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Synthesis and Characterization of $ReCl(H_2)(AsMePh_2)_4$, a Classical Hydride Complex; Reexamination of $ReCl(H_2)(PMePh_2)_4$ and Theoretical Calculations on Model Compounds

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The synthesis of $ReCl(H_2)(AsMePh_2)_4$ is reported and verified on the basis of ^1H NMR and FAB-MS. The minimum T_1 time for the metal-bonded hydrogen atoms was determined to be 44 ms (−78 °C) and 89 (−48 °C) ms at 200 and 400 MHz, respectively. From this minimum T_1 time, and, allowing for contributions from other nuclei to the relaxation, a metal-bonded H to H atom distance of 1.57 Å can be assessed. The complex is reversibly oxidized at a potential $E_{1/2}(\mathrm{ox}) = +0.07$ V. The J_{HD} coupling in the related $ReCl(HD)(AsMePh_2)_4$ compound was at 3.3 Hz. These data for $ReCl(H_2)(AsMePh_2)_4$ suggest that this molecule contains classical hydrides, and interpretations on T_1 and X-ray data published previously for $ReCl(H_2)(PMePh_2)_4$ suggest that this molecule contains a very long metal-bonded H−H interaction of 1.39 Å. Theoretical calculations on model compounds $ReCl(H_2)(XR_3)_4$ (X = P, As; R = H, Me) give virtually identical average d_{H-H} values of 1.5 (XH_3) and 1.63 (XMe_3) Å.

Introduction

The characterization by Kubas[1] of two metal-bonded H-atoms attached to each other within the compound $W(CO)_3(P^iPr_3)_2(\eta^2\text{-}H_2)$ ushered in a period of intensive research into transition metal η^2-dihydrogen complexes. The importance of this area of research lies in the elucidation of the nature of metal−hydrogen and hydrogen−hydrogen bonding. More recently, there has been an evolution in thinking for the nature of an η^2-H_2 ligand from those containing a short H to H interaction (ca. 0.85 Å) to now a wide range of distances extending out to those due to classical metal hydride bonding (ca. >1.65 Å).[2] One way of probing these interaction was accomplished by the observation that a decrease in T_1 time as halides of greater size were substituted trans to the ligand of interest in $IrXH_2(H_2)(PR_3)_2$ complexes occurs.[3] The thermodynamic stability of these complexes follows the $I^- > Br^- > Cl^-$ trend in σ-donor strengths and thereby increases the metal d to H−H σ^* interaction for the metal−hydrogen bond in the same order. These results coincide with the electronegativities of the trans halogens; chlorine, being the most electronegative, draws the most electron density away from the metal.

We have previously conducted research aimed at determining the effect that changing the identity of the halogen trans to the dihydrogen ligand in $ReCl(\eta^2\text{-}H_2)(PMePh_2)_4$[4] would have on the (H−H) interaction, as it is anticipated that the nature of the dihydrogen ligand will change as the trans halogen is varied.[5] Thus the compounds $ReX(H_2)(PMePh_2)_4$, X = Br^- and I^-, were synthesized and on the basis of their respective T_1(min) values (92, 62, and 101 ms for the Cl^-, Br^-, and I^-, respectively), did not follow the same trend as that discovered for the Ir complex mentioned above.

Additionally, the complexes $ReCl(H_2)(dppe)_2$ and $ReCl(H_2)(dppee)_2$ were previously synthesized and characterized.[6] These complexes have similar T_1(min) times (43 ms at −40 °C and 29 ms at 26 °C, by 200 MHz NMR) and J_{HP} values (20 Hz for both) to $ReCl(H_2)(PMePh_2)_4$, but have greatly lessened reactivity to H_2 displacement reactions. Interestingly enough, the greater rigidity of the dppee ligand as compared to dppe resulted in a higher temperature at which the minimum T_1 was obtained, perhaps reflective of a more hindered rotation.

This work describes what effect changing the cis atoms has on the hydride ligands. This is accomplished by the synthesis of the complex $ReCl(H_2)(AsMePh_2)_4$, **1**. Theory has been very successful in predicting geometries of transition metal polyhydride complexes.[7] Therefore, we have also used MP2 and B3LYP calculations to compare the geometries of the phosphine and arsine complexes.

Experimental Section

Materials. $AsPh_3$, Li, $ReCl_5$, and Na were used as purchased from commercial sources. THF and hexane were dried over sodium benzophenone ketyl and distilled under dinitrogen. Methanol was dried over magnesium methoxide. Reactions were carried out under inert atmospheres, either Ar or N_2, using Schlenk techniques. The IR spectra were recorded using a KVB/Analect IR instrument. Mass spectral data were obtained at the Michigan State University Mass Spectrometry Facility, which is supported, in part, by a grant (DRR-00480) from the Biotechnology Research Technology Program, National Center for Research Resources, National Institutes of Health. The ^1H NMR spectrum were recorded on Varian XL 200 and XL400 spectrometers in either acetone-d_6 or benzene-d_6. The cyclic voltammetry measurements were carried out on a BAS CV50 electrochemical analyzer in a 0.1 M $[^nBu_4N][BF_4]$ solution in THF (0.82 g of $[^nBu_4N][BF_4]$ in 25 mL of THF) with a glassy carbon electrode reference to a Ag/AgCl reference electrode.

Synthesis of $AsMePh_2$. This ligand does not appear to be available commercially and thus had to be synthesized. $AsPh_3$ (5.0 g) was dissolved in 25 mL of dry THF under Ar. Li metal (0.023 g), cut and beaten into flat pieces, was added to the solution and the mixture heated overnight with stirring at reflux temperature. The solution changed from

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clear with a slight yellow tinge to red-brown and opaque when all of the Li chips had reacted. In a separate flask, 4.69 g of MeI was added to 25 mL of THF and this solution added slowly via a cannula over a period of 20 min. Upon completion, the mixture was stirred for 2 h. MeOH was added to destroy unreacted compounds. The volume of the resulting solution was reduced by 50% by vacuum distillation and the remaining slurry washed with 3 × 10 mL of H_2O using a syringe. This removed most of the LiI salt. The mixture was then subjected to a dynamic vacuum overnight. The product, a clear yellow viscous oil, was obtained by vacuum distillation (0.5 mmHg, 110 °C) using a short distillation pathway. The quantity obtained weighed 2.38 g corresponding to a 48% yield. ^{1}H NMR (400 MHz, acetone-d_6) δ 1.44 (s, 3H CH_3AsPh$_2$), 7.25−7.45 (m, 10H, MeAsC$_6$$H_5$).

Preparation of $ReCl(H_2)(AsMePh_2)_4$, 1. This compound was prepared in a manner identical to that for the phosphine analogue $ReCl(H_2)(PMePh_2)_4$[4] except that $AsMePh_2$ was used instead of $PMePh_2$. A typical reaction consisted of 1.5 g of $AsMePh_2$, 0.14 g of Na, 1.5 mL of Hg, 0.58 g of $ReCl_5$, and 25 mL of THF. These components were mixed in a flask which was surrounded by an ice/water slush and this was stirred overnight. The resulting solution was filtered through Celite and concentrated and MeOH added, yielding a light gray material 0.535 g (28% yield) on this occasion. On other occasions lower yields were obtained. IR data (Nujol mull) 2922−2854 m, 1260 s, 1080 m, 1017 s, 799 s, 734 s, 694 s, 403 s. ^{1}H NMR (200 MHz, acetone-d_6) δ −9.15 (s, 2H, H_2−Re), 1.52 (s, 12H, CH_3As), 6.80−7.60 (m, 52H, ($C_6H_5)_2$-As). This compound lost dihydrogen if recrystallized in a dinitrogen filled glovebox, and we were not able to purify it under Ar using vacuum line Schlenk techniques. Satisfactory elemental analyses were not obtained for this compound, and a ^{1}H NMR spectrum in acetone-d_6 is supplied as Supporting Information in order for an assessment of the kind of bulk purity that the reduction reaction produces. Additionally, the complex ReCl(HD)($AsMePh_2)_4$ was prepared by conducting the synthesis under an HD atmosphere. The HD gas was generated by reacting NaH with D_2O. The ^{1}H NMR spectrum in the hydride region for this molecule presented as Figure 1 consists of a singlet at δ −9.13 and an uneven three-line pattern at δ −9.16, J_{HD} = 3.3 Hz. The small bump at δ −9.2 may be due to resonances from the ortho-substituted complexes $ReCl(H_2)(AsMe(C_6D_2H_3)_2)_4$ and/or $ReCl(HD)(AsMe(C_6D_2H_3)_2)_4$.

Theoretical

Calculations were performed on model compounds of both phosphine and arsine compounds $ReCl(H_2)(XR_3)_4$; XR_3 (X = P, As; R = H, Me). Geometries were optimized using MP2 (XH_3) and B3LYP (XH_3 and XMe_3) using the GAMESS−UK package.[8] Several basis sets were used for calculations on XH_3 complexes based upon the modified Ermler−Christiansen relativistic effective core potentials (RECPs) for Re,[9,10] the Wadt−Hay bases for P, As, and Cl,[11] and the Dunning triple-ξ basis for H.[12]

BSI: Re: (5s6p4d)/[3s3p3d]; H_{Re}: (5s1p)/[3s1p]; P/As: (3s3p)/[2s2p]; Cl: (3s3p)/[2s2p]; H_P: (3s)/[2s]

BSII: Re: (5s6p4d1f)/[4s4p4d1f] (ξ_f = 0.8); H_{Re}: (5s1p)/[3s1p] ((ξ_p = 1.0); P/As: (3s3p1d)/[2s2p1d] ($\xi_{d(P)}$ = 0.37, $\xi_{d(As)}$ = 0.293); Cl: (3s3p1d)/[2s2p1d] (ξ_d = 0.6); H_P: (3s)/[2s]

BSIII: Re: (5s7p5d1f)/[3s4p4d1f](ξ_p = 0.015, ξ_d = 0.033, ξ_f = 0.8); H_{Re}: (7s2p)/[5s2p] (ξ_s = 0.033, 0.011; ξ_p = 1.0, 0.33); P/As: (5s5p2d)/[4s4p2d] ($\xi_{s(P)}$ = 0.04, 0.013; $\xi_{p(P)}$ = 0.033, 0.011; $\xi_{d(P)}$ = 0.37, 0.123, $\xi_{s(As)}$ = 0.0469, 0.015; $\xi_{p(As)}$ = 0.033, 0.011; $\xi_{d(As)}$ = 0.3, 0.1); Cl: (5s5p2d)/[4s4p2d] (ξ_s = 0.15, 0.05; ξ_p = 0.06, 0.02; ξ_d = 0.6, 0.2); H_P: (3s)/[2s]

Table 1. T_1 Times for the Metal-Bonded Hydrogen Atoms in 1 at 200 and 400 MHz in Acetone-d_6

200 MHz		400 MHz	
temp, °C	T_1, ms	temp, °C	T_1, ms
23	152	25	160
2.3	107	0	128.3
−18.2	79.6	−20	103
−38.2	58.5	−40	90
−58.4	47.8	−55	89.3
−78.4	43.8	−60	96.3
−88.7	51.7	−80	121.3

The basis set for the XMe_3 calculations was as above (BSI) except methyl groups were represented by STO-5g bases.[13] Re: (5s6p4d)/[3s3p3d]; H_{Re}: (5s1p)/[3s1p]; P/As: (3s3p)/[2s2p]; Cl: (3s3p)/[2s2p]; C_P: (10s5p)/[2s1p]; H_{Me}: (5s)/[1s]

Discussion

The synthesis of **1** is accomplished by the reduction of $ReCl_5$ using Na/Hg in the presence of $AsMePh_2$. The compound does not appear to be thermally stable and, unlike the more robust $PMePh_2$ analogue,[4] decomposes if dissolved in CH_2Cl_2 and loses dihydrogen if recrystallized in a dinitrogen-filled glovebox. Spectroscopic measurements were determined on freshly prepared samples of **1**. We did not obtain a reasonable elemental analysis for **1**. However, it was possible to characterize this compound by a variety of spectroscopic techniques.

Convincing evidence that the complex was produced is evident in the results of a FAB-MS experiment. Peaks indicative of the molecular ion $[ReCl(H_2)(AsMePh_2)_4]^+$ (1200 *m/z*) and fragments $[ReCl(H_2)(AsMePh_2)_3]^+$ (956 *m/z*), $[ReCl(AsMePh_2)_3]^+$ (954 *m/z*), $[ReCl(AsMePh_2)_2]^+$ (710 *m/z*), $[AsMePh_2]^+$ (244 *m/z*), $[AsPh_2]^+$ (229 *m/z*), and $[AsMePh]^+$ (167 *m/z*), where the number in parentheses indicates the highest peak of the various isotopic patterns observed. The profile of these patterns matched the calculated isotopic patterns. It is noteworthy that in the case of **1** the molecular ion was the species observed in the FAB-MS experiment whereas in the case of $ReCl(H_2)(PMePh_2)_4$, the protonated molecule (i.e., $[HReCl(H_2)(PMePh_2)_4]^+$) was produced.[4a] In both cases an identical matrix was used, namely, *m*-nitrobenzyl alcohol.

Additionally, it is clear from the ^{1}H NMR spectrum that the complex contains a hydride and the ligand $AsMePh_2$. The resonance at δ −9.15 (s, acetone-d_6) is in the region where the metal-bonded H atoms in $ReCl(H_2)(PMePh_2)_4$ were observed (δ −8.88, (q, CD_2Cl_2)).[4b] Table 1 lists the T_1 data obtained using instruments at two different frequencies, namely 200 and 400 MHz, and these are illustrated graphically in Figure 2. The minimum T_1 at 200 and 400 MHz were observed at −78 °C and −48 °C and this is simply a reflection of the fact that the lower frequency instrument requires a lower temperature for the rotation of the molecule to match the Larmor frequency.[14] Equation 1 was first suggested[15] and then quantitatively used to assess the rate of relaxation for an ^{1}H−^{1}H dipole−dipole interaction for various hydride complexes.[14,16] This equation

$$R_{HH} = \frac{1}{T_{1_{dd(\mathrm{intra})}}} = \frac{3\gamma^4\hbar^2}{10\mathrm{r}^6}\left\{\frac{\tau_c}{1+\tau_c^2\omega^2} + \frac{4\tau_c}{1+4\tau_c^2\omega^2}\right\} \quad (1)$$

does not afford units of s^{-1} as stated in reference[14] if one conducts an "evaluation of the constants." However, the formulation of the relaxation rate given in eq 2[17] does afford units of s^{-1} as evident in eq 3 using SI units for the various constants.[18] Therefore, it is clearly necessary to have this (μ_0/4π)^2 term when one evaluates T_1 relaxation data using SI units.

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$$\frac{1}{T_{1_{dd(\mathrm{intra})}}} = \frac{3}{10}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma^4 \hbar^2 r^{-6}[\tau_c/(1+\omega^2\tau^2) + 4\tau_c/(1+4\omega^2\tau^2)\} \tag{2}$$

$$\frac{1}{T_{1_{dd(\mathrm{intra})}}} = \frac{3}{160}\,\frac{(4\pi\times10^{-7})^2\mathrm{T}^4\frac{m^6}{J^2}(2.67515255\times10^8)^4\frac{1}{s^4T^4}(1.05457266\times10^{-34})^2J^2s^2(4.53\times10^{-10})s}{\pi^2r^6} = \frac{77.505\times10^{-59}m^6}{r^6s} \rightarrow \frac{1}{T_{1_{dd(\mathrm{intra})}}} = \frac{77.505\ \text{Å}^6}{r^6s} \tag{3}$$

This quantity is equivalent to 1 G^2 cm^3 erg^{-1}, and including this into eq 1 would afford units of cm^6 s^{-1} if cgs units are used. A similar reformulation, given in eq 4, should be employed when dealing with relaxation between an H atom and some other non-H element.[14,17] The results afforded by use of equations 2

$$R_{\mathrm{HX}} = \frac{2}{15}\left(\frac{\mu_0}{4\pi}\right)^2\frac{\gamma_{\mathrm{H}}^2\gamma_{\mathrm{X}}^2\hbar^2}{r^6}S(S+1)\times\left\{\frac{\tau_c}{1+\tau_c^2\omega_-^2} + \frac{3\tau_c}{1+\tau_c^2\omega_{\mathrm{H}}^2} + \frac{6\tau_c}{1+\tau_c^2\omega_+^2}\right\} \tag{4}$$

and 4 are identical to those reported previously.[14] The only point here is that these are the expressions to use if one employs SI units, which was suggested to be the standard.[19]

In addition to the many constructive uses of eq 1 pointed out earlier,[14] we would like to utilize it to address the nature of $ReCl(H_2)(PMePh_2)_4$ which was assessed on the basis of a short T_1 (ms at 200 MHz) and a single-crystal X-ray determined structure ($d_{\mathrm{HH}} = 1.17(13)$ Å) as possessing an asymmetric stretched or long metal-bonded H to H atom interaction.[4] If we examine the distances between the metal-bonded H atoms in that structure and other nuclei capable of contributing to the relaxation (as suggested earlier[14]), we calculate that the rate of relaxation should be on the order of 11.3 ms at 200 MHz, with the contributions given in eq 5 for the rate calculated at 500

$$R_{\mathrm{calc}} = R_{\mathrm{H(Re)H}} + R_{\mathrm{H(ligand)H}} + R_{\mathrm{HP}} + R_{\mathrm{HRe}} = 29.908 + 2.80 + 0.111 + 2.577 = 35.396\ \mathrm{s}^{-1} \tag{5}$$

MHz. This analysis is somewhat compromised by the fact that the positions of the atoms were assessed using X-ray diffraction and, with this technique, the positions of the hydrogen atoms nuclei and the centroids of electron density assessed using X-ray do not coincide.[20] However, the calculated relaxation rate at 11.3 ms is lower than the 25 ms observed at 200 MHz. By assuming that the other rates of relaxation do not change significantly, we can calculate what the metal-bonded H−H distance should be so that there is agreement between the calculated and experimental T_1 minimum times, eq 6. This translates into a relaxation rate of 10.512 s^{-1} for the H−H dipole

$$R_{\mathrm{expt}} = 16 = R_{\mathrm{H(Re)H}} + 2.80 + 0.111 + 2.577 \rightarrow R_{\mathrm{H(Re)H}} = 10.512 \rightarrow \mathrm{d}_{(\mathrm{H-H})} = 1.395\ \text{Å} \tag{6}$$

mechanism or an H−H distance of 1.395 Å. On this basis, we can conclude that $ReCl(H_2)(PMePh_2)_4$ contains a very long and weak metal-bonded H−H atom interaction. Others have concluded[21] that distances greater than 1.1 Å between the metal-bonded H atoms indicate "little H−H bonding." This longer distance with the T_1 minimum time analysis compared to the shorter one assessed crystallographically illustrates the difficulties of refining metal-bonded H-atoms using X-ray data and this was previously suggested to be an artifact of the X-ray experiment.[22]

Unfortunately, we were unsuccessful in attempts to obtain crystals of the complex $ReCl(H_2)(AsMePh_2)_4$. Therefore, to use the T_1 data, it is necessary to construct a structural approximation to the molecule. This analysis, presented as Supporting Information, suggests that the H−H atom separation in $ReCl(H_2)(AsMePh_2)_4$ is on the order of 1.57 Å, which is larger than that obtained for the $PMePh_2$ analogue, eq 7.

$$R_{\mathrm{meas}} = R_{\mathrm{H(Re)H}} + R_{\mathrm{H(ligand)H}} + R_{\mathrm{HAs}} + R_{\mathrm{HRe}} \rightarrow 9.091 = (77.51/d_{(\mathrm{H-H})}{}^6) + 2.00 + \{(11.31/(3.141 - 0.515d_{(\mathrm{H-H})})^6)\} + 2(11.31/(3.076)^6) + \{(11.31/(3.109 + 0.360d_{(\mathrm{H-H})})^6)\} + 1.907 \rightarrow d_{(\mathrm{H-H})} \approx 1.57\ \text{Å} \tag{7}$$

Therefore it can be said that changing the ligands cis to the metal-bonded H atoms did have an effect on their interaction.

It is also interesting that in the case of **1**, the minimum T_1 observed is directly proportional to the resonance frequency of the instrument in accordance with the equation $[T_1(\mathrm{min})]^{-1} = \gamma^2/\omega_o[\mathrm{B}_{xL}^0]^2$, where ω_0 represents the resonance frequency of the instrument.[23] This is different to what was observed with the phosphine analogue $ReCl(H_2)(PMePh_2)_4$ where the T_1 at 200 MHz of 25 ms did not directly scale to that at 400 MHz reported at 92 ms.[4c] This apparent lack of direct scale is not easily explained, but may be accounted for by the contribution of the metal−hydrogen and ligand-hydrogen dipole−dipole interactions. As magnetic field strength increases, so does the temperature at which T_1 is a minimum because the rate of tumbling

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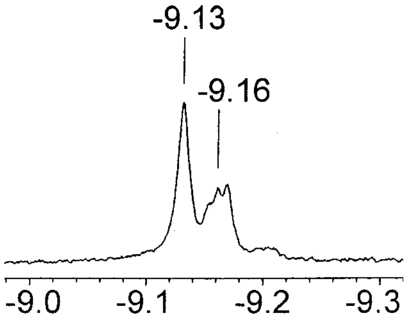

Figure 1. The ^1H NMR spectrum of $ReCl(HD)(AsMePh_2)_4$ in the Hydride Region.

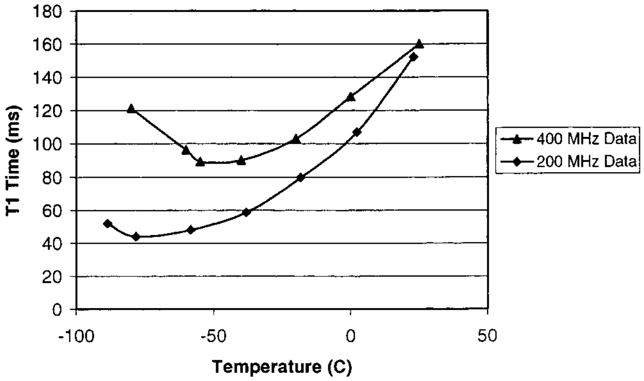

Figure 2. T_1 Times vs Temperature for Complex 1.

needed to match the Larmor frequency is greater. The contributions of heteronuclear dipole−dipole interactions may vary with temperature as the ligands change configuration with temperature.[4c] Additionally, the $^{31}P\{^1H\}$ NMR spectrum of this molecule in the hydride region shows variation over a temperature range which could be attributed to different rotamers of the phosphine ligands, or differing orientations of the dihydrogen ligand, or both. These rotamers will have different temperatures at which the respective T_1 minimums are obtained. In the case of **1**, a longer ReAs bond may suggest that the different rotamers are not observed.

The HD analogue to **1**, i.e., $ReCl(HD)(AsMePh_2)_4$ was also synthesized. This was accomplished by conducting the experiment to prepare **1** (normally done under Ar) under an HD atmosphere (produced by reacting NaH in D_2O). An HD coupling of 3.3 Hz was observed with $ReCl(HD)(AsMePh_2)_4$, see Figure 1, in contrast to the case with the $^1H\{^{31}P\}$ NMR spectrum of $ReCl(HD)(PMePh_2)_4$ where no HD coupling was resolved.[5] This HD coupling (assuming $^2J_{HD} \cong 2 \pm 2$ Hz indicates a hydride−deuteride[24] (i.e., Re(H)(D) coupling) is in the range of classical hydride deuteride coupling and thus it is not constructive to use the equation $d_{HH} = -0.0168J(H,D) + 1.44$[25,26] to calculate the distance between the two atoms.

Theoretical calculations were performed on four model systems: $ReCl(H_2)(XR_3)_4$ (X = P, As; R = H, Me). The MP2 and DFT results for the PH_3 and AsH_3 cases are very similar with d_{H-H} on the border of classical dihydride distances (Table 2). Additionally, a notable difference between these theoretical results and the X-ray structure of $ReCl(H_2)(PMePh_2)_4$ is that the dihydrogen ligand lies between the planes of the phosphine ligands and the chloride rather than along one of the planes. Theoretical geometries of XMe_3 complexes are similar to the X-ray structure with ∼5° variations in the Cl−Re−P angles. Comparison of the MP2 PH_3 structure with experiment shows that this level of theory tends to underestimate the bond lengths between the Re−Cl and Re−P atoms. Luck and Cotton observed d_{Re-Cl} and average d_{Re-P} distances of 2.54 and 2.42 Å, respectively.[4a] The MP2 values in the largest basis set gave errors of around 0.06 Å while DFT calculations were much closer (>0.02 Å). Therefore the DFT values for the arsine complexes may be more reliable.

Table 2. Theoretical Parameters for $ReCl(H_2)(XR_3)_4$ (X = P, As; R = H, Me)

		MP2	MP2	MP2	DFT	DFT	DFT
		BSI	BSII	BSIII	BSI	BSII	BSIII
X = P	*d*(H−H), Å	1.470	1.452	1.461	1.466	1.505	1.501
R = H	*d*(Re−H), Å	1.630	1.637	1.641	1.654	1.661	1.661
	d(Re−Cl), Å	2.557	2.454	2.470	2.578	2.517	2.545
	d(Re−P), Å	2.405	2.342	2.342	2.431	2.396	2.400
X = As	*d*(H−H), Å	1.467	1.452	1.458	1.484	1.506	1.495
R = H	*d*(Re−H), Å	1.631	1.639	1.638	1.657	1.660	1.656
	d(Re−Cl), Å	2.563	2.459	2.479	2.587	2.522	2.541
	d(Re−As), Å	2.472	2.429	2.432	2.504	2.491	2.496
X = P	*d*(H−H), Å				1.639		
R = Me	*d*(Re−H), Å				1.659		
	d(Re−Cl), Å				2.661		
	d(Re−P), Å				2.428		
	d(Re−P′), Å				2.507		
	∠(Cl−Re−P), deg				96.7		
	∠(Cl−Re−P′), deg				76.1		
X = As	*d*(H−H), Å				1.619		
R = Me	*d*(Re−H), Å				1.659		
	d(Re−Cl), Å				2.662		
	d(Re−As), Å				2.488		
	d(Re−As’), Å				2.553		
	∠(Cl−Re−As), deg				95.2		
	∠(Cl−Re−As’), deg				76.7		

Unfortunately, the calculations did not reveal a significant difference between the d_{H-H} values for the two R = H complexes. We expected this might have resulted from basis set error, but even large bases with diffuse and polarization functions on all important atoms show no difference in the bond length. The average d_{H-H} values for the PH_3 and AsH_3 complexes are 1.5 Å, only 0.1 Å longer than the theoretical d_{H-H} in the isoelectronic, but less electron-rich, $[Os(H_2)(NH_3)_4Cl]^+$ complex.[27] The bond length in the osmium complex is very close to the neutron diffraction for $[OsAc(H_2)(en)_2]^{+}$[28] indicating good agreement between theory and experiment. The difference between the T_1-derived distance and theory may result from the steric effects present in the true complex. Because the potential energy surface for stretching the H−H bond is so shallow,[7b,27,29] small changes in the coordination sphere may drastically affect the H−H bond distance. Therefore, we also calculated geometries for the XMe_3 derivatives. No real difference in d_{H-H} was shown between the PMe_3 and $AsMe_3$ derivatives, again possibly due to an incomplete description of the ligand sphere, but there was an increase in the d_{H-H} lengths, Table 2. Significant differences between theoretical studies and T_1 have been reported previously.[30] Experimental studies of

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Table 3. Electrochemical Data

complex	$E_{1/2}$(ox) (measured), V vs Ag/Ag$^+$	conditions	reference
$ReCl(H_2)(PMePh_2)_4$	−0.02	20 °C, 0.1M [$^nBu_4N$][BF_4] in THF, scan rate 100 mV/s	this work
$ReCl(H_2)(AsMePh_2)_4$, **1**	0.07	*a*	*a*
ferrocene	0.67	*a*	*a*
$ReCl_3(PMePh_2)_4$	0.90	22 °C, 0.1M [$^nBu_4N$][BF_4] in CH_2Cl_2, scan rate 200 mV/s	4b
$ReCl(H_2)(PMePh_2)_4$	−0.07	*a*	4b
$ReH_3(PMePh_2)_4$	−0.17	*a*	4b
ferrocene	0.52	*a*	4b

[a] Same as above entry.

$Cp^*MH_4(H_2)(PMe_3)^+$ (M = Mo, W) gave T_1 values for the Mo complexes as half that for the W complex, suggesting some significant structural difference between the two species. However, theoretical calculations gave very similar structures and d_{H-H} distances for the two complexes.

To assess the reducing capability on **1**, the oxidative potentials measured using cyclic voltammetric methods were assessed. Table 3 contains these data together with those reported for closely related compounds. As is evident in Table 3, the measurements for the other complexes were conducted in CH_2Cl_2. Unfortunately, complex **1** is not stable in this solvent as evident by the disappearance of the hydride resonance in a ^1H NMR spectrum in CD_2Cl_2. Thus the measurements had to be conducted in THF. It is clear from the difference in oxidation potentials of ferrocene in CH_2Cl_2 and THF that we cannot directly compare the potentials for the compounds determined in different solvents. Further, the fact that the oxidation potential for $ReCl(H_2)(PMePh_2)_4$ in the two solvents (using the Fe^{2+}/Fe^{3+} couple as a scale) does not correlate exactly suggests that we should not attempt to reduce the data to one scale. Clearly the effects of solvation and differing ion transport capabilities in different solvents may contribute to determine the oxidation potentials. However, comparisons in the same solvent under similar conditions are meaningful and, in that regard, **1** with a reversible oxidation at 0.07 V is clearly more difficult to oxidize than the phosphine analogue $ReCl(H_2)(PMePh_2)_4$ at −0.02 V. These values are in agreement with the MP2/BSIII Koopman's theorem ionization potentials for $ReCl(H_2)(PH_3)_4$ (IP = 7.8 eV) and $ReCl(H_2)(AsH_3)_4$ (IP = 8.0 eV). This difference is directly related to a less electron rich metal-center and this may be due to the fact that the rupture of the stretched H_2 ligand is now complete by changing the P atoms to As. However, note that the complex $ReCl_3(PMePh_2)_4$ oxidized at 0.90 V which for a Re^{3+} compound is much higher than the potential for **1**. Additionally, the potential for the compound $Re(H_3)(PMePh_2)_4$ at −0.17 V indicated that the metal center here was more electron rich than in $ReCl(H_2)(PMePh_2)_4$ at −0.07 V. Clearly this illustrates the fact that the electronic effects of a H^- are not equivalent to that in a Cl^- ligand.

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Supporting Information Available: The analysis of the T_1 data and a figure displaying the ^1H NMR spectrum of $ReCl(H_2)(AsMePh_2)_4$, **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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