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Theoretical Investigations of Classical and Nonclassical Structures of MH_7L_2 Polyhydride Complexes of Re and Tc

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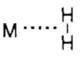
Abstract: The geometries, energies, and electronic properties of ReH_7L_2 and TcH_7L_2 complexes have been calculated using ab initio theoretical techniques including relativistic effective core potentials for Re and Tc. Classical nine-coordinate MH_7L_2 polyhydride forms and nonclassical $M(H_2)H_5L_2$ and $M(H_2)_2H_3L_2$ structures containing molecular dihydrogen ligands have been investigated. Molecular geometries were optimized at the Hartree–Fock SCF level with L = PH_3 model ligands for the various structures of Re and Tc. Electron correlation effects were treated using configuration interaction (CI) techniques at the optimized geometries. Results are compared with experimental structural determination and with solution NMR studies of Re complexes. The classical structure is found to be more stable than the eight-coordinate structure by 2–4 kcal/mol for the case of Re, depending on the level of calculation, and 7–10 kcal/mol lower than seven-coordinate forms. The nonclassical seven-coordinate structures, by contrast, are predicted to be 2–12 kcal/mol lower in energy than the classical form for Tc depending on the basis set and treatment of electron correlation effects. Although the small differences in energy between these forms make predictions of the most stable form of MH_7P_2 species with bulkier phosphine ligands in solution more difficult, these results indicate a greater tendency for Tc to display nonclassical structures relative to Re. The positive ions of ReH_7L_2 and $Re(H_2)H_5L_2$ are also investigated, with the IP of the latter form calculated to be 2.1 eV lower in energy than the classical structure.

Introduction

Transition-metal polyhydride complexes have been the subject of extensive experimental[1] and theoretical[2] studies in recent years since the discovery by Kubas and co-workers[3] of $W(\eta^2\text{-}H_2)(CO)_3(PR_3)_2$ with a nonclassical structure containing molecular hydrogen. These activities have resulted in the synthesis of many new transition-metal complexes containing dihydrogen and the observation of equilibrium between classical hydride and nonclassical dihydrogen forms in certain cases. One of the main issues in this unfolding story has been the identification of factors influencing the relative stability of metal–dihydrogen forms (**1**) compared to traditional-metal dihydride (**2**) forms.



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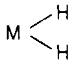

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Re polyhydrides have been studied extensively[4-12] and present a rich class of compounds with the possibilities of both polyhydride and dihydrogen forms. Experimental studies to determine whether these complexes assume classical or nonclassical forms have generated considerable controversy. This is especially true for studies in solution where the complexes could show fluxional behavior between several different structures. Only recently has structural information from X-ray and neutron diffraction studies been emerging[5,6,9,11,13-16] that locates the position of the hydrogen atoms in the crystal. Neutron diffraction studies which have found classical polyhydride structures have been reported for ReH_7L_2 by Howard et al.[13] and for ReH_5L_3 crystals by Emge et al.[15] where L denotes phosphine ligands. An X-ray diffraction study of ReH_5L_3 by Cotton and Luck[9] also found a classical eight-coordinate structure. The existence of η^2-bonded H_2 has been shown by the same investigators[8] in the case of the pseudooctahedral complex $ReCl(\eta^2\text{-}H_2)L_4$. Earlier X-ray diffraction studies[13,14] did not locate the position of the hydrogen atoms in ReH_7L_2 species.

The preceding structural studies of eight- and nine-coordinate structures in the solid state contrast with NMR studies in solution which have been interpreted in terms of nonclassical structures.[1b,4] NMR relaxation times (T_1) have provided a diagnostic means of discerning classical and nonclassical structures in solution, since the dominant dipolar relaxation time varies strongly as a function of the distance, R, between hydrogens (i.e., as R^6). Classical hydrides typically exhibit longer relaxation times with $T_1 > 350$ ms, while dihydrogen complexes usually have times in the range $4 < T_1 < 100$ ms. NMR relaxation studies by Crabtree et al.[1b,11] and by Cotton et al.[8,9] however, showed that the interpretation of T_1 times is extremely subtle, since T_1 also depends on temperature. Typically there is a characteristic minimum value T_1(min) as a function of temperature, from which the most reliable structural information can be inferred. Earlier studies of $ReH_7(PPh_3)_2$ found a T_1 of 78 ms at 205 K, which suggested a possible nonclassical structure in solution. Subsequent experimental studies, coupled with the above neutron diffraction information, led to the interpretation of a classical structure in solution to be most consistent with the data. Electrochemical studies,[7] however, suggested the existence of both a nonclassical $Re(H_2)H_5P_2$ form as well as a classical form with separate half-wave oxidation potentials. Similarly for the ReH_5P_3 complexes, the solution NMR data are consistent with a nonclassical structure, while the structural information on crystals shows only classical polyhydrides.[15]

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In this paper we report the results of ab initio electronic structure calculations on the model complex $ReH_7(PH_3)_2$ for both the classical nine-coordinate form as well as several nonclassical structures. These calculations were carried out using the MESA set of electronic structure codes.[17] For each structure a full geometry optimization at the Hartree–Fock level is carried out using analytic gradient techniques. The calculations employ relativistic effective core potentials to replace the inner core electrons of the P and Re atoms. Electron correlation effects were investigated at the Hartree–Fock optimized geometries with configuration interaction techniques. A comparison of the resultant geometries and relative energies of these forms provides information to guide the experimental search for classical and nonclassical forms in solution. In addition, similar information is reported on the Tc analogues of these complexes, for which very little experimental information is currently available.

Details of the Calculation

Electronic structure calculations were carried out on the $MH_7(PR_3)_2$ complexes at the Hartree–Fock level using a flexible contracted Gaussian basis. The calculations employed relativistic effective core potentials (RECPs)[18,19] to replace the inner core electrons of Re and Tc as well as to treat the effects of the relativistic mass–velocity and Darwin terms on the valence electrons. In each case, the outer core electrons with the same principal quantum number as the valence d electrons were explicitly treated in the calculation. Thus, for Re, the [Kr] $4d^{10}$ core is replaced by the RECP and the remaining electrons corresponding to the $5s^2\,5p^6\,5d^6\,6s^1$ ground-state configuration were explicitly treated in the calculation. Similarly for Tc, the [Ar] $3d^{10}$ core was replaced. Previous experience has shown that inclusion of these outer core electrons is essential in calculations including electron correlation effects involving transition metals.[20] The presence of these electrons also becomes important in cases of high valence states as represented by these formally d^0 classical polyhydride complexes.

Two basis sets were employed in the calculations reported here. The majority of the calculations used a valence double-ζ (VDZ) basis. A [3s3p2d] contracted basis[18] was used for Re, in which the inner 5s and 5p orbitals are described by a single contracted function, while the outer 5d, 6s, and 6p orbitals are represented by two functions (and analogously for Tc). Similarly for P, a [2s2p] contracted basis[19] was used to represent the 3s and 3p orbitals, and a (4s) – [2s] contracted double-ζ basis[21] was used on all hydrogen atoms.

A valence double-ζ plus polarization (VDZP) basis was used for selected cases in which the VDZ basis has been augmented by f functions on the metal and p functions on the hydrogen atoms directly bound to the metal. For Re a three-term Gaussian fit[22] to a Slater-type 4f orbital was used, where the effective exponent of 2.19 was optimized from CI calculations on the $5d^6\,6s^1$ state of the atom. An effective exponent of 2.56 was adopted from the compilation by Walch et al.[23] for the second transition series elements. A 2p exponent of 1.0 was used for the seven hydrogen atoms.

For each structure a full geometry optimization was carried out at the Hartree–Fock level using analytic gradient techniques. The P–H bond lengths (1.4 Å) and M–P–H bond angles (119°) were held fixed during this procedure. For the resultant local minimum geometry, a configuration interaction calculation was carried out comprising all single and double excitations (CI) involving the valence electrons. The six lowest core orbitals and the three highest virtual orbitals were excluded in the CI calculations. (In the VDZP calculations, no exclusions were placed on the virtual orbitals, although it was determined later that these highest orbitals affect the energy at most 0.1 kcal/mol.) The resultant CI calculations involved 41 682 to 82 609 spin eigenfunctions for C_{2v} and C_s molecular symmetries in the VDZ basis, compared to 130 052 to 258 664 spin eigenfunctions for the analogous cases in the VDZP basis. The effects of higher order excitations were estimated using the Davidson correction[24] for quadruple excitations as denoted by CI+Q results.

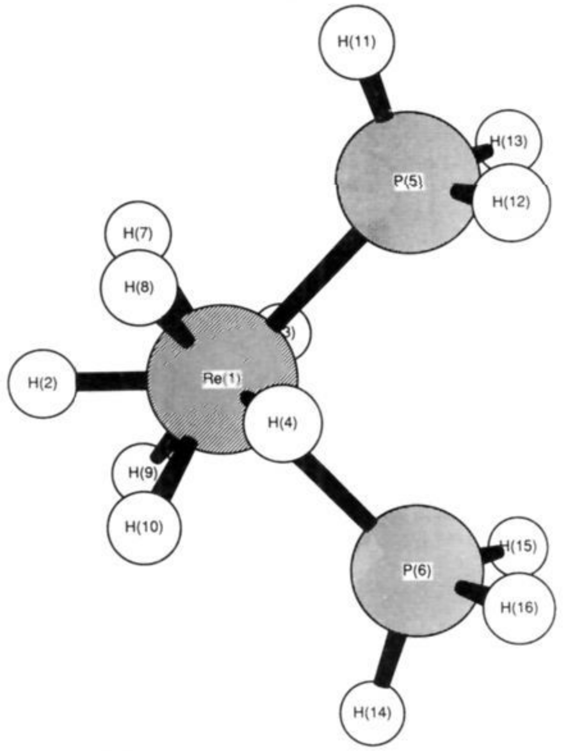

Figure 1. Calculated geometric structure of the classical form (**3**) of $ReH_7(PH_3)_2$.

Table I. Calculated Geometrical Parameters for Nine-Coordinated $ReH_7(PH_3)_2$ Complexes

Bond Lengths (Å)

ReH_7L_2 **3**		ReH_7L_2 **4**		ReH_7L_2 **3a**	
Re–H_2	1.632	Re–H_3	1.659	Re–H_2	1.677
Re–H_3	1.687	Re–H_6	1.671	Re–H_3	1.695
Re–H_8	1.664	Re–H_7	1.700	Re–H_8	1.667
H_2–H_8	1.738	H_4–H_8	1.750	H_2–H_8	1.940
H_4–H_8	1.843	H_3–H_9	1.772	H_4–H_8	1.982
H_7–H_8	1.895	H_6–H_{10}	1.997	H_7–H_8	1.879
		H_6–H_9	1.906		
Re–P_5	2.549	Re–P_2	2.495	Re–P_5	2.481
		Re–P_5	2.503		

Bond Angles (deg)

ReH_7L_2 **3**		ReH_7L_2 **4**		ReH_7L_2 **3a**	
H_2–Re–H_3	108.9	H_3–Re–H_4	138.6	H_2–Re–H_3	70.2
H_3–Re–H_4	142.2	H_7–Re–H_8	73.6	H_3–Re–H_4	140.5
H_7–Re–H_8	69.4	H_6–Re–H_9	69.6	H_7–Re–H_8	68.6
H_2–Re–H_8	63.6	H_4–Re–H_{10}	74.4	H_2–Re–H_8	131.7
P_5–Re–P_6	93.9	P_2–Re–P_5	143.7	P_5–Re–P_6	144.9
P_5–Re–H_8	78.3	P_5–Re–H_{10}	76.9	P_5–Re–H_8	74.6
P_5–Re–H_3	77.2	P_2–Re–H_{10}	139.4	P_5–Re–H_3	84.1
		P_2–Re–H_6	73.5		
		P_5–Re–H_7	78.1		

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Table II. Geometrical Parameters for Nine-Coordinate TcH$_7$L$_2$ Structures

Bond Lengths (Å)

TcH$_7$L$_2$ **3**		*cis*-Tc(H$_2$)$_2$H$_3$L$_2$ **7**		*trans*-Tc(H$_2$)$_2$H$_3$L$_2$ **8**	
Tc–H$_2$	1.616	Tc–H$_2$	1.686	Tc–H$_2$	1.858
Tc–H$_3$	1.675	Tc–H$_3$	1.611	Tc–H$_3$	1.865
Tc–H$_8$	1.678	Tc–H$_4$	1.690	Tc–H$_4$	1.737
		Tc–H$_5$	1.953	Tc–H$_5$	1.916
		Tc–H$_7$	1.938	Tc–H$_7$	1.681
Tc–P$_5$	2.556	Tc–P$_9$	2.507	Tc–P$_9$	2.523
H$_2$–H$_8$	1.691	H$_5$–H$_6$	0.768	H$_2$–H$_3$	0.789
H$_4$–H$_8$	1.765	H$_7$–H$_8$	0.784	H$_5$–H$_6$	0.766
H$_7$–H$_8$	1.851	H$_2$–H$_3$	1.653	H$_7$–H$_8$	1.581

Bond Angles (deg)

TcH$_7$L$_2$ **3**		*cis*-Tc(H$_2$)$_2$H$_3$L$_2$ **7**		*trans*-Tc(H$_2$)$_2$H$_3$L$_2$ **8**	
H$_2$–Tc–H$_3$	104.4	H$_2$–Tc–H$_3$	60.1	H$_4$–Tc–H$_8$	151.6
H$_3$–Tc–H$_4$	151.2	H$_3$–Tc–H$_4$	60.1	H$_4$–Tc–H$_8$	151.6
H$_7$–Tc–H$_8$	68.6	H$_4$–Tc–H$_5$	80.0	H$_7$–Tc–H$_8$	56.1
H$_2$–Tc–H$_8$	62.6	H$_2$–Tc–H$_7$	79.0	H$_4$–Tc–H$_5$	88.6
				H$_4$–Tc–H$_3$	81.6
P$_5$–Tc–P$_6$	91.8	P$_9$–Tc–P$_{10}$	167.4	P$_9$–Tc–P$_{10}$	155.1
P$_5$–Tc–H$_8$	80.1	P$_9$–Tc–H$_2$	86.6	P$_9$–Tc–H$_3$	91.0
P$_5$–Tc–H$_3$	80.0	P$_9$–Tc–H$_3$	83.7	P$_9$–Tc–H$_4$	85.8

Results and Discussion

Nine-Coordinate Classical Structures. We first consider the classical nine-coordinate structure MH$_7$L$_2$ (**3**), the optimized geometry for which is shown in Figure 1. This structure, having C_{2v} symmetry, corresponds to a tricapped trigonal prism (TPP) where the top and bottom triangular faces are formed by one phosphine (P$_5$) and two H atoms (H$_7$ and H$_8$). The equatorial hydrogens (H$_2$, H$_3$, and H$_4$) cap the three sides of the prism. The calculated bond lengths and bond angles for the ReH$_7$(PH$_3$)$_2$ structure corresponding to **3** are given in Table I. Structural information for the TcH$_7$L$_2$ analogue, which has apparently not yet been synthesized, is given in Table II. Similar geometrical parameters are obtained, with the Tc–H bond lengths 0.016–0.026 Å shorter than the corresponding Re–H values.

The calculated values are compared to the experimental neutron diffraction results[5] for the ReH$_7$(dppe) complex in Table III. The predicted metal–hydrogen bond lengths range from 1.63 to 1.69 Å and agree quite well with the experimental values (within 0.01 Å except for M–H$_2$, which is within 0.03 Å). The unique Re–H$_2$ bond is shortest, the four equivalent bonds to H$_7$, H$_8$, H$_9$, and H$_{10}$ are intermediate in length, and the two bonds to H$_3$ and H$_4$ are the longest, also in agreement with the experimental trend. Metal–phosphine bond lengths are generally considerably overestimated at the Hartree–Fock level, as is also observed in this case where the calculated M–PH$_3$ bond length (2.549 Å) is 0.12 Å longer than the M–dppe experimental value. The calculated P–M–P angle (93.9°) is somewhat larger, as expected, than the experimental angle (83°) constrained by the bridging CH$_2$ groups in the bidentate dppe moiety.

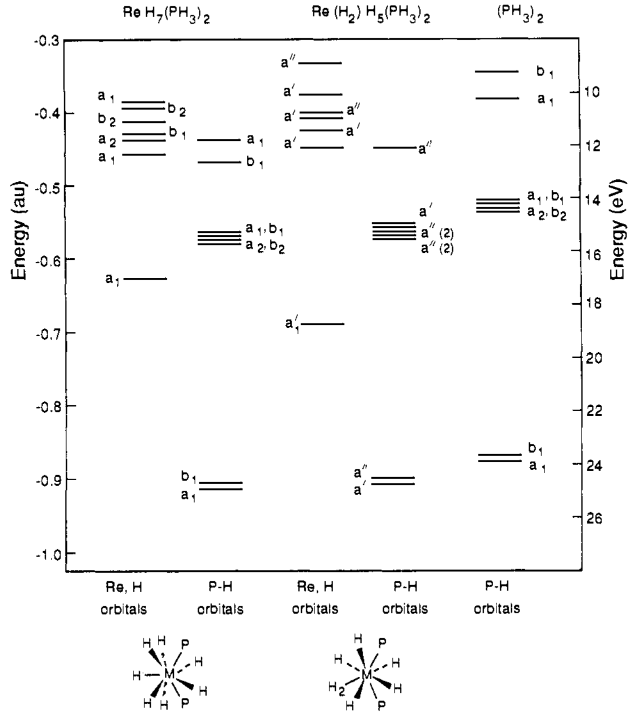


Figure 2. Energies of highest occupied levels of ReH$_7$(PH$_3$)$_2$ and Re(H$_2$)H$_5$(PH$_3$)$_2$.

Although this structure might be viewed as a d^0 complex from an electron-counting perspective where the hydride ligands are regarded as H$^-$ entities, the electronic structure is considerably more covalent in character as reflected in the Mulliken population analysis, which yields a 5d population of 6.5 electrons and a (6s,6p) population of 2.3 electrons. (One should add the customary cautionary note that such analyses typically overestimate the valence s and p character of transition metals in complexes and hence overestimate the total electronic population on metal centers. Indeed, the Mulliken analysis gives an overall net charge of −1.8 on the Re that is clearly unphysical.)

Ignoring the metal–phosphine interactions for the moment, there remain seven bonding orbitals involved in the formation of Re–H bonds, as shown in the Hartree–Fock orbital energies of the highest occupied orbitals in Figure 2. In C_{2v} symmetry these involve three orbitals of a$_1$ symmetry, two of b$_2$, and one each of b$_1$ and a$_2$. In the coordinate system used in Figure 2, the 5d orbitals span the a$_1$ (d_{z^2}, $d_{x^2-y^2}$), b$_2$ (d_{xz}), b$_1$ (d_{yz}), and a2 (d_{xy}) representations.

The nine-coordinate structure discussed thus far corresponds to the observed neutron diffraction structure by Howard et al.[5] In solution such high-coordination complexes could be quite fluxional and may have several local minima on the global potential energy surface. Another possible nine-coordinate structure in solution was suggested by NMR studies[11] which indicated the presence of inequivalent phosphine ligands, in contrast with the situation with the C_{2v} structure where the phosphines are equivalent. An alternative structure (**4**) was investigated in which one phosphine and two hydrogen ligands occupy the equatorial capping

Table III. Comparison of Calculated and Experimental Bond Lengths (Å) and Angles (deg) for MH$_7$(PR$_3$)$_2$ Complexes

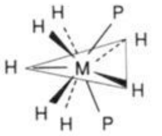
	ReH$_7$(PH$_3$)$_2$ calc **3**	ReH$_7$(dppe)[a] exptl **3**	ReH$_7$(PR$_3$)$_2$ exptl	TcH$_7$(PH$_3$)$_2$ calc **3**	ReH$_7$(PH$_3$)$_2$ calc **3a**	ReH$_7$(PR$_3$)$_2$ exptl **3a**, distorted
M–H$_2$	1.632	1.660		1.616	1.676	1.676
M–H$_3$, H$_4$	1.687	1.689		1.675	1.695	1.697, 1.684
M–H$_7$, H$_8$, H$_9$, H$_{10}$	1.664	1.669 1.671		1.638	1.667	1.673, 1.678 1.679, 1.683
M–P$_5$	2.549	2.425	2.427[b] 2.396[c]	2.556	2.481	2.403, 2.405
P$_5$–M–P$_6$	93.9	83.0	138.9[b] 146.8[c]	91.8	144.9	151.3

[a] dppe = 1,2-bis(diphenylphosphino)ethane, ref 5. [b] L = PPh$_3$, ref 13. [c] L = PMe$_2$Ph, ref 14. [d] L = P(p-tolyl)$_3$, ref 25.

Table IV. Relative Energies and Total Energies of ReH_7L_2 and TcH_7L_2 Species

	relative energy (kcal/mol)		
structure	SCF	CI	CI + Q
	VDZ Basis		
ReH_7P_2 **3**	0.0	0.0	0.0
ReH_7P_2 **4**	10.4	8.2	7.4
$Re(H_2)H_5P_2$ **5**	−5.2	1.2	2.8
$Re(H_2)_2H_3P_2$ **7**	−2.5	6.8	10.5
ReH_7P_2 **3a**	1.6	0.7	0.6
	VDZP Basis		
ReH_7P_2 **3**	0.0	0.0	0.0
$Re(H_2)H_5P_2$ **5**	−1.9	3.2	4.4
	VDZ Basis		
TcH_7P_2 **3**	0.0	0.0	0.0
$Tc(H_2)H_5P_2$ **5**	[−17.9], unstable		
$Tc(H_2)_2H_3P_2$ **7**	−31.4	−11.8	−7.7
$Tc(H_2)_2H_3P_2$ **8**	−28.2	−5.0	−7.5
	VDZP Basis		
TcH_7P_2 **3**	0.0	0.0	0.0
$Tc(H_2)_2H_3P_2$ **7**	−24.2	−5.6	−1.5
	Total Energy (au)		
	VDZ Basis		
ReH_7P_2 **3**	−98.301499	−98.620138	−98.668216
TcH_7P_2 **3**	−99.234891	−99.572064	−99.625579
	VDZP Basis		
ReH_7P_2 **3**	−98.340416	−98.801531	−98.868110
TcH_7P_2 **3**	−99.288226	−99.739755	−99.811320

positions as opposed to the situation with three equatorial hydrogen ligands in **3**. Two views of the resultant optimized structure is shown schematically in Figure 3, and selected geometrical parameters for **3** and **4** are given in Table I. The structure **4** is found to be 10.4 kcal/mol higher in energy than the C_{2v} nine-coordinate structure **3** and 8.2 kcal/mol higher when electron correlation effects are included at the CI level. The relative energies of various structures considered are given in Table IV at both SCF and CI levels of treatment.



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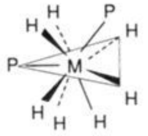

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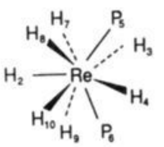

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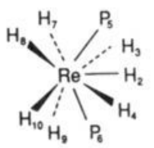

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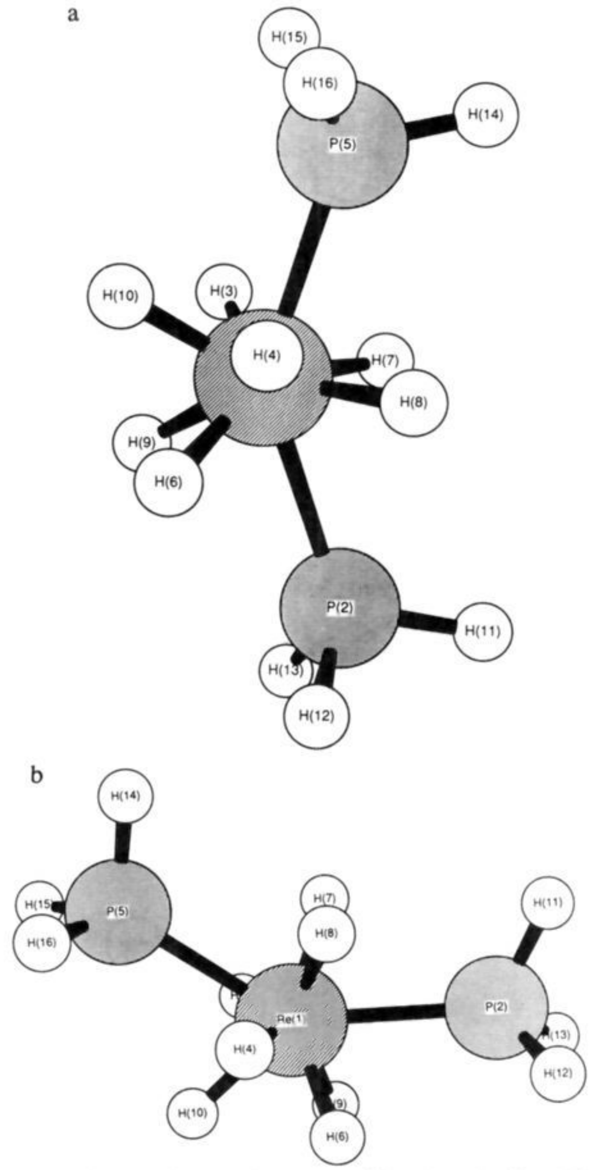

Figure 3. Calculated geometric structure of the alternative form (**4**) of $ReH_7(PH_3)_2$: (a) view analogous to Figure 1 and (b) view showing equatorial phosphine group and two hydride ligands capping a trigonal prism.

Another form of a Re heptahydride complex has been observed recently in a neutron diffraction study by Brammer et al.[25] of $ReH_7(PR_3)_2$ where R = *p*-tolyl. The idealized structure resembles the monocapped square antiprism depicted in structure **3a**, where H_2 is the capping atom of the H_3–P_5–H_4–P_6 face of the square antiprism. The relationship to structure **3** can be derived by viewing **3** as a square antiprism with H_2 now capping the "bottom" H_7–H_8–H_{10}–H_9 face instead of the "top" H_3–P_5–H_4–P_6 face as in **3a**. This form was also investigated for the model $ReH_7(PH_3)_2$ complex, and the geometrical parameters of the optimized C_{2v} structure **3a** also appear in Table I. The experimental structure is considerably distorted from the idealized form, as shown in Table III where the observed bond lengths are compared to the calculated values. A salient feature of the neutron diffraction study is the distinct nonequivalence of the four hydrogens on the face opposite the capping hydrogen H_2. The separation for two of the hydrogens corresponding to H_8 and H_{10} is found to be only 1.357 Å, a value intermediate between the 1.6–1.8 Å distances typically found in classical polyhydrides and the 0.8 Å characteristic of dihydrogen complexes.

At the SCF level the calculated energy of the alternative form (**3a**) lies only slightly more than 1 kcal/mol higher than the classical nine-coordinated structure (**3**), and at the CI level the separation diminishes to less than 1 kcal/mol (Table IV). This indicates that both classical forms are likely to be present in solution. In addition, the results discussed in the section place the nonclassical eight-coordinate $Re(H_2)H_5P_2$ species within 1–4 kcal/mol of the classical structure, so that it is not unreasonable to regard the distorted structure described by Brammer et al. as a species along a path between classical and nonclassical forms.

Eight-Coordinate $M(\eta^2\text{-}H_2)H_5L_2$ and Seven-Coordinate $M(\eta^2\text{-}H_2)_2H_3L_2$ Structures. The structures discussed in the previous section all correspond to classical nine-coordinate polyhydride

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(25) Brammer, L.; Howard, J. A. K.; Johnson, O.; Koetzel, J. F.; Spencer, J. L.; Stringer, A. M. *J. Chem. Soc., Chem. Commun.* **1991**, 241.

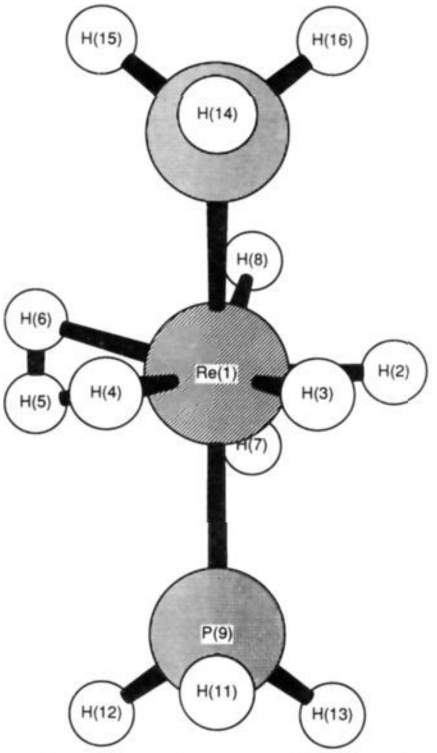
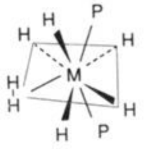


Figure 4. Calculated geometric structure of eight-coordinate complex (**5**), $Re(H_2)H_5(PH_3)_2$.

structures of MH_7L_2 species. In this section we discuss various nonclassical structures that were investigated containing one or more dihydrogen ligands.

A dodecahedral structure was investigated as an eight-coordinate nonclassical structure for $M(\eta^2\text{-}H_2)H_5(PH_3)_2$ as depicted in **5**. In the plane of symmetry of this form are three hydride ligands and the center of the H_2 ligand, which is perpendicular to the plane. The two phosphine ligands and remaining two hydride ligands lie symmetrically on either side of the central plane. The optimized structure for $Re(H_2)H_5L_2$ is shown in Figure 4, and the geometrical parameters are summarized in Table V. The H_2 ligand is characterized by a longer Re–H bond length (1.88 Å), compared to Re–H distances between 1.66 and 1.72 Å for the other ligands, and a H–H distance of 0.79 Å, slightly longer than the bond length of uncoordinated H_2 (0.74).



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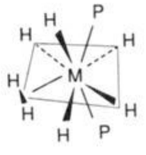

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The energies of the occupied orbitals are compared to their counterparts in the nine-coordinate polyhydride structure in Figure 2. The primary change is the conversion of two Re–H bonding orbitals into an H–H bonding orbital (the lowest a_1 orbital in the figure) and a dπ lone pair orbital directed toward the H_2 ligand. As shown schematically in Figure 5, the nominally H_2 bonding orbital delocalizes slightly onto the metal, and the dπ orbital mixes in some antibonding σ^* character on the H_2. These interactions are familiar from other metal complexes such as d^6 $ML_5(\eta^2\text{-}H_2)$ systems where σ donation from the H_2 onto the metal and π donation from the metal onto H_2 characterize the bonding. The Mulliken populations, which are notoriously misleading in general for transition-metal complexes, do not reflect significant redistribution of charge, however, as two M–H bonds are converted into an H_2 bond and a 5d lone pair on the metal. In the case of Re, for example, the gross populations of the valence electrons are $s^{0.48}$ $p^{1.81}$ $d^{6.54}$ for ReH_7P_2 compared to $s^{0.47}$ $p^{1.57}$ $d^{6.55}$ for $Re(H_2)H_5P_2$. Similarly for TcH_7P_2 and *cis*-$Tc(H_2)H_3P_2$ the d populations, which are more reliably given by Mulliken populations compared to the diffuse s and p contributions, change relatively little in the gross populations of $s^{0.44}$ $p^{1.67}$ $d^{6.75}$ and $s^{0.38}$ $p^{0.90}$ $d^{6.78}$, respectively.

Table V. Geometrical Parameters for Eight- and Seven-Coordinate ReH_7L_2 Species

Bond Lengths (Å)

$Re(H_2)H_5L_2$ **5**		$Re(H_2)_2H_3L_2$ **7**	
$Re\text{-}H_2$	1.656	$Re\text{-}H_2$	1.691
$Re\text{-}H_3$	1.661	$Re\text{-}H_3$	1.645
$Re\text{-}H_4$	1.721	$Re\text{-}H_8$	1.853
$Re\text{-}H_5$	1.888	$Re\text{-}P_9$	2.456
$Re\text{-}H_7$	1.682	$H_5\text{-}H_6$	0.828
$Re\text{-}P_9$	2.473	$H_2\text{-}H_3$	1.720
$H_2\text{-}H_3$	1.701		
$H_3\text{-}H_4$	1.971		
$H_4\text{-}H_5$	0.796		
$H_3\text{-}H_8$	1.720		
$H_2\text{-}H_7$	1.999		

Bond Angles (deg)

$Re(H_2)H_5L_2$ **5**		$Re(H_2)_2H_3L_2$ **7**	
$H_2\text{-}Re\text{-}H_3$	61.7	$H_2\text{-}Re\text{-}H_3$	64.1
$H_3\text{-}Re\text{-}H_4$	71.3	$H_3\text{-}Re\text{-}H_4$	64.1
$H_4\text{-}Re\text{-}H_5$	77.5	$H_4\text{-}Re\text{-}H_5$	76.4
$H_5\text{-}Re\text{-}H_7$	74.5	$H_2\text{-}Re\text{-}H_7$	76.4
$H_7\text{-}Re\text{-}H_8$	63.5	$P_9\text{-}Re\text{-}P_{10}$	163.9
$H_2\text{-}Re\text{-}H_7$	73.4	$P_9\text{-}Re\text{-}H_2$	86.6
$P_9\text{-}Re\text{-}P_{10}$	151.5	$P_9\text{-}Re\text{-}H_3$	86.5
$P_9\text{-}Re\text{-}H_7$	72.2		
$P_9\text{-}Re\text{-}H_2$	91.5		

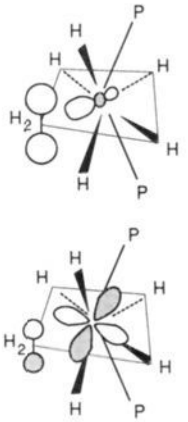


Figure 5. Schematic drawing of the H_2 bonding orbital and the Re 5d π orbital in $Re(H_2)H_5(PH_3)_2$.

The results in Table IV also provide information on the rotational barrier of coordinated dihydrogen about the metal–H_2 bond. In the case of the eight-coordinate complex, the upright form (**5**) lies 4.5 kcal/mol lower than the form (**6**) with the H_2 rotated 90° into the plane of the other hydride ligands. Since in both cases there is an occupied dπ lone pair on the metal, the preference for the upright form would be consistent with the dπ back-bonding, albeit weak, that can occur into the vacant σ^* H_2 orbital in this orientation.

For the case of Tc, no stable eight-coordinate structure could be located analogous to structure **5** of Re. Instead, the molecule collapsed to a seven-coordinate form during the geometry optimization. Attempts to locate other possible eight-coordinate minima also failed to identify stable structures. The possible origins of these differences between Tc and Re will be discussed below.

Of possible seven-coordinate complexes, one structure for $Re(H_2)_2H_3(PH_3)_2$ that was considered here (**7**) consists of five

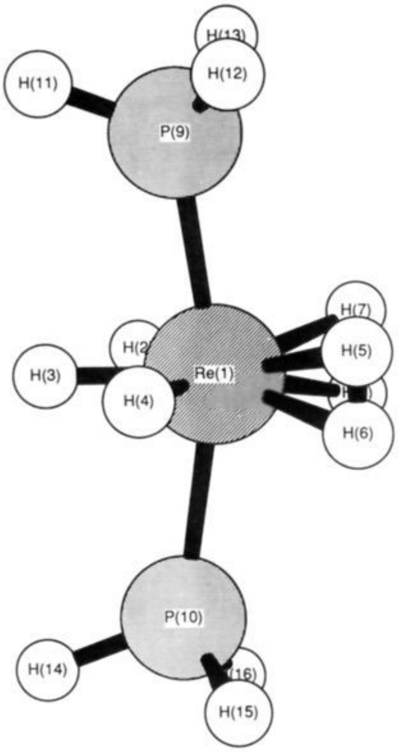
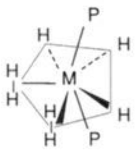


Figure 6. Calculated geometric structure of the cis form (**7**) of Re-$(H_2)_2H_3(PH_3)_2$.

ligands about the central Re atom in a planar arrangement (three hydride and two H_2 ligands) with the phosphine ligands lying above and below the plane. The optimized structure appears in Figure 6, and the geometrical parameters are summarized in Table V. The H–H distances of 0.828 Å for the H_2 ligands are slightly longer than the calculated H_2 distance of 0.796 Å in the eight-coordinate dihydrogen complex.



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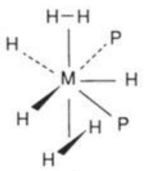

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The nature of the bonding in seven-coordinate *cis*-ReH-$(H_2)H_3(PH_3)_2$ closely resembles the features of the eight-coordinate structure shown in Figure 2. In the seven-coordinate case, there are now two H_2 bonding orbitals at low energy and two predominantly 5d π lone pair orbitals on Re. As shown in Figure 7, there is significant backbonding into the σ^* H_2 orbitals. These two orbitals (with energies 8.3 and 8.6 eV) are the highest occupied levels in the complex, with the metal–hydrogen bonding orbitals lying at lower energies (10.2 eV and below). This picture is quite consistent, then, with the formal designation of the complex as a d^4 species.

The structure for the analogous *cis*-$Tc(H_2)_2H_3(PH_3)_2$ complex corresponding to **7** is shown in Figure 8a, and the geometrical parameters are given in Table II. As will be discussed in a later section, this form corresponds to the global minimum of TcH_7L_2 structures studied here in contrast to Re, where the classical nine-coordinate structure represents the global minimum.

In addition, a trans complex (**8**) was also investigated, which can be viewed as having three hydride and two phosphine ligands in the central plane with the H_2 ligands in axial positions above and below the plane. Two views of this form are shown in Figure 8 (parts b and c), and the structural parameters also appear in Table II. The calculated H–H separations in the Tc complexes lie in the range 0.78–0.80 Å, typical values for dihydrogen ligands. The bonding in the Tc seven-coordinate complexes mirrors the situation for the Re complex discussed above. Two 4dπ orbitals appear at 8.5 and 8.7 eV as the highest occupied orbitals in **7** separated by over an eV from the manifold of Tc–H bonding orbitals. In **8**, however, a third Tc–H bonding orbital lies very close to the nominally nonbonding 4d orbitals.

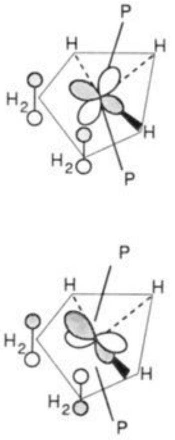

Figure 7. Schematic drawing of the Re 5d π orbitals in *cis*-$Re(H_2)H_5(PH_3)_2$.

In the d^2 eight-coordinate structure and the d^4 seven-coordinate structures discussed above, the formally occupied d orbitals are different from the ones in traditional ligand field analysis of eight-coordinate[26–29] and seven-coordinate[30] complexes. For example, in the idealized MA_4B_4 dodecahedron, the occupied d orbital was the $x^2–y^2$ component, where the *xy* plane was defined perpendicular to the 4-fold axis. In the eight-coordinate Re-$(H_2)H_5L_2$ structure, by contrast, the occupied d orbital is the d_{xz} orbital with π symmetry relative to the plane defined by the three hydride ligands and the midpoint of the H_2 molecule. Much of these differences can be attributed to the following factors: (1) the complexes studied here have very low symmetry and are not easily described in terms of idealized structures, (2) the bonding is considerably more covalent here than in the ionic limit often assumed in ligand field analyses, and (3) some stabilization arises from the dπ interaction with the H_2 σ^* orbital.

A few comments should be made regarding (1) the possible existence of other structures and (2) the stability of the structures that were found. In view of the many likely structures that could exist, the structures obtained from the geometry optimizations should be considered representative nonclassical structures. While attempts to find other stable structures did not lead to lower energy forms, the possibility of other structures with comparable or lower energies should not be precluded. On the latter issue of stability, the calculation of vibrational frequencies would provide a definitive test of stability since a local minimum would exhibit all positive force constants. In nearly all cases here, however, the geometry optimizations were carried out with sufficiently flexible degrees of freedom to allow the structure to relax to lower energy forms.

Effects of Electron Correlation and Basis Set Size on Relative Stabilities. In the discussion to this point the results have been based primarily on optimized geometries obtained at the Hartree–Fock level (SCF) in the VDZ basis and energies from CI calculations at these geometries. There are three main factors which could influence the predicted relative stabilities derived from this procedure: (1) the quality of the VDZ basis set employed, (2) the reliability of using a Hartree–Fock single-reference function in a CI calculation limited to single and double excitations, and (3) the use of PH_3 ligand to model alkyl phosphine ligands. While the first two factors will have been explored in the following section, any detailed discussion about the use of PH_3 will be deferred to future papers. More basic alkyl phosphines could alter the relative energies of classical and nonclassical forms, presumably toward the former type, and bulker phosphine substituents would add steric interactions not present in the model complex. Nevertheless, excellent agreement was obtained recently in studies of the structures and rotational barriers of $W(PR_3)_2(CO)_3(H_2)$

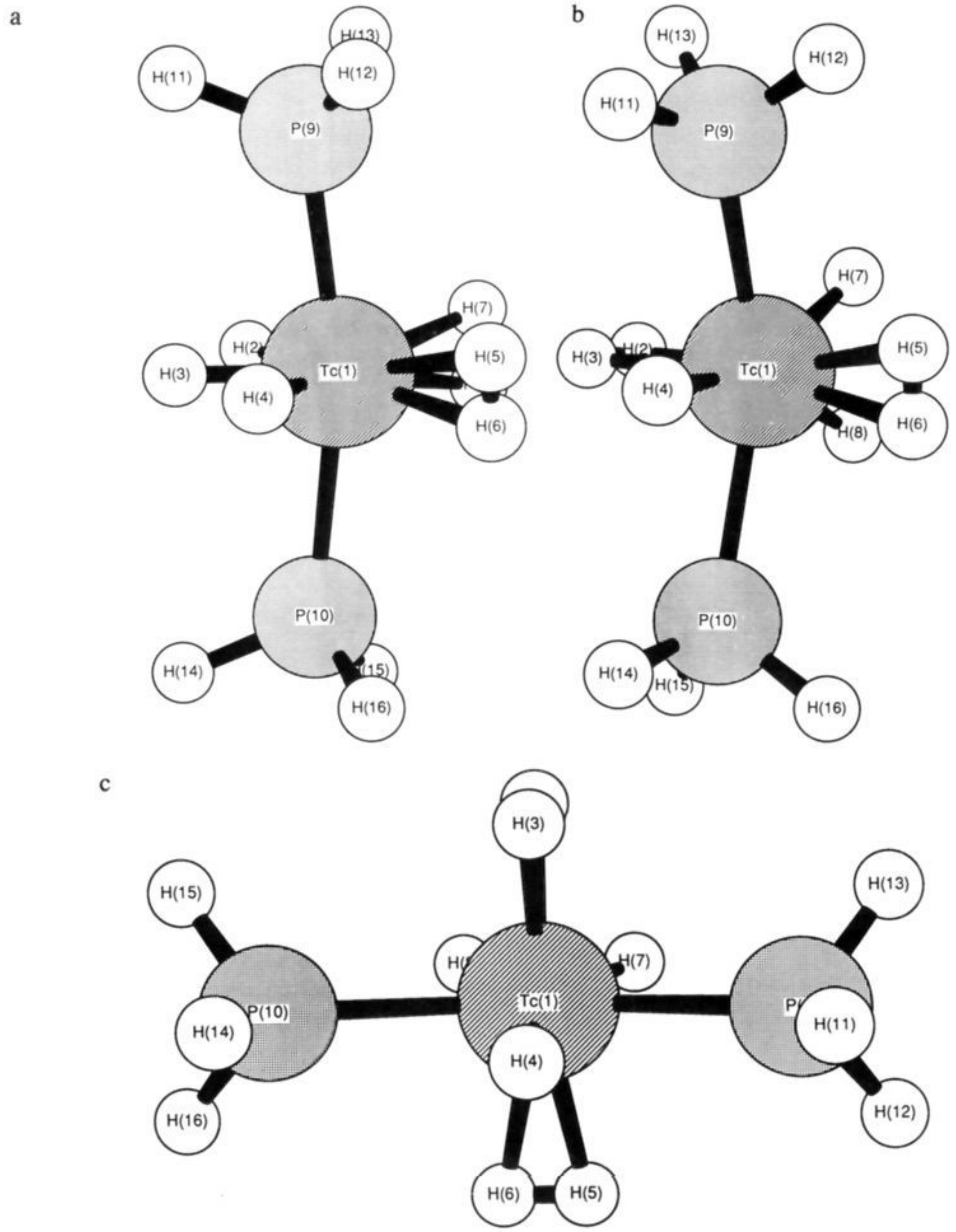

Figure 8. Structure corresponding to optimized geometries of $TcH_7(PH_3)_2$: (a) cis form (**7**) and (b) and (c) two views of trans form (**8**).

complexes[26] using PH_3 model ligands as well as more realistic $P(CH_3)_3$ ligands.

As to the effects of basis set size, the effects of enlarging the basis to include polarization functions (f functions on the metal p functions on H atoms bound to the metal) in the VDZP basis are summarized in Table IV. For Re and Tc, the lowest energy classical and nonclassical species found in the VDZ basis were investigated. In each case, the effect of the added functions in the VDZP basis is to stabilize the classical form to a small degree relative to the VDZ result. The difference between structures **3** and **5** for Re is −5 and +1 kcal/mol for SCF and CI, respectively, in the VDZ basis compared to −2 and +3 kcal/mol, respectively, in the VDZP basis. For Tc, the nonclassical structure **7** is still calculated to be the lowest energy structure at all levels of calculation, but the difference has been reduced from 31 and 12 kcal/mol, for SCF and CI in the VDZ basis, and to 24 and 6 kcal/mol in the larger basis.

The effects of higher order excitations, as estimated by the CI+Q procedure, also leads to changes of the order of 1–4 kcal/mol in relative stabilities generally in favor of the classical structures as shown in Table IV. Relatively little difference (about 1 kcal/mol) is observed between the stabilities of the Re nine- and eight-coordinate species, while effects of up to 4 kcal/mol are evident between nine- and seven-coordinate structures for both Re and Tc. (Another approach to explore these effects involves multi-reference CI calculations based on CAS-SCF or GVB reference functions. Recent calculations[31] indicate that results using these approaches lead to even greater stabilization of classical relative to nonclassical structures.)

Relative Energies of Classical and Nonclassical Polyhydrides of Re and Tc. The relative energetics of the nine-, eight-, and seven-coordinate species are summarized in Table IV. Electron

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(26) Orgel, L. E. J. *Inorg. Nucl. Chem.* **1960**, *14*, 136.

(27) Lippard, S. J. *Prog. Inorg. Chem.* **1967**, *8*, 109; **1976**, *21*, 91.

(28) (a) Muetterties, E. L.; Wright, C. M. *Quart. Rev., Chem. Soc.* **1967**, *8*, 109. (b) Parish, R. V. *Coord. Chem. Rev.* **1966**, *1*, 439. (c) Clark, R. J. H.; Kepert, D. L.; Nyholm, R. S.; Lewis, J. *Coord. Chem. Rev.* **1977**, *24*, 179.

(29) Burdett, J. K.; Hoffmann, R.; Fay, R. C. *Inorg. Chem.* **1978**, *17*, 2553.

(30) Hoffmann, R.; Beier, B. F.; Muetterties, E. L.; Rossi, A. R. *Inorg. Chem.* **1977**, *16*, 511.

(31) Hall, M. B., private communication.

correlation effects, as treated in the CI calculations, are seen to be crucial in obtaining relative orderings of various species. For example, at the SCF level in the VDZ basis, the eight-coordinate $Re(H_2)H_5L_2$ and seven-coordinate $Re(H_2)_2H_3L_2$ structures lie 5 and 2 kcal/mol, respectively, below the classical nine-coordinate structure. At the CI level, by contrast, the classical structure is predicted to be the most stable, although only by 1 and 7 kcal/mol, respectively, relative to the eight- and seven-coordinate structures.

For the Tc analogues, there are two major qualitative differences relative to the Re complexes. In the VDZ basis, the seven-coordinate structure is predicted to be the most stable form by 12 kcal/mol even at the CI level—just the reverse of the situation for Re, where the seven-coordinate structure was the *least* stable form. As noted above, at the highest level of theory (CI+Q in the VDZP basis), this difference is reduced to 1.5 kcal/mol. The other major difference concerns the existence of a stable eight-coordinate structure for $Tc(H_2)H_2L_2$, since our attempts to obtain a local minimum corresponding to this form resulted in collapse to the seven-coordinate form.

On the basis of the previous theoretical results for the model MH_7L_2 complexes, the classical nine-coordinate structure is energetically favored for Re with the ordering

$$ReH_7L_2 < Re(H_2)H_5L_2 < Re(H_2)_2H_3L_2$$

relative to eight- and seven-coordinate nonclassical structures, while for Tc the ordering

$$Tc(H_2)_2H_3L_2 < [Tc(H_2)H_5L_2] < TcH_7L_2$$

is found. (The placement of the apparently unstable eight-coordinate structure is based on estimates from structures with geometrical constraints.) This overall preference suggests that dihydrogen-containing complexes should be more readily found for Tc than for Re. Since the chemistry of Tc–hydrogen complexes has yet to be explored, these theoretical predictions will have to await further experimental studies. These results are consistent with the general notion that second-row transition metal complexes show a greater tendency to favor dihydrogen complex to dihydride forms than their third-row counterparts. For example, in the case of $M(CO)_3(PR_3)_2(H_2)$ complexes recent dynamical studies[3c] place the dihydrogen form only 1 kcal/mol lower in energy than the dihydride form in the case of M = W. The analogue with M = Mo, by comparison, appears to exist only in the dihydrogen form. A complicating factor is the apparent lower overall stability of either form for second transition-metal hydrogen complexes, but in general the "more basic" third-row elements are more effective in "activating" the hydrogen ligand toward the dihydride form.

As one lowers the effective coordination number in the Re complexes one finds the electronic structure to have no 5d lone pairs in the nine-coordinate form, one 5d lone pair for eight-coordinate, and two 5d lone pairs for seven-coordinate. The remaining 5d and 6s,6p hybrid orbitals are involved in Re–H bonding interactions. It is perhaps helpful to examine the relative energies of the states of the metal atoms themselves[32] to understand the difference in trends between Re and Tc for nine, eight, and seven coordination in that the states are ordered

$$6s^25d^5 \text{ (0.0 eV)}, 6s^15d^6 \text{ (1.76 eV)}, 5d^7 \text{ (5.80 eV) for Re}$$

$$5s^24d^5 \text{ (0.0 eV)}, 5s^14d^6 \text{ (0.75 eV)}, 4d^7 \text{ (3.67 eV) for Tc}$$

where experimental splittings are quoted for the first two states and calculated energies for the d^7 states for which there is no experimental value. For these states there are

no d lone pairs, 1 d lone pair, and 2 d lone pairs

respectively, indicating there is roughly 1 eV (23 kcal/mol) difference between Tc and Re in promotion energy for exciting an electron from the s shell to the d shell as successive numbers of doubly occupied d orbitals are formed. This is also consistent with the greater stabilization of the 6s orbital in Re relative to the 5s orbital in Tc by relativistic effects which are more pronounced in the third transition series. These factors could account for the preference of Tc to have lower coordination number complexes than Re.

Table VI. Energies of Nine-Coordinate and Eight-Coordinate Forms of ReH_7L_2 Complexes and Their Positive Ions

	nine-coord	eight-coord
	Ionization Energies (eV)	
$-\epsilon_i$[a]	10.51	9.12
SCF[b]	8.93	6.80
CI[c]	9.11	7.01
	Total Energies (au)	
SCF neutral	−98.301499	−98.309892
SCF ion	−97.973194	−98.059878
CI neutral	−98.620138	−98.618157
CI ion	−98.285343	−98.360481

[a] Using orbital energy and Koopmans' theorem. [b] Using separate restricted HF calculations on each neutral and ionic species. [c] Using CI calculations including single and double excitations from the SCF reference state for each species.

Positive Ions of Re Polyhydrides. In an effort to provide information on the ionization energies of classical and nonclassical Re polyhydrides, the results of various calculations on the classical structure $ReH_7(PH_3)_2$ and the nonclassical form $Re(H_2)H_5(PH_3)_2$ are reported in Table VI. One motivation for these calculations is the recent electrochemical study of Costello and Walton,[7] who attempted to identify a nonclassical form of ReH_7L_2 by comparing the redox processing occurring in ReH_5L_3 and ReH_7L_2 complexes in solution. The theoretical results in Table VI compare the difference in IPs between nine-coordinate ReH_7L_2 and eight-coordinate $Re(H_2)H_5L_2$ at three increasingly sophisticated levels: (1) simply by comparing the highest occupied orbital energies using Koopmans' theorem, (2) carrying out separate SCF calculations on the neutral and positive ions of each species, and (3) for each SCF wave function in step (2) performing a CI calculation containing all single and double excitations. Although the relative difference in IPs between the classical and nonclassical forms is comparable in all three calculations, the most accurate CI results predict a difference of 2.1 eV between the IPs of the nine-coordinate (9.11 eV) and eight-coordinate (7.01 eV) structures. Since the ionization in the nine-coordinate structure arises from a Re–H bonding orbital as compared to a nonbonding 5d orbital in the eight-coordinate structure, it is not surprising that the former has a higher ionization energy. Returning to the cyclic voltammetry studies of Costello and Walton, these investigators found two oxidations—at +0.35 and +1.0 V relative to Ag/AgCl—for ReL_5L_3, which exhibits classical behavior. The former peak was assigned to the complex itself and the latter to a product of the oxidation. A single peak that was found at +1.64 V in ReH_7L_2 was interpreted to indicate a metal-based oxidation that would be consistent with a nonclassical form. The observed difference of 1.3 V between the "classical" and "nonclassical" forms is suggestive and may be compared to the calculated "gas-phase" difference of 2.1 eV between two MH_7L_2 forms. Nevertheless, more studies of the chemistry of these complexes and their ions is clearly needed before definitive confirmation of nonclassical structures can be made.

Conclusions

The geometries, energies, and electronic properties of ReH_7L_2 and TcH_7L_2 complexes have been calculated using ab initio theoretical techniques. Relative energies at the SCF and CI levels are summarized in Table IV. Results are compared with experimental structural determination and with solution NMR studies of Re complexes. The classical ReH_7L_2 structure is found to be 2–4 kcal/mol more stable than eight-coordinate $Re(H_2)H_5L_2$ and 7–10 kcal/mol more stable than seven-coordinate $Re(H_2)_2H_3L_2$. The nonclassical seven-coordinate structures, by contrast, are predicted to be 2–12 kcal/mol lower in energy than the classical form for Tc, depending on the level of calculation. Although the small differences in energy between these forms

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make predictions of the most stable form of MH_7P_2 species with bulkier phosphine ligands in solution more difficult, these results indicate a greater tendency for Tc to display nonclassical structures relative to Re. The positive ions of ReH_7L_2 and $Re(H_2)H_5L_2$ are also investigated, with the IP of the latter form calculated to be 2.1 eV lower in energy.

Acknowledgment. The author thanks Drs. Greg Kubas and Carol Burns for helpful discussions and suggestions and Prof. Michael Hall for unpublished results on multireference CI and perturbation theory results on classical and nonclassical hydrides. This work was carried out under the auspices of the U.S. Department of Energy.

Ethynamine: The Remarkable Acid-Strengthening and Base-Weakening Effect of the Acetylenic Linkage. A Comparison with Ethenamine and Methylamine

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Abstract: Ab initio molecular orbital calculations predict that ethynamine is a substantially stronger acid but a substantially weaker base than other amines such as methylamine and ethenamine in the gas phase, as previously observed experimentally for other ynamine systems in aqueous solution. The high relative acidity of ethynamine can be attributed largely to stabilization of the ethynylamide anion and the low relative basicity to a destabilization of the ethynylammonium cation. The preferred site of protonation in both ethynamine and ethenamine is at carbon rather than nitrogen, a result which can be rationalized in terms of stabilizing interactions in the C-protonated species. High-level (G2) theoretical data are presented for the related oxygen-containing systems, ethynol, vinyl alcohol, ketene, and acetaldehyde, and used to derive new values of the heats of formation for these molecules.

Introduction

In a recent experimental study of ynamines ($RC{\equiv}CNH_2$) in aqueous solution, Kresge and co-workers[1] reported basicities and acidities which differ dramatically from those of standard saturated amines. For example, phenyl(cyclohexylamino)acetylene ($PhC{\equiv}CNHC_6H_{11}$) was found to be more than 10 orders of magnitude less basic than cyclohexylamine, while phenylaminoacetylene ($PhC{\equiv}CNH_2$) was found to be more than 17 orders of magnitude more acidic than ammonia. The $C{\equiv}C$ triple bond clearly has a massive effect, and an understanding of the operative mechanism is highly desirable.

In previous related experiments, it had been found that ynols were considerably more acidic than enols.[2] For example, phenylynol ($PhC{\equiv}COH$) was found to be more acidic than $PhCH{=}CHOH$ by more than 7 pK_a units. We subsequently examined the acidity of ynols using ab initio molecular orbital theory to see whether the very high acidity carried over to the gas phase.[3] Indeed, deprotonation of the prototype ynol, ethynol ($HC{\equiv}COH$), was calculated to require 101 kJ mol^{-1} less energy than deprotonation of its enol analogue, vinyl alcohol ($CH_2{=}CHOH$). By careful analysis of bond separation energies (BSEs), we were able to show that this greater acidity could be attributed to two contributing factors: (1) destabilization of the neutral ynol relative to the enol and (2) stabilization of the ynolate anion relative to the enolate anion.

Table I. Calculated Total Energies (hartrees) and Zero-Point Vibrational Energies (kJ mol^{-1})[a]

no.	species		HF/6-31+G*	MP4/6-311+G**	ZPVE[b]
1	$CH_3CHNH_2^+$	C_s	−133.44382	−133.99182	232.2
2	$CH_2{=}CHNH_3^+$	C_s	−133.41418	−133.96992	236.4
3	$CH_3CH{=}NH$	C_s	−133.07708	−133.63297	193.7
4	$CH_2{=}CHNH_2$	C_1	−133.06884	−133.62639	194.4
5	$CH_2{=}CHNH^-$	C_s	−132.44951	−133.01338	152.2
6	$CH_2{=}CNH_2^+$	C_{2v}	−132.21228	−132.72702	161.7
7	$HC{\equiv}CNH_3^+$	C_{3v}	−132.16913	−132.69350	169.2
8	$CH_2{=}C{=}NH$	C_s	−131.87654	−132.39942	123.6
9	$HC{\equiv}CNH_2$	C_s	−131.85287	−132.37584	126.5
10	$HC{\equiv}CNH^-$	C_1	−131.25263	−131.78571	84.3
11	$HC{\equiv}CNH^-$	C_s	−131.24952	−131.77949	81.9[c]
12	$CH_3NH_3^+$	C_{3v}	−95.57416	−95.98963	223.5
13	CH_3NH_2	C_s	−95.21417	−95.63086	180.7
14	CH_3NH^-	C_s	−94.54326	−94.96940	133.0
15	CH_3CH_3	D_{3d}	−79.22945	−79.61480	208.8
16	$CH_3CH_2^+$	C_{2v}	−78.31018	−78.65325	170.7
17	$CH_2{=}CH_2$	D_{2h}	−78.03582	−78.38334	143.6
18	$CH_2{=}CH^+$	C_{2v}	−77.07607	−77.39225	96.1
19	$HC{\equiv}CH$	$D_{\infty h}$	−76.82307	−77.14000	77.2
20	$CH_2{=}NH$	C_s	−94.03267	−94.41205	113.4
21	$CH_2{=}O$	C_{2v}	−113.87116	−114.26728	76.5
22	CH_4	T_d	−40.19567	−40.40513	125.1
23	H_2	$D_{\infty h}$	−1.12683	−1.16764	27.8

[a] HF/6-31+G* optimized structures. [b] Zero-point vibrational energies (HF/6-31+G*). [c] Structure has one imaginary frequency.

It is the purpose of the present study to carry out a similar investigation of the acidities and basicities of ethynamine, the prototype ynamine. Ethynamine has attracted theoretical attention as a possible interstellar species.[4] It was observed for the first time by Schwarz, Holmes, and co-workers in neutralization–reionization mass spectrometry experiments,[5] and subsequently some of its infrared absorptions have been recorded by Wentrup et al.[6] The focus in this paper will be on the acid–base properties of ethynamine. Comparisons will be presented with ethenamine, the prototype enamine, and with methylamine. A particular point of interest is to understand why the preferred site of protonation

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