrometer at 146 MHz. Infrared data were collected on a Nicolet 510P FT-IR. Most of the complexes studied here are known; their properties and preparation are described: $Os(H_2)(H)_2(CO)L_2$ (L = P(i-Pr)$_3$, P(t-Bu)Me$_2$),[3,4] $OsH(H_2)Cl(CO)L_2$,[35] $Os(H_2)Cl_2(CO)(P(i\text{-}Pr)_3)_2$.[36] $W(H_2)(CO)_3(P(i\text{-}Pr)_3)_2$ was a gift from Dr. G. J. Kubas. $OsH(H_2)I(CO)(P(i\text{-}Pr)_3)_2$ was prepared under H_2 from $OsHI(CO)(P(i\text{-}Pr)_3)_2$.

$Os(H)_2(H_2)(CO)(P(t\text{-}Bu)_2Me)_2$. (a) To $OsHCl(CO)(P(t\text{-}Bu)_2Me)_2$ (34.0 mgs, 0.591 mmol), partially dissolved in 15 mL of pentane, was added 1.01 equiv of 1.75 M PhLi (34 μL, 0.595 mmol). The reaction mixture turned from orange to red-orange within 1 min of addition. The solution was then filtered and the solvent removed to give $OsH(Ph)(CO)(P(t\text{-}Bu)_2Me)_2$. ^1H NMR (298 K, C_6D_6): OsH, −39.3, (t, 1H, [J_{P-H}] = 14 Hz); PCH_3, 0.79 (vt, 6H, [J_{P-H}] = 3 Hz); PCCH_3, 1.13 (vt, 18H, [J_{P-H}] = 6 Hz); PCCH_3, 1.16 (vt, 18H, [J_{P-H}] = 6 Hz); o-Ph, 7.58 (d, 1H, [J_{H-H}] = 6 Hz); o-Ph, 6.97 (d, 1H, [J_{H-H}] = 6 Hz); m-Ph, 7.34 (t, 1H, [J_{H-H}] = 6 Hz); m-Ph, 7.29 (t, 1H, [J_{H-H}] = 7 Hz); p-Ph, 7.07 (t, 1H, [J_{H-H}] = 8 Hz). $^{31}P\{^1H\}$ NMR (298 K, C_6D_6): 37.1 (s). IR (C_6D_6): ν(CO) = 1865 cm^{-1}.

(b) One atmosphere of H_2 (excess) was added to a solution of $OsHPh(CO)(P(t\text{-}Bu)_2Me)_2$. The mixture turned a pale yellow in time of mixing. The yield of $Os(H)_2(H_2)(CO)(P(t\text{-}Bu)_2Me)_2$ was quantitative by ^{31}P NMR. ^1H NMR (298 K, C_6D_6): OsH, −7.95, (t, 4H, [J_{P-H}] = 10.8 Hz); PCH_3, 1.65, (vt, 6H, [J_{P-H}] = 3 Hz); PCCH_3, 1.24, (vt, 36H, [J_{P-H}] = 6 Hz). $^{31}P\{^1H\}$ NMR (298 K, C_6D_6): 41.6 (s). IR: in (C_6D_6) ν(CO and Os-H) 1950, 1887, 1867 cm^{-1}; (in KBr) 2020, 1948, 1908, 1883, 1867 cm^{-1}. IR of $OsD_4(CO)(P(t\text{-}Bu)_2Me)_2$ in C_6D_6: ν(CO) 1910 cm^{-1}. For comparison, IR of $OsH_4(CO)(P(i\text{-}Pr)_3)_2$ in C_6D_6: 1948, 1884, 1867 cm^{-1}. IR for $OsD_4(CO)(P(i\text{-}Pr)_3)_2$ in C_6D_6: 1910 cm^{-1}.

$OsHI(CO)(P(i\text{-}Pr)_3)_2$ was prepared from the reaction of $OsHCl(CO)(P(i\text{-}Pr)_3)_2$ (0.0799 g, 0.19 mmol) with LiI (0.1868 g, 1.4 mmol, 7.3 equiv) in dry acetone (15 mL). After 3 h of stirring, the reaction was evacuated to dryness and extracted with toluene. The resultant

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solution was evacuated to leave a red-brown solid. $^{31}P\{^1H\}$ NMR (298 °K, C_6D_6): 49.0 (s). ^1H NMR (298 °K, C_6D_6): PC*H*, 2.84 (m, 6H); PCC*H*, 1.22 (quin, 36H); Os*H*, −30.47 (s, 1H). IR: ν(CO) = 1891 cm^{-1}.

$Os(H_2)Cl_2(CO)(P(i\text{-}Pr)_3)_2$ was prepared by addition of HC(O)OEt (0.06 mL, 0.74 mmol) to 24 mg $Os(H)_2Cl_2(P(i\text{-}Pr)_3)_2$, in 0.6 mL. Product formation (growth of ^{31}P NMR signal at 15.0 ppm) achieved 50% in 2 h at 25 °C and was complete after 24 h. The broad triplet of $Os(H_2)Cl_2(CO)_2(P(i\text{-}Pr)_3)_2$ was observed at −7.81 ppm (J(P−H) = 9.4 Hz) in the ^1H NMR spectrum. Spectral data agreed with those reported.[35]

Proton NMR measurements were done on a Varian XL-300 spectrometer using standard software for T_1 determination. Dynamic NMR spectra of the $OsH(H_2)Cl(CO)L_2$ complexes, which showed coalesced free and coordinated H_2 at 0 °C, were simulated with the DNMR5 program. From the exchange-broadened (not coalesced) spectra of $W(H_2)(CO)_3(P(i\text{-}Pr)_3)_2$ and $OsH(H_2)I(CO)(P(i\text{-}Pr)_3)_2$ at 0 °C, the rate constant k_1 was determined using the free H_2 line width (Δ), T_1, and H_2(free)/H_2(bound) ratio (R) as $k_1 = \pi R[\Delta - 1/(\pi T_1)]$. This rate k_1 can also be determined from the width of coordinated H_2 as $k_1 = \pi\Delta - 1/T_1$ (note that here the spectroscopic data are for *coordinated* H_2). Both determinations provide consistent results, but we prefer the first approach, since the free H_2 line width is determined by exchange only (that of coordinated H_2 may include unresolved couplings).

The slow-exchange spectra of $Os(H_2)(H)_2(CO)(P(t\text{-}Bu)_2Me)_2$ could only be analyzed by using the free H_2 line width, because the resonance in the hydride region is averaged (OsH_4) and coupled to two ^{31}P. If the exchange occurs by the mechanism of eq 3, the following equation applies for the lifetime τ_{H_2} of free H_2:

$$\frac{1}{\tau_{H_2}} = \frac{1}{[H_2]}\left(\frac{d[H_2]}{dt}\right) = k_{-1}[Os(H)_2(CO)L_2] = \frac{k_1[OsH_4(CO)L_2]}{[H_2]}$$

The temperature-dependence of k_1 in $Os(H_2)(H)_2(CO)(P(t\text{-}Bu)_2Me)_2$, determined at high temperatures (60−90 °C), was extrapolated to 0 °C to give the value in Table 1.

Because of the slower rates for $OsH_4(CO)(P(i\text{-}Pr)_3)_2$, it was only possible to obtain significantly broadened lines at five temperatures before a practical high temperature limit was reached. Because these data are over a considerably smaller temperature range (85−105 °C), and because slow rates (10−45 s^{-1}) involve the greatest error, we prefer to report these results only as a $\Delta G^\ddagger$ at 368 K (19.6 kcal/mol). Extrapolation to extract $\Delta H^\ddagger$ and $\Delta S^\ddagger$ is not justified by the limited data available.

Selected Spectroscopic Data. **$OsHCl(H_2)(CO)(P(i\text{-}Pr)_3)_2$** ($CD_2Cl_2$, −10 °C): δ −1.85 (br, $Os(H_2)$), −6.73 (t, ^2J(H-P) = 18.6 Hz, OsH). The hydride resonance broadens below −90 °C, probably because of slow phosphine rotation. **$OsHCl(H_2)(CO)(P(t\text{-}Bu)_2Me)_2$** ($CD_2Cl_2$, −40 °C): δ −2.06 (br, $Os(H_2)$), −7.67 (br, OsH). Phosphine rotation is relatively slow in this complex, which makes the hydride resonance broad at −40 °C. At −90 °C, when this dynamic process is stopped on the NMR time scale, there are well-resolved resonances of three rotamers, δ −6.84 (1%), −7.30 (26%), and −7.83 (73%) (all triplets, ^2J(H−P) = 17.0 Hz). The H_2 resonance is a single broad line at −90 °C with a line width that is broader than expected based on T_1. This suggests that different rotamers also have somewhat different chemical shifts $\delta(H_2)$. **$OsHI(H_2)(CO)(P(i\text{-}Pr)_3)_2$** ($CD_2Cl_2$, 0 °C): δ −3.45 (br, $Os(H_2)$), −7.82 (t, ^2J(H−P) = 18.7 Hz, OsH). At −95 °C, three rotamers are in slow exchange with δ(OsH) −6.68 (15%), −7.36 (35%), −8.11 (50%). The resonance of coordinated H_2 is broader than expected from its T_1 for the same reason as suggested for $OsH(H_2)Cl(CO)(P(t\text{-}Bu)_2Me)_2$. **$W(H_2)(CO)_3(P(i\text{-}Pr)_3)_2$** ($CD_2Cl_2$, −80 °C): δ −4.25 (br, $W(H_2)$). Two additional resonances are observed for $W(H)_2(CO)_3(P(i\text{-}Pr)_3)_2$ at −2.36 (dd, ^2J(H−P) = 38.8, 45.6 Hz, WH) and −5.06 (dd, ^2J(H−P) = 20.8, 36.1 Hz, WH). Note that, unlike that in toluene-d_8, all resonances are well-separated in CD_2Cl_2. In this solvent, the stability is limited and measurements are possible only below −20 °C. For comparison, we have measured in toluene-d_8 at −90 °C: δ −4.23 (br, $W(H_2)$), −2.07 (dd, ^2J(H−P) = 38.5, 44.5 Hz, WH), −4.43 (dd, ^2J(H−P) = 20.5, 38.2 Hz, WH). The T_1(H−D)/T_{1min}(H−H) ratio was calculated to be 15.9 at the temperature of T_{1min}(H−H), i.e., when $\omega\tau_c$ is *ca.* 0.62.[14a] The ratio, T_{1min}(H−D)/T_{1min}(H−H) = 14.6, here takes into account that T_{1min}(H−D) is observed at a lower temperature, where $\omega\tau_c$ = 0.94.

Computational Details. The calculations were performed using the Gaussian 92 package of programs[37] and the Density Functional Method (Becke 3LYP).[38] Effective core potentials (ECP) were used for Os (relativistic) and Ru.[39] The 5s and 5p (Os) and 4s and 4p (Ru) were included in the valence shell with basis sets of triple ζ quality. For P, the ECP of Stevens and Bash was chosen with a double ζ basis set plus polarization.[40] Double ζ basis with polarization were also used for C and O. The hydrides are represented by a triple Hζ basis set quality[41] with polarization and the H of PH_3 by a single H basis set.[42] Geometrical optimization was done with a gradient method at the Becke 3LYP level, freezing the rotation of the PH_3 groups, the PH bond length and the H−P−H angles.

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