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Transition metal polyhydride complexes: a theoretical view

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CONTENTS

ABSTRACT

The factors governing the stabilities of classical and non-classical isomers in transition metal polyhydride complexes are summarized in this review. Diagonal lines in the Periodic Table, which divide

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the classical (left-hand side of the line) and non-classical (right-hand side of the line) isomers, were defined for neutral (through Ru and Ir) and cationic (between Tc/Ru and Os/Ir) complexes with only phosphine ligands. The carbonyl ligand was found to stabilize significantly the non-classical isomers due to its strong π-accepting ability. The strong "σ"- and "π"-donating ability of the Cp ligand makes most of its polyhydride complexes adopt classical structures. In this review, we also discuss some unique structural features in several types of polyhydride complex, such as the orientation of η^2-H_2 ligands in non-classical structures and the distortions in the "four-legged piano-stool" complexes ($MH_nL_{4-n}Cp$) and the pseudo-pentagonal-bipyramidal complexes ($MH_nL_{6-n}Cp$).

LIST OF ABBREVIATIONS

bq	7,8-benzoquinolato
CASSCF	complete active space self consistent field
CI	configuration interaction
CISD	configuration interaction with all-single and all-double excitations
Cp	η^5-C_5H_5
Cp*	η^5-C_5Me_5
Cy	cyclohexyl
depe	1,2-bis(diethylphosphino)ethane
diphpyH	2-Ph-6-(*o*-C_6H_4)(C_5H_3N)
dmpe	1,2-bis(di-methylphosphine)ethane
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
en	ethylenediamine
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
MCSCF	multiconfiguration self consistent field
MP2	second-order Møller–Plesset perturbation
MP3	third-order Møller–Plesset perturbation
MP4	fourth-order Møller–Plesset perturbation
MRCI	multireference configuration interaction
PP_2	$PPh(CH_2CH_2PR_2)_2$
PP_3	$P(CH_2CH_2PPh_2)_3$
py	pyridine
RHF	restricted Hartree–Fock
SOJT	second-order Jahn–Tellere
tolyl	$-C_6H_4CH_3$

1. INTRODUCTION

Since the first discovery of a stable non-classical dihydrogen complex, $W(CO)_3[P(i\text{-}Pr)_3]_2(\eta^2\text{-}H_2)$, by Kubas et al. [1], transition metal polyhydride complexes have been the subject of considerable interest [2–5]. Research in this field has focused on the synthesis, characterization, structure and reactivity of polyhydride complexes. The study of polyhydride complexes has become a significant branch of coordination chemistry, resulting in the discovery of many complexes containing non-classical dihydrogen ligands or classical hydride ligands. Although more than 170 dihydrogen complexes have been reported thus far [5], only a few η^2-H_2 complexes have been characterized unequivocally in the solid state by both X-ray and neutron diffraction techniques [1,6–8]. The existence of most other η^2-H_2 complexes has been inferred mainly by NMR spectroscopic studies or from X-ray crystallographic determinations without specific location of the hydrogen atom positions. Although most η^2-H_2 complexes characterized thus far by neutron diffraction typically show H–H distances of 0.82 Å [1,6–8], a recent study showed the existence of a complex with an H–H separation of 1.10 Å [9].

In spectroscopic studies, the ^{1}H NMR relaxation time (T_1) has been used as a criterion to distinguish between classical and non-classical structures in solution [10]. However, recent studies have revealed that several examples of polyhydrides, originally identified as having non-classical structures according to this criterion, e.g. $[OsH_5(PR_3)_3]^+$ [11], $ReH_5(PPh_3)_3$ [12] and ReH_7 (dppe) [13], are classical complexes. The T_1 criterion was later redefined by taking into account all factors that contribute to the relaxation time [14]. The measurement of H–D coupling constants in the ^{1}H NMR experiments is also commonly used in the characterization of non-classical dihydrogen complexes [5]. Other physical techniques, such as IR and electrochemical methods [15,16], have also been used to predict the stability of the non-classical dihydrogen complexes. Despite these advances in experimental methodology, accurate locations of hydrogen atoms can only be obtained experimentally through solid-state neutron diffraction, which requires larger, well-formed crystals, long collection times and sophisticated equipment.

All these experimental interests have led to an increasing number of quantum chemical studies of the electronic structures and relative stabilities of classical and non-classical polyhydrides [17–26]. In a series of theoretical papers [26], we examined the effect of electron correlation and suggested that MP2 calculations provide reliable results for the determination of the relative stability of classical and non-classical isomers. Although oscillations were found in the application of perturbation theory to some first-row transition metal fluoride and carbonyl complexes [27], no such behavior was found in the second- and third-row transition metal polyhydrides. We also examained the factors that contribute to the stabilization of one isomer over another and provided some qualitative rules governing the stability of these metal hydride complexes. In general, non-classical isomers are preferred for complexes with strong π-acceptor ligands or late transition metals.

Various reviews of the experimental aspects have appeared [2–5]. Here, we summarize theoretical work on the structure, bonding and stabilities of classical and non-classical transition metal polyhydride complexes.

2. BONDING MODEL AND THEORETICAL ASPECTS

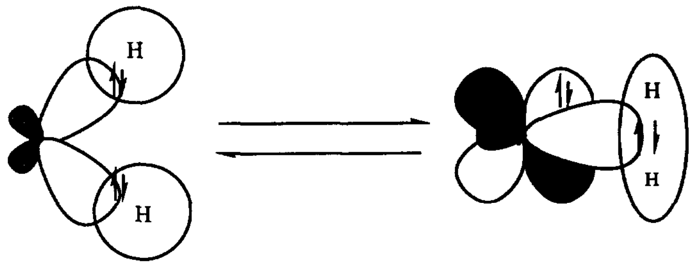
Early theoretical calculations, based on the semi-empirical, extended Hückel method, were performed to obtain qualitative information [17]. The metal–dihydrogen bonding in the non-classical dihydrogen complexes was then described using a model similar to that used for metal–ethylene interaction. The H–H σ bond donates its electron density to an empty metal orbital, with a weaker, secondary back donation of metal d electrons to the H–H σ^* antibonding orbital. This qualitative idea remains widely accepted and has been further supported by ab initio quantum chemical calculations [19,26b].

Ab initio quantum mechanical methods, which, in principle, can provide quantitative predictions, have been applied to this field since 1987. Earlier ab initio calculations were restricted to the lower quality RHF level. The importance of electron correlation in this class of metal complexes has been noted only since 1991 [19c,23,24,26b]. In the calculations of the $ReH_7(PH_3)_2$ polyhydride complex, RHF gave a stable non-classical isomer while CI calculations gave a stable classical isomer [19c]. In a conformational study of the $FeH_2(\eta^2\text{-}H_2)(PH_3)_3$ complex, the inclusion of the correlation energy (MCSCF calculations) drastically modified the RHF results [24].

In a systematic study [26b], we examined the use of different levels of electron correlation calculations on model complexes, IrH_5L_2 ($L \equiv Be$, PH_3 and PMe_3). The molecular complex $IrH_5[P(i\text{-}Pr)_3]_2$ was characterized by neutron diffraction [28] and its structure was compared with the calculated structures. Electron correlation was included in several different ways: CISD, CASSCF, MRCI, MP2, MP3 and MP4 calculations. The Be model was used for theoretical simplicity in the higher level calculations. This systematic study suggested that the economical MP2 method provides a reliable result for the determination of relative energies between classical and non-classical isomers when compared with the time consuming, higher level MRCI results. The conventional substitution of PR_3 by PH_3 causes an error of about 2.0 kcal mol^{-1} by overestimating the stability of the non-classical isomer [26b].

More recently, theoretical studies [24b] on $Ir(\eta^2\text{-}H_2)HCl_2(PH_3)_2$, a model complex of $Ir(\eta^2\text{-}H_2)HCl_2[P(i\text{-}Pr)_3]_2$ [9], showed that an MP2 calculation gave a separation of 1.40 Å in the $\eta^2\text{-}H_2$ unit, while a coupled pair functional calculation gave 1.06 Å (the experimental value is 1.10 Å [9]). This result indicates that MP2 may not reproduce well those structures with H---H separations in the range 1.00–1.50 Å. For example, our attempt (previously unpublished) failed to reproduce the 1.37 Å H---H separation found in the neutron structure of the $ReH_7[P(p\text{-tolyl})_3]_2$ complex [13a] with an MP2 geometry optimization on the model complex, $ReH_7(PH_3)_2$. With heavy atom positions fixed at the experimental values of $ReH_7[P(p\text{-tolyl})_3]_2$, the MP2 calculation gave an H---H separation of 1.48 Å. However, the energy difference between the experimental and optimized geometries is only about 2.0 kcal mol^{-1} at the MP2 level. This result implies that the potential surface is very flat in the intermediate region.

Based on an analysis of the laplacian of the valence electron density (i.e. $\nabla^2\rho$) [29] on the classical and non-classical isomers of the $IrH_5(PH_3)_2$ complex [26b], we provided a bonding scheme (see Scheme I) to describe the metal–hydride and metal–dihydrogen bonding interaction. Similar bonding descriptions have been provided previously [17a,19d]. For the $M(H)_2$ classical form, the central metal atom formally transfers its d electrons to the hydrides and forms polar–covalent M–H bonds. For the non-classical isomer, the H_2 unit uses its two σ electrons to form a dative bond with the metal and the extra two electrons are localized at the metal center by occupying a metal d orbital. Based on this analysis we concluded that a non-classical isomer is preferred for complexes with strong π-accepting ligands and contracted metal d orbitals.



$M(H)_2$ Classical form

$M(\eta^2\text{-}H_2)$ Nonclassical form

Scheme I

Throughout this paper, (η^2-H_2) indicates a dihydrogen ligand, $(H)_n$ ($n=1, 2, \ldots$) denotes a classical hydride and H_n ($n=1, 2, \ldots$) is used when we do not want to indicate the structural form. In this review, we refer to the molecule as a non-classical isomer when the H–H separation is less than 1.0 Å and a classical isomer when the H---H separation is greater than 1.5 Å. Those complexes with an H---H separation greater than 1.0 Å, but less than 1.5 Å, are referred to as having an intermediate structure [4a]. In terms of H–H bonding, we speculate that these intermediate structures may be more like classical hydrides because we do not expect significant electron density accumulation between a pair of H atoms with a separation of greater than 1.0 Å. Further theoretical studies on the electronic structural change with the H---H separation are necessary to determine how reasonable this classification is and if the speculation is true.

TABLE 1

Neutral and cationic model complexes without strong π-acceptor ligands, and relative energies (kcal mol^{-1}) of classical and non-classical isomers (MP2 results)

Neutral model complexes	$MoH_2(PH_3)_5$	$TcH_3(PH_3)_4$	$RuH_4(PH_3)_3$	$RhH_5(PH_3)_2$
	−1.1(**1**→**2**)	5.4(**3**→**4**)	3.3(**5**→**6**)	−5.0(**8**→**9**)
			23.9(**5**→**7**)	−22.6(**8**→**10**)
	$MoH_4(PH_3)_4$	$TcH_5(PH_3)_3$	$RuH_6(PH_3)_2$	$RhH_7(PH_3)$
	18.3(**13**→**14**)	10.4(**16**→**17**)	−0.3(**19**→**20**)	−17.4(**22**→**23**)
	25.9(**13**→**15**)	20.2(**16**→**18**)	−6.4(**19**→**21**)	−38.8(**22**→**24**)
	$WH_2(PH_3)_5$	$ReH_3(PH_3)_4$	$OsH_4(PH_3)_3$	$IrH_5(PH_3)_2$
	6.4(**1**→**2**)	11.5(**3**→**4**)	13.6(**5**→**6**)	10.5(**8**→**9**)
			27.9(**5**→**7**)	−0.9(**8**→**10**)
	$WH_4(PH_3)_4$	$ReH_5(PH_3)_3$	$OsH_6(PH_3)_2$	$IrH_7(PH_3)$
	24.9(**13**→**14**)	15.2(**16**→**17**)	5.9(**19**→**20**)	0.8(**22**→**23**)
	41.0(**13**→**15**)	31.8(**16**→**18**)	17.0(**19**→**21**)	−5.4(**22**→**24**)
Cationic model complexes		$TcH_2(PH_3)_5^+$	$RuH_3(PH_3)_4^+$	$RhH_4(PH_3)_3^+$
		2.0(**1**→**2**)	−7.2(**3**→**4**)	−24.8(**5**→**6**)
	$MoH_3(PH_3)_5^+$	$TcH_4(PH_3)_4^+$	$RuH_5(PH_3)_3^+$	$RhH_6(PH_3)_2^+$
	21.9(**11**→**12**)	13.9(**13**→**14**)	−6.8(**16**→**17**)	−34.3(**19**→**20**)
		18.9(**13**→**15**)	−5.8(**16**→**18**)	−71.2(**19**→**21**)
		$ReH_2(PH_3)_5^+$	$OsH_3(PH_3)_4^+$	$IrH_4(PH_3)_3^+$
		5.3(**1**→**2**)	1.9(**3**→**4**)	−8.2(**5**→**6**)
	$WH_3(PH_3)_5^+$	$ReH_4(PH_3)_4^+$	$OsH_5(PH_3)_3^+$	$IrH_6(PH_3)_2^+$
	24.1(**11**→**12**)	17.4(**13**→**14**)	3.7(**16**→**17**)	−12.4(**19**→**20**)
		26.7(**13**→**15**)	17.7(**16**→**18**)	−31.7(**19**→**21**)

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3. STABILITY RULES FOR CLASSICAL AND NON-CLASSICAL ISOMERS

3.1. Polyhydride complexes with phosphine ligands only

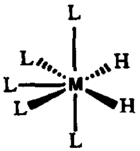
3.1.1. Results

A large number of transition metal polyhydride complexes with only phosphine ligands have been synthesized and structurally characterized. Systematic calculations were performed on the model complexes (neutral and cationic species) listed in Table 1, and the geometries for each model complex with different isomers are illustrated in Chart I. Details of these theoretical calculations can be found in a previous paper [26c]. In Table 1, the calculated energy differences between classical and non-classical isomers for different model complexes are also given. The energy difference between two isomers is defined as

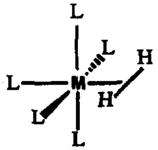
$$\Delta E = E(\text{non-classical isomer}) - E(\text{classical isomer}) \tag{1}$$

The bold numbers in Table 1 indicate the pair of classical and non-classical isomers

MH_2L_5



(C_{2v})
1



(C_{2v})
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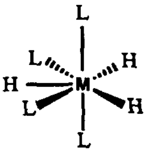
MH_3L_4



(C_{2v})
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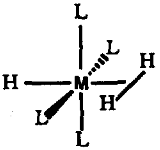
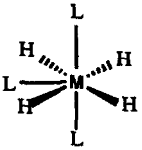
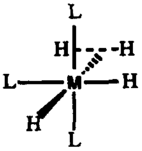


(C_{2v})
4

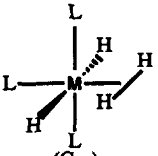
MH_4L_3



(C_{2v})
5

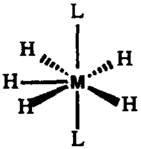


(C_s)
6

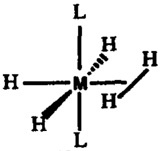


(C_{2v})
7

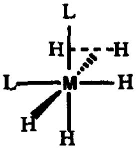
MH_5L_2



(C_{2v})
8

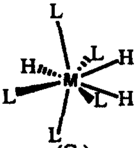


(C_{2v})
9

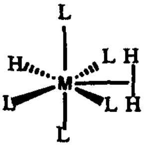


(C_1)
10

MH_3L_5

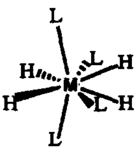


(C_s)
11

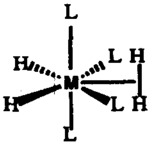


(C_s)
12

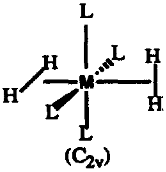
MH_4L_4



(C_{2v})
13

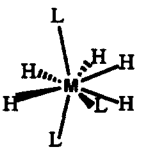


(C_{2v})
14



(C_{2v})
15

MH_5L_3


(C_s)
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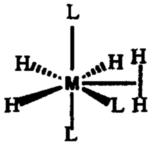
(C_s)
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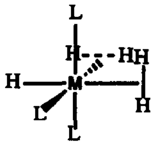
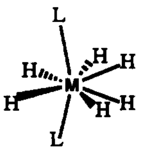
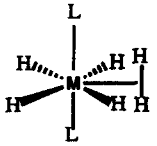
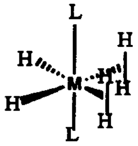

(C_s)
18

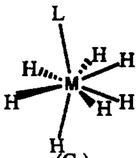
MH_6L_2


(C_{2v})
19


(C_{2v})
20


(C_{2v})
21

MH_7L


(C_s)
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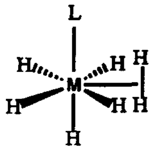
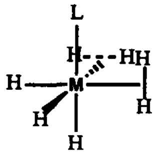

(C_s)
23


(C_1)
24

(Chart I) for the calculated energy difference. In most cases, the first ΔE value is the energy difference between a classical isomer and a non-classical isomer with one η^2-H_2 ligand, while the second is the energy difference between a classical isomer and a non-classical isomer with two η^2-H_2 ligands. However, for $RuH_4(PH_3)_3$, $RhH_5(PH_3)_2$, $OsH_4(PH_3)_3$, and $IrH_5(PH_3)_2$, the second ΔE value is the energy difference between a classical isomer and a second non-classical isomer with one η^2-H_2 ligand (see Chart I).

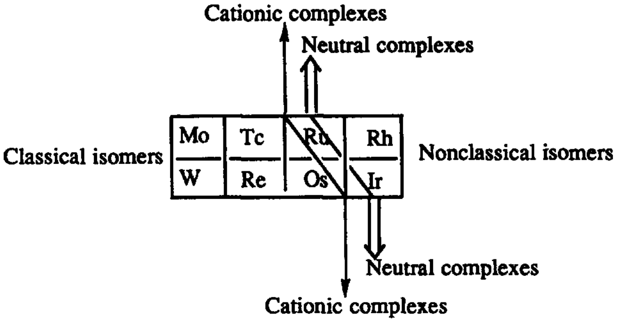
3.1.2. Periodic trends

Systematic calculations on the class of metal complexes with phosphine ligands only showed that the classical hydrides are preferred for those transition metals with more diffuse d orbitals, i.e. early transition metals. The preference of the third row for the classical isomer has its origin in the increasingly diffuse nature of the d orbitals on descending the transition metal group. For transition metals from the same series, the diffuse nature of the d orbitals decreases from left to right in the Periodic Table. From the conclusion made in the previous section, we can easily understand the trend by which the energy differences between classical and non-classical isomers decrease from Mo to Rh and W to Ir.

From the periodic trend in the size and vaporization enthalpy of the transition metals, we expect to find a similarity in the diffuse nature of the d orbitals along a diagonal line in the Periodic Table. In a previous paper [26c], we postulated that a diagonal line divides the transition metals into those that prefer classical forms (left side of the line) and those that prefer non-classical forms (right side of the line). For those complexes along the diagonal line, both classical and non-classical isomers may exist. From Table 1, we can see that this diagonal line crosses through Ru and Ir for neutral phosphine complexes.

For cationic complexes, the corresponding diagonal line shifts towards early transition metals, and crosses through Tc/Ru and Os/Ir metals. This left shift supports, once again, the idea of the diffuse nature of metal d orbitals governing the relative stabilities of classical and non-classical isomers, since increasing the charge on a hydride complex makes its metal d orbitals contract and therefore stabilizes its non-classical isomer.

Scheme II summarizes the periodic trends for both neutral and cationic species for those polyhydride complexes with only phosphine ligands. The scheme illustrates the shift of the diagonal lines from neutral to cationic complexes and the locations of classical and non-classical isomers. It should be noted here that these diagonal lines could be ligand sensitive, a point which will be discussed later.



Scheme II

3.1.3. *Comments*

Generally, our conclusions apply to the second- and third-row transition metal complexes. For the first-row transition metal complexes, the division between classical and non-classical forms is likely to shift to the left in the Periodic Table, because the d orbitals of the first-row transition metals are significantly more contracted than those of the second- and third-row transition metals. Therefore $Mn(\eta^2\text{-}H_2)H(dmpe)_2$ probably exists [30a], although Mn is located to the left of the extrapolated diagonal line defined for neutral second- and third-row complexes.

From Table 1, calculations predict a slightly more stable non-classical isomer (**2**) for $MoH_2(PH_3)_5$. This contrasts with the X-ray crystal structure of $MoH_2(PMe_3)_5$ [30b] which shows a pentagonal-bipyramidal classical geometry with two non-adjacent hydrogens. This result may be due to the computational error caused by the replacements of PMe_3 by PH_3. The PH_3 substitution slightly overestimates the stability of the non-classical isomer [26b].

For neutral complexes, those complexes with transition metals on the diagonal line (Ru and Ir) can either adopt classical or non-classical isomers. A solid state NMR study [30c] showed that $RuH_4(PPh_3)_3$ adopts a non-classical isomer with an H---H separation of 0.93 Å. The left shift of the diagonal line for cationic complexes is strongly supported by numerous reports indicating that the protonation of neutral classical polyhydride complexes leads to the formation of non-classical isomers [31,32]. For example, $[Ir(H)_2(\eta^2\text{-}H_2)_2(PCy_3)_2]^+$ was obtained through protonation of $IrH_5(PCy_3)_2$, and $[M(H)(\eta^2\text{-}H_2)(dppe)_2]^+$ ($M \equiv$ Fe, Ru and Os) through protonation of $M(H)_2(dppe)_2$. Most $[MH_3(PR_3)_4]^+$ ($M \equiv$ Fe, Ru or Os) complexes are classified as non-classical isomers. The theoretical calculations (see Table 1) support these observations. For the $[OsH_3(PH_3)_4]^+$ complex, the classical isomer is predicted to be slightly more stable by 1.9 kcal mol^{-1} (see Table 1) than its non-classical isomer. This small difference implies that both classical and non-classical isomers exist for $[OsH_3(PR_3)_4]^+$ complexes. This conclusion is supported by reports indicating that $[OsH_3(depe)_2]^+$ is either an intermediate structure or a mixture of a dihydride and dihydrogen species in fast equilibrium [31b] and $[OsH_3(dppe)_2]^+$ is an octahedral non-classical complex with an H---H separation of 0.96 Å in the $\eta^2\text{-}H_2$ ligand [31c].

Other Ir cationic complexes, such as $[IrH(\eta^2\text{-}H_2)(PR_3)_2(bq)]^+$ [10,32] and $[IrH(\eta^2\text{-}H_2)(diphpyH)(PR_3)_2]^+$ [33], have been reported as non-classical species because Ir is located on the right-hand side of the relevant diagonal line. Several dicationic Os complexes are claimed as non-classical isomers with a molecular formula of $[Os(\eta^2\text{-}H_2)(NH_3)_4L]^{2+}$ ($L \equiv NH_3$, Py, D_2O, CH_3CN, Cl^- I^-) or $[Os(\eta^2\text{-}H_2)(en)_2L]^{2+}$ ($L \equiv$ Py or Cl^-) [34]. The results for these Os complexes are expected because more charge is carried by the dicationic Os complexes which further stabilizes the non-classical structures.

One significant result of our calculations is the prediction of a stable classical structure for $[OsH_5L_3]^+$ complexes ($L \equiv PPh_3$ or PMe_2Ph), although the complexes were classified as non-classical on the basis of a spectroscopic study [32]. Our prediction has been supported by recent theoretical calculations on more than 20 possible isomers of the $[OsH_5(PH_3)_3]^+$ model complex [25a] and has been confirmed by the result of a neutron diffraction study [11]. Several early transition metal polyhydride complexes with only phosphine ligands, such as ReH_7L_2 ($L \equiv P(p\text{-}C_6H_4F)_3$ or PCy_3) [10], are also predicted to be classical isomers. We also predict the complexes $[ReH_6(PP_2)]^+$ to be classical structures, although X-ray diffraction and ^1H NMR T_1 studies suggest that each complex contains an elongated $\eta^2\text{-}H_2$ ligand [35a,b].

3.2. *Polyhydride complexes with Cp and phosphine ligands*

3.2.1. $MH_nL_{4-n}Cp$ *complexes*

A large number of transition metal polyhydride complexes containing one or more $\eta^5\text{-}C_5R_5$ ligands have been structurally characterized either in the solid state or in solution [36–42]. A systematic series of theoretical calculations has been carried out on model complexes with a general molecular formula of $MH_nL_{4-n}Cp$ ($n = 1$–4), where $M \equiv Ru$, Rh, Os and Ir and $L \equiv PH_3$. The relative energies between the different isomers of these complexes are given in Table 2 [26e]. The various geometries of these model complexes are illustrated in Chart II.

TABLE 2

Some neutral and cationic model Cp complexes, and the relative energies of classical and non-classical isomers (MP2 results)

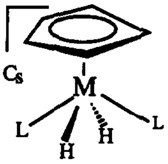
Neutral model complexes	$RuH_3Cp(PH_3)$	RhH_4Cp
		0.0(**30**→**31**)
	15.5(**28**→**29**)	11.8(**30**→**32**)
	$OsH_3Cp(PH_3)$	IrH_4Cp
		0.7(**30**→**31**)
	21.9(**28**→**29**)	23.1(**30**→**32**)
Cationic model complexes	$RuH_2Cp(PH_3)_2^+$	$RhH_3Cp(PH_3)^+$
	5.7(**25**→**26**)	
	12.5(**25**→**27**)	−0.5(**28**→**29**)
	$OsH_2Cp(PH_3)_2^+$	$IrH_3Cp(PH_3)^+$
	5.8(**25**→**26**)	
	17.8(**25**→**27**)	11.7(**28**→**29**)

Adapted from Z. Lin and M.B. Hall, Organometallics, 11 (1992) 3801.

Surprisingly, the results in Table 2 show that, for most complexes, the classical hydrides with "four-legged piano-stool" structures are preferred. Only the $[RhH_3(PH_3)Cp]^+$ complex shows a slightly more stable non-classical isomer (by only 0.50 kcal mol^{-1}). The energy difference between the two classical isomers for each complex is relatively small and that with two hydrogen atoms trans (also referred to as "angular trans") [43] to each other (with respect to the four legs) is always found to be more stable. These calculations indicate that the Cp ligand is a very strong "σ" and "π" donor. The strong "σ" and "π"-donating ability of the Cp ligand increases the tendency of the central metal to transfer d electrons to hydrides and stabilizes the classical isomers. Therefore the diagonal line which divides the classical and non-classical isomers [observed in MH_nL_{7-n}, and MH_nL_{8-n} ($n = 2$–7 and $L \equiv PH_3$) complexes] is shifted towards late transition metals in the Periodic Table when three phosphine ligands are replaced by a Cp ligand.

Experimental results [36–42] indicate that most $MH_nL_{4-n}Cp$ ($L \equiv$ phosphine) polyhydrides adopt classical isomers. In general, this is in agreement with the theoretical calculations (see Table 2). An exception is seen for cationic Ru complexes ($[RuH_2L_2Cp]^+$) [5,39]. Most experimental studies [5,39] have concluded that these Ru complexes are non-classical. However, the calculations suggest that the $[RuH_2(PH_3)_2Cp]^+$ complex prefers the trans classical isomer (**25**) over the non-classical isomer (**27**) by 12.5 kcal mol^{-1} (see Table 2), a significant energy difference.

MH_2CpL_2



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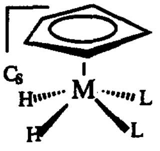

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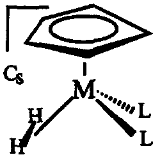
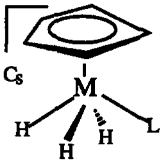


27

MH_3CpL



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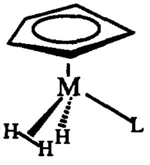

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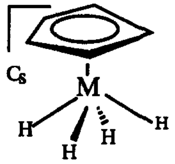
MH_4Cp



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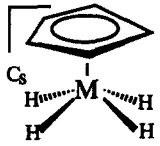

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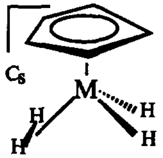


32

Recently, the X-ray crystal structure of the $[RuH_2(\eta^5\text{-}C_5Me_5)(dppm)]^+$ complex indicated that the non-classical form (**27**) is preferred [39a]. Because of the bidentate ligand and the bulky phenyl groups in the dppm unit, the Ru complex may be forced to adopt a non-classical isomer (**27**), although the calculated energy difference between **26** and **27** for the $[RuH_2(PH_3)_2Cp]^+$ complex is 6.8 kcal mol^{-1} (see Table 2) with a preference for the cis classical form (**26**). A very recent neutron diffraction study shows that $[RuH_2(dppm)Cp]^+$ adopts an intermediate isomer with an H---H distance of 1.09 Å [31c]. In view of the periodically diagonal similarity in the transition metals, we would expect that $[RuH_2(PR_3)_2Cp]^+$ complexes would be classical with the two phosphine ligands trans to each other. This is because the $[IrH_3(PR_3)Cp]^+$ complex is characterized by neutron diffraction as a classical isomer and both Ir and Ru are located along the same diagonal line in the Periodic Table.

A recent spectroscopic (^1H NMR) study [42] has shown that both $RuH_2X(PR_3)Cp^*$ ($X \equiv$ halide, OR and SiR'_3) and $RuH_3(PR_3)Cp^*$ complexes are classical hydrides. When the X group is taken as an anion, the former complex looks like a cationic species. These results further support the conclusion [26e] that $RuH_2(PR_3)_2Cp^+$ complexes are likely to be classical, while $[RuH_2(\text{bidentate phosphine})Cp]^+$ could adopt intermediate structures.

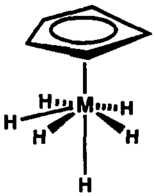
3.2.2. $MH_nL_{6-n}Cp$ complexes

In addition to the cyclopentadienyl polyhydride complexes discussed in Section 3.2.1., a new class of cyclopentadienyl polyhydrides containing an even higher coordination number, i.e. $MH_n(PR_3)_{6-n}Cp$ ($n=5$ or 6), has been found in both the solid state and solution [44,45]. The ^1H NMR measurements [44] of $MH_5(PR_3)Cp$ ($M \equiv Mo$ or W) complexes indicate that they are classical, pentagonal-bipyramidal structures with five equivalent hydrogens. A classical, pentagonal-bipyramidal structure was suggested for the ReH_6Cp complexes from both X-ray and electron diffraction. However, none of the polyhydrides in this class has been unequivocally characterized by neutron diffraction.

For MH_6Cp complexes, four isomers (**33**–**36**) illustrated in Chart III were studied [26f]. Their relative energies are listed in Table 3. It has been concluded, based on the results in Table 3, that a diagonal line in the Periodic Table through Ru and Ir atoms divides the classical forms (left side of the line) and non-classical forms (right side of the line) for this class of polyhydride complexes. For the $[RuH_6Cp]^+$ complex, the classical (**33**) and non-classical (**36**) isomers are of almost equal energy. For both $[RhH_6Cp]^{2+}$ and $[IrH_6Cp]^{2+}$ complexes, the non-classical isomer (**36**) is more stable than the classical isomer (**33**). As the charge increases on a complex, its metal d orbitals contract and are stabilized, and therefore its non-classical isomers will eventually be favored.

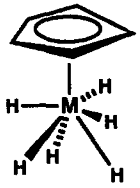
When the two classical isomers (**33** and **34**) are compared, the pentagonal-bipyramidal structure (Cp one site) (**33**) is always more stable then the capped

MH_6Cp



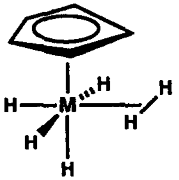
C_{5v}

33



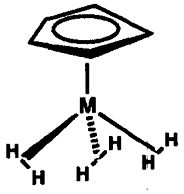
C_s(pseudo C_{3v})

34



C_s

35



C_s(pseudo C_{3v})

36

TABLE 3

$CpMH_6$ complexes and the relative energies (kcal mol^{-1}) of classical and non-classical isomers (MP2 results)[a,b]

Isomer	$CpTcH_6$	$CpRuH_6^+$	$CpRhH_6^{2+}$	$CpReH_6$	$CpOsH_6^+$	$CpIrH_6^{2+}$
33	0.0	0.0	0.0	0.0	0.0	0.0
34	14.0	12.2	*	15.9	15.0	12.1
35	(23.9)	7.8	−9.6	(23.4)	(18.2)	2.1
36	(47.5)	0.3	−71.0	(58.8)	(38.5)	−13.7

[a] Asterisk denotes that the isomer is not a minimum.

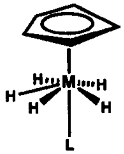
[b] Numbers in parentheses indicate that the isomer is not a minimum at the MP2 level, but is a minimum at the HF level. The MP2 energy is calculated on the basis of the corresponding HF geometry.

Adapted from Z. Lin and M.B. Hall, Organometallics, 12 (1993) 4046.

trigonal antiprism (Cp three sites) (**34**). Few, if any, MH_6Cp complexes adopt the structure of the analogous $[ReH_9]^{2-}$ complex, which is a tricapped trigonal prism. Since the transition metal atom in the classical hydride MH_6Cp has a formal d^0 configuration, we expect that the ligand–ligand repulsive interaction will play a role in the gross stability of different classical isomers (geometries). Interestingly, the potential energy hypersurface for an MA_6B type, obtained by Kepert [46] from ligand–ligand repulsion calculations, shows that a pentagonal-bipyramid with the short M—B bond in one of the axial sites is the most stable structure. If, due to its large size, Cp effectively acts like a ligand with a short, strong metal–ligand bond, i.e. like the B ligand above, a pseudo-pentagonal-bipyramidal structure might be expected for the MH_6Cp complexes.

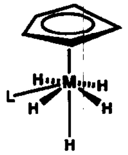
Four MH_5LCp complexes, $MH_5(PH_3)Cp$ (M≡Mo and W) and $[MH_5(PH_3)Cp]^+$ (M≡Tc and Re), were also studied [26f]. No non-classical isomer was found in these complexes, and therefore only two classical isomers (see Chart IV) were calculated. Chart IV shows their relative energies. The energy differences between **37** and **38** are not very large for any of the complexes studied here. For both $MoH_5(PH_3)Cp$ and $WH_5(PH_3)Cp$, isomer **37** has a lower energy than isomer **38**. However, isomer **38** is slightly lower in energy than isomer **37** for $[TcH_5(PH_3)Cp]^+$ and $[ReH_5(PH_3)Cp]^+$ complexes. From the viewpoint of ligand–ligand repulsion, we would expect greater ligand–ligand repulsion in **38** than in **37**, since isomer **37** has a Cp—M—P angle of 180.0°, while isomer **38** has an angle of near 110.0° [26f]. Electronically, when the phosphine ligand occupies the axial position, it pushes all equatorial hydrogens away from it because of its donation of an electron pair to the metal. This effect, which will be discussed later, decreases the Cp—M—H_e angle, and therefore weakens the M—H_e bonds. The steric factor favors isomer **37** while the electronic factor does not. The results indicate that the two factors are of nearly

$CpMLH_5$



C_{5v}

37

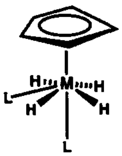


C_s
(optimized within C_1)

38

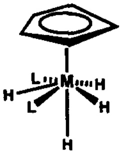
	37	38
$CpMo(PH_3)H_5$	0.0kcal/mol	2.1kcal/mol
$CpW(PH_3)H_5$	0.0kcal/mol	3.2kcal/mol
$CpTc(PH_3)H_5^+$	0.0kcal/mol	-0.9kcal/mol
$CpRe(PH_3)H_5^+$	0.0kcal/mol	-0.9kcal/mol

$CpML_2H_4$



C_s

39



C_s

40

	39	40
$CpNb(PH_3)_2H_4$	0.0kcal/mol	-0.3kcal/mol
$CpTa(PH_3)_2H_4$	0.0kcal/mol	0.0kcal/mol
$CpMo(PH_3)_2H_4^+$	0.0kcal/mol	-1.8kcal/mol
$CpW(PH_3)_2H_4^+$	0.0kcal/mol	-0.9kcal/mol

equal importance in the determination of the relative stabilities, at least for complexes containing small phosphines.

For complexes of the general type $[MH_4L_2Cp]^{x+}$ ($x=0$ or 1), only classical isomers **39** and **40** (see Chart IV) were studied [26f]. For this type of complex, the transition metal must be of Group 5 or 6. From the periodical trend discussed earlier, we expect all the complexes studied here to have classical structures as the most stable isomer. From Chart IV, we can see that isomers **39** and **40** are almost of equal energy for $NbH_4(PH_3)_2Cp$, $TaH_4(PH_3)_2Cp$, $[MoH_4(PH_3)_2Cp]^+$ and $[WH_4(PH_3)_2Cp]^+$. Isomer **39** has two Cp–phosphine repulsions, while isomer **40** has one Cp–phosphine and one phosphine–phosphine repulsion. An axial occupation of one phosphine ligand makes isomer **39** unfavorable electronically, as will be discussed later.

3.3. Polyhydride complexes with strong π-accepting ligands

A limited number of model complexes, listed in Table 4, were studied to examine the most important trends in systems with π-accepting ligands [26c]. Table 4 also lists their relative energies. The geometries for these model complexes are illustrated in Chart V. The first stable non-classical complex, $W(CO)_3[P(i\text{-}Pr)_3]_2(\eta^2\text{-}H_2)$, synthesized by Kubas et al. [1], has three carbonyls. The carbonyl ligands play a

TABLE 4

Some neutral and cationic model complexes with strong π-acceptor ligands, and the relative energies of classical and non-classical isomers (MP2 results)

Neutral model complexes	$WH_2(PH_3)_5$	$WH_2(CO)(PH_3)_4$	$WH_2(CO)_2(PH_3)_3$	$WH_2(CO)_3(PH_3)_2$
	6.4(**1**→**2**)	−1.3(**41**→**42**)	−4.5(**43**→**44**)	−17.6(**45**→**46**)
	$MoH_4(PH_3)_4$	$MoH_4(CO)(PH_3)_3$		
	18.3(**13**→**14**)	−0.4(**47**→**48**)		
	25.9(**13**→**15**)	5.9(**47**→**49**)		
	$WH_4(PH_3)_4$	$WH_4(CO)(PH_3)_3$	$WH_4(CO)_4$	
	24.9(**13**→**14**)	8.1(**47**→**48**)	3.8(**50**→**51**)	
	41.0(**13**→**15**)	22.6(**47**→**49**)	−0.3(**50**→**52**)	
Cationic model complexes	$TcH_4(PH_3)_4^+$	$TcH_4(CO)(PH_3)_3^+$		
	13.9(**13**→**14**)	−1.8(**47**→**48**)		
	18.9(**13**→**15**)	2.0(**47**→**49**)		
	$ReH_4(PH_3)_4^+$	$ReH_4(CO)(PH_3)_3^+$		
	17.4(**13**→**14**)	2.0(**31**→**32**)		
	26.7(**13**→**15**)	9.9(**31**→**33**)		

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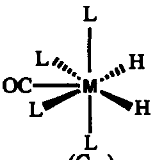
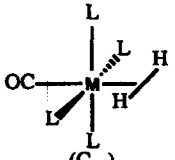
significant role in stabilizing the non-classical structure [17d]. When these carbonyls are substituted by phosphine ligands, the most stable isomer is classical [see Table 4 for $WH_2(PH_3)_5$]. The calculated energy difference of −17.6 kcal mol^{-1} between **45** and **46** for $WH_2(CO)_3(PH_3)_2$ differs substantially from the NMR-derived quantity of −1.2 kcal mol^{-1} for $WH_2(CO)_3[P(i\text{-}Pr)_3]_2$ [1d]. A more recently reported non-classical complex $Mo(CO)(\eta^2\text{-}H_2)(dppe)_2$ has one carbonyl [8]. Interestingly, $Mo(CO)(H)_2(depe)_2$ gives a classical pentagonal-bipyramidal structure [8]. The conformational transformation due to the slight change in the ligand environment (the depe ligand is a better σ donor than the dppe ligand) helps to illustrate the difficulty encountered in the theoretical prediction for $MoH_2(PMe_3)_5$ and other complexes, where there is a fine balance between the relative stabilities of the isomers.

The stabilizing effect of the carbonyl ligand(s) on non-classical isomers is also seen in model calculations (see Table 4). Calculations on other transition metal model complexes, $MH_4(CO)(PH_3)_3$ (M ≡ Mo, W, Tc$^+$, Re$^+$) (see Chart V for structures), were also completed. The results (see Table 4) indicate that both isomers are possible for the Mo complex. The classical isomer is preferred for the W complex. Again, results for $[MH_4(CO)(PH_3)_3]^+$ (M ≡ Tc and Re) show that the most stable isomer is non-classical (**48**) with one η^2-H_2 ligand for the Tc complex and classical (**47**) (slightly more stable) for the Re complex. Apparently, the trend from the second- to third-row metal complexes, i.e. the more diffuse d orbitals of the third-row transition metals, is responsible for the results of these calculations. On going from Group 6 to Group 7 metal complexes, the effect of an overall positive charge in the

$MH_2(CO)L_4$

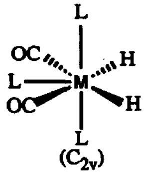


(C_{2v})
41

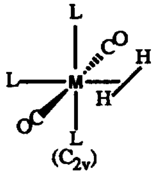


(C_{2v})
42

$MH_2(CO)_2L_3$

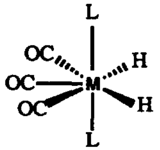


(C_{2v})
43

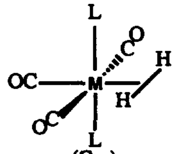


(C_{2v})
44

$MH_2(CO)_3L_2$

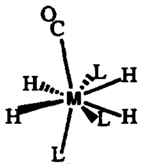


(C_{2v})
45

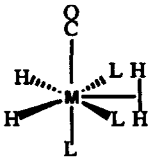


(C_{2v})
46

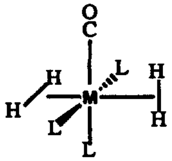
$MH_4(CO)L_3$



(C_s)
47

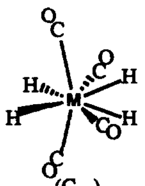


(C_s)
48

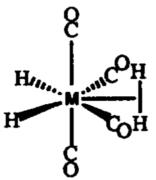


(C_s)
49

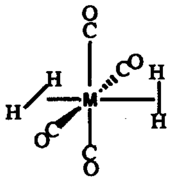
$MH_4(CO)_4$



(C_{2v})
50



(C_{2v})
51



(C_{2v})
52

Group 7 complexes also plays an important role. For the $[ReH_4(PH_3)_3L]^+$ complexes, the replacement of a phosphine ligand by a carbonyl significantly stabilizes the non-classical isomer (**48**). This significant stabilization leads to a very exciting observation, i.e. both classical and non-classical isomers coexist in a solution of the $[ReH_4(CO)(PMe_2Ph)_3]^+$ complex [26g,47], while only the classical isomer is observed for the corresponding non-carbonyl complex, $[ReH_4(PMe_2Ph)_4]^+$ [48a].

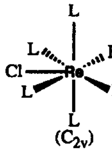
The observation that the stabilities of the non-classical isomers increase with the number of carbonyls (see Table 4) is strikingly clear, although no linear relationship was found. These results suggest that the stability of non-classical complexes depends on the number of π-accepting ligands and the diffuse nature of the transition metal d orbitals. In general, non-classical isomers are more likely to be found in complexes with a larger number of π-accepting ligands.

Recently reported $[ReH_2(CO)_3(PR_3)_2]^+$ ($R \equiv Cy$ or i-Pr) complexes have been characterized as non-classical forms based on NMR studies [48b]. From the first non-classical isomer, $W(\eta^2\text{-}H_2)(CO)_3[P(i\text{-}Pr)_3]_2$ [1], we can easily derive a similar conclusion from a theoretical point of view because Re is located to the right of W in the Periodic Table, and the Re complexes carry a positive charge. It has also been reported [48b] that both classical and non-classical isomers exist for $[ReH_2(CO)_2(PR_3)_3]^+$ and $[ReH_2(CO)(PR_3)_4]^+$ complexes. These results can again be understood from the theoretical calculations on the analogous W complexes shown in Table 4.

3.4. Polyhydride complexes with chloride ligands

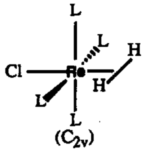
Previously, only two model chloride complexes have been studied, shown in Chart VI [26c]. These are models for the reported chloride complexes $ReH_2Cl(PMePh_2)_4$ and $IrH_4Cl[P(i\text{-}Pr)_3]_2$ [12c,49]. NMR spectroscopic studies suggest that both complexes adopt non-classical structures. However, calculations (see Chart VI) give a classical structure for the Re complex and a non-classical structure for the Ir complex.

$ReH_2(Cl)L_4$



(0.0 kcal/mol)

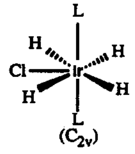
53



(14.1 kcal/mol)

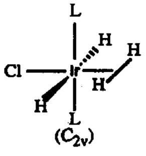
54

$IrH_4(Cl)L_2$



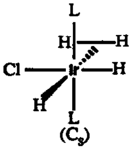
(0.0 kcal/mol)

55



(20.7 kcal/mol)

56



(-7.4 kcal/mol)

57

For the Re complex, the X-ray structural determination suggests an intermediate structure [12]. In the optimized classical $Re(H)_2Cl(PH_3)_4$ structure (**53**), the calculated structural parameters for the heavy atoms are very close to the X-ray result [12c]. For example, the calculated Cl–Re–P bond angle in the equatorial plane of the pentagonal-bipyramidal structure is 81.3°, while the X-ray result is approximately 83°. All other calculated structural parameters for the classical isomer are in agreement with the heavy atom positions of the X-ray structure; a final structural determination by neutron diffraction is needed to test the accuracy of the theoretical prediction. For the Ir complex, one non-classical isomer (**56**) is much higher in energy than the other (**57**). This result is due to the trans influence, which will be discussed in more detail later.

The results of the calculations on the two chloride complexes (Re classical structure; Ir non-classical structure) can be understood by considering the strong electron-withdrawing ability of the chloride ligand which makes the two complexes cation-like. Therefore, in the Periodic Table, Re is located to the left of the diagonal line defined earlier (see Scheme II) and the Re complex prefers a classical isomer, while Ir is located to the right of the line and the Ir complex adopts a non-classical structure.

More recently, several reports of other chloride polyhydride complexes have appeared [9,50,51]. A neutron diffraction study of the $IrH_3Cl_2[P(i\text{-}Pr)_3]_2$ complex shows that it contains an η^2-H_2 ligand with a pseudo-octahedral structure in which the η^2-H_2 is trans to one chloride ligand [9]. This result is consistent with our stability rule for cationic complexes. In the η^2-H_2 unit, however, the H–H bond distance is 1.11 Å. This Ir complex is viewed as an intermediate structure according to the classification mentioned above, together with the reported $ReH_7[P(p\text{-tolyl})_3]_2$ complex [13a] with an H---H separation of 1.37 Å. The long H---H separation in this Ir complex can be explained in the following manner. Although the chloride ligand is primarily taken as a strong σ-electron-withdrawing ligand which makes the relevant complexes cation-like, its π-donating ability (secondary factor) plays an important role in the situation in which the Cl ligand is trans to a dihydrogen unit. The π-donating nature of the trans chloride ligand greatly destabilizes the d orbitals (accommodating two d electrons, see Scheme I) in the non-classical structure. This destabilization strengthens the back donation of d electrons to the H–H σ^* antibonding orbital, and therefore weakens the H–H bond. This argument finds support in $Ir(\eta^2\text{-}H_2)H_2Cl[P(i\text{-}Pr)_3]_2$ where the H---H distance in the η^2-H_2 unit is reported to be 0.78 Å [9b]. In the latter complex, the trans ligand of η^2-H_2 is a hydride instead of chloride as in the former complex.

It is believed that the $OsH_4Cl_2[P(i\text{-}Pr)_3]_2$ complex can be formulated as $Os(\eta^2\text{-}H_2)_2Cl_2[P(i\text{-}Pr)_3]_2$ based on an X-ray crystal study [50]. This complex can be viewed as a dicationic species, and therefore the classification is again consistent with our stability rule for cationic complexes. We believe that the H–H separations in the assumed η^2-H_2 units will again be long, as observed in the $IrH(\eta^2\text{-}$

H_2)Cl_2[P(i-Pr)$_3$]$_2$ complex [9]. The X-ray diffraction study of $TcH_2Cl(dppe)_2$ suggests that the Tc complex is a non-classical isomer, i.e. it may be formulated as Tc(η^2-H_2)Cl(dppe)$_2$, in which the Cl ligand is trans to the η^2-H_2 ligand and the H---H separation is 1.1 Å [51]. Scheme II shows that Tc is located on the left-hand side of the diagonal line for cationic complexes and the Tc complex is expected to be classical. MP2 geometry optimization based on the $TcH_2Cl(PH_3)_4$ model (with a starting geometry similar to **54**) gave a separation of 1.44 Å between the two H atoms. Therefore, we classify this Tc complex as an intermediate structure in which the H---H separation ranges from 1.0 to 1.5 Å. As expected for these complexes with intermediate structures, the MP2 geometry predicts H---H separations which are too long [[24b]. It has also been reported [51b] that $TcH_3(dppe)_2$ is a trihydride complex because it does not have an electron-withdrawing chloride ligand.

3.5. *Other polyhydride complexes*

Sections 3.1–3.4 provide general rules for the determination of the relative stabilities of classical and non-classical isomers. Some exceptions to these rules have been discussed in the individual sections. Here, we comment on several recently reported complexes in which other electronic and steric factors must be considered. For early transition metal complexes, L_yMH_x, the non-classical isomer exists when the L_yM fragment does not have enough d electrons to form x M–H bonds. For example, $WH_5(SiPh_3)(PP_2)$ is classical, while its protonation product is non-classical [35c], because the parent complex has a formal d^0 configuration. In addition, the protonation of $ReH_7(PR_3)_2$ gives a non-classical structure and double protonation of $MoH_4(dppe)_2$ generates $[MoH_4(\eta^2\text{-}H_2)(dppe)_2]^{2+}$ [35d,e].

Although we have concluded that most Cp complexes will adopt classical structures, non-classical isomers may exist if the considered complexes have a very crowded ligand environment, or if they have π-acceptor ligands. For example, the $MH_2(CO)_3Cp$ (M≡V, Nb or Ta) complexes [51c], which have three strong π-accepting ligands, will be sterically crowded if they adopt a classical isomer.

4. HIGHLY STABLE NON-CLASSICAL ISOMERS WITH OCTAHEDRAL STRUCTURES

4.1. *Stability trends*

The five firmly established (i.e. determined by neutron diffraction techniques) non-classical polyhydride complexes adopt octahedral structures when we count the η^2-H_2 unit as a single ligand [1,6–9]. In addition to these complexes, the majority of non-classical polyhydride complexes reported adopt an octahedral structure [5]. Interestingly, previous theoretical calculations [26d] on $MH_n(PH_3)_{8-n}$ model complexes (with 18 valence electrons) also show the same trend, i.e. those complexes which prefer non-classical isomers have an octahedral structure as the most stable geometry. In Fig. 1, the calculated relative energies of the different isomers are plotted vs. the coordination number for this class of complex. ΔE_1 and ΔE_2 in Fig. 1 are defined as

$$\Delta E_1 = E\{M(H)_nL_{8-n}\} - E\{M(H)_{n-2}(\eta^2\text{-}H_2)L_{8-n}\} \tag{2}$$

$$\Delta E_2 = E\{M(H)_nL_{8-n}\} - E\{M(H)_{n-4}(\eta^2\text{-}H_2)_2L_{8-n}\} \tag{3}$$

In Fig. 1 the ratio of ΔE_1 to ΔE_2, i.e. $\Delta E_2/\Delta E_1$, for each model complex is also presented.

It can be concluded from Fig. 1 that one group has a classical structure with a maximum coordination number of eight as the most stable geometry, while the other has a six-coordinate non-classical structure as the most stable geometry [26d]. Seven-coordinate non-classical complexes are intermediate in energy between six-

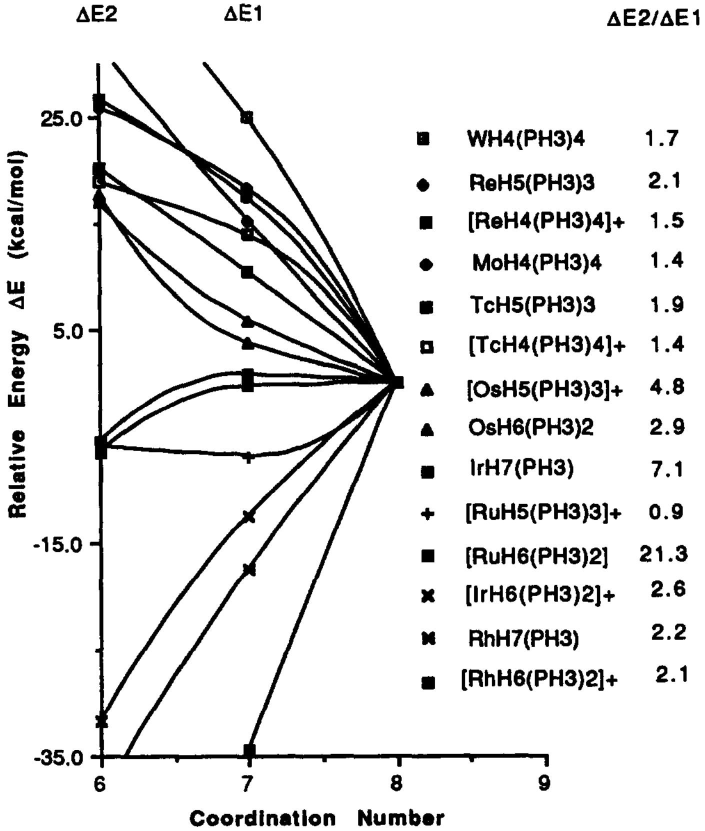


Fig. 1. Plots of the relative energies of different isomers of polyhydride complexes vs. coordination number. ΔE_1 and ΔE_2 are defined in eqns. (2) and (3) respectively. The complexes listed on the right follow the order of decreasing ΔE_2. Each complex in the list has three isomeric structures which can be found in Chart I. (Reproduced with permission from Z. Lin and M.B. Hall, Inorg. Chem., 31 (1992) 4262.)

and eight-coordinate complexes. These findings imply that, for a polyhydride complex, a six-coordinate octahedral geometry will be favored when a non-classical isomer is adopted and a seven-coordinate non-classical complex is unusually difficult to stabilize.

4.2. Molecular orbital model

A molecular orbital argument provides a simple explanation of the stability trends discussed above [26d]. Figure 2 illustrates the changes in relevant energy levels from one isomer to another for an 18-electron model complex, MH_nL_{8-n} ($n=$ 4–8). The M–L energy levels are omitted from the figure for clarity, since they are relatively constant from one isomer to another. ΔE_1 and ΔE_2 in Fig. 2 have the same definitions as in eqns. (2) and (3). When the dodecahedral classical isomer, $M(H)_nL_{8-n}$, transforms into the pentagonal-bipyramidal non-classical isomer,

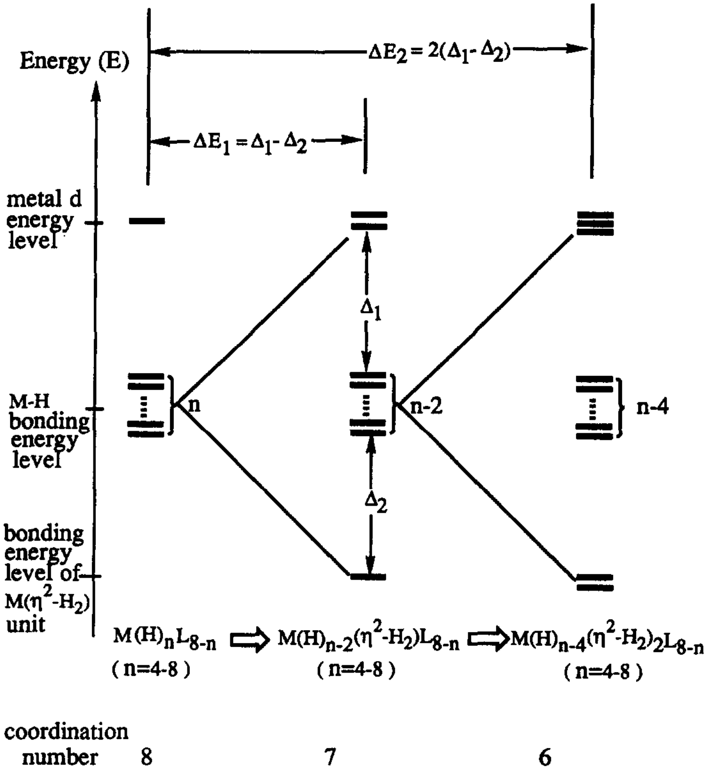


Fig. 2. Illustration of the changes in relevant energy levels in the dodecahedral→pentagonal-bipyramidal→octahedral isomerization process for an 18-electron model complex, MH_nL_{8-n} ($n=4$–8). ΔE_1 and ΔE_2 are defined in eqns. (2) and (3). (Reproduced with permission from Z. Lin and M.B. Hall, Inorg. Chem., 31 (1992) 4262.)

$M(H)_{n-2}(\eta^2\text{-}H_2)L_{8-n}$, two M–H bonds become a pair of d electrons and an $M(\eta^2\text{-}H_2)$ unit. A similar transformation leads from the pentagonal-bipyramidal isomer to the octahedral non-classical isomer, $M(H)_{n-4}(\eta^2\text{-}H_2)_2L_{8-n}$. In Fig. 2 $|\Delta_1|$ is the energy level difference between M–H and the metal d orbital and $|\Delta_2|$ is the energy level difference between the $M(\eta^2\text{-}H_2)$ unit and the M–H bond. When $|\Delta_1|>|\Delta_2|$, the classical isomer with the maximum coordination number will be the most stable. When $|\Delta_1|<|\Delta_2|$, the octahedral non-classical isomer with the maximum number of d electrons will be the most stable. This model clearly explains the trends observed both theoretically and experimentally.

Further support for this model is obtained from calculations of the $\Delta E_2/\Delta E_1$ ratios for the different complexes (see the right column of Fig. 1). The model illustrated in Fig. 2 predicts a $\Delta E_2/\Delta E_1$ ratio of 2.0 (see top of Fig. 2). Of the 14 complexes (see Fig. 1), ten have $\Delta E_2/\Delta E_1$ ratios in the range 1.4–2.9, and one has a slightly larger ratio (4.8). For the three complexes with abnormal $\Delta E_2/\Delta E_1$ ratios, the transition metals (Ru and Ir) are on (or near) the diagonal lines which divide the classical and non-classical isomers; here, $|\Delta_1|$ and $|\Delta_2|$ are close in magnitude.

In this simple molecular orbital model [26d], we assume that the energy level of the metal d orbitals does not change significantly on going from one isomer to another (see Fig. 2). The excellent agreement between this model and MP2 calculations implies that this assumption is reasonable, and therefore that the M–H bond in the majority of polyhydrides must be substantially covalent. Otherwise, we would expect a significant change in the effective charge carried by the metal in the transformation from the classical to non-classical isomer. Such a change would greatly affect the energy level of the metal d orbitals.

Cationic complexes have more greatly contracted d orbitals, and therefore the line which divides the transition metals into classical and non-classical complexes occurs earlier in the series. In the model discussed above, the contraction is intimately related to a decrease in the metal d orbital energy levels (see Fig. 2) ($|\Delta_1|$ decreases). In addition, the contraction weakens the metal–hydrogen interaction ($|\Delta_2|$ increases). Therefore the relative stability of the non-classical isomer increases when the complex is cationic or has electron-withdrawing ligands.

We could continue the condensation of two hydride ligands in the systems discussed above into an $\eta^2\text{-}H_2$ ligand, so that a five-coordinate non-classical isomer could be formed. However, a five-coordinate non-classical isomer is expected to be unstable. The instability of a five-coordinate non-classical isomer can be understood as follows. For an 18-electron ML_5 complex, the transition metal has a formal d^8 configuration. The eight valence electrons occupy $e''(d_{xz}, d_{yz})$ and e'(d–p mixing) orbitals. Therefore the trigonal-bipyramidal non-classical isomer is not favored since four of the eight valence electrons would be forced to occupy the high-energy e' orbitals. The instability of the trigonal-bipyramidal non-classical isomer is closely related to the reason why the trigonal-bipyramidal geometry is found to be a transition state rather than an intermediate in the oxidative addition of dihydrogen to a d^8 square-planar iridium complex [52].

A five-coordinate non-classical structure has been suggested for $[M(\eta^2\text{-}H_2)(PP_3)]^+$ ($M \equiv Co$ or Rh) complexes [53]. This observation is probably due to the fact that MPP_3 forms a trigonal-pyramidal structure and has only one vacant site for coordination. In addition, the metals in these complexes are all late transition metal atoms so that more d electrons can localize at the metal center.

5. STRUCTURAL FEATURES IN SOME POLYHYDRIDE COMPLEXES

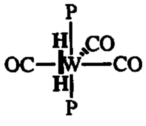
5.1. *Trans influence*

The trans influence [54] was used to predict the relative stabilities of some isomeric hydride complexes [52]. Since H is a strong trans influencing ligand, it is particularly significant in the polyhydride complexes where more than two H ligands are present. In the model complex, $RuH_4(PH_3)_3$, isomer **7** with two H ligands trans to each other is energetically higher by 20.6 kcal mol^{-1} than isomer **6** with two H ligands cis to each other. Likewise, in $OsH_4(PH_3)_3$, isomer **7** is 14.3 kcal mol^{-1} higher than isomer **6**. A similar comparison can be made between isomers **9** and **10** for the model complexes $RhH_5(PH_3)_2$ and $IrH_5(PH_3)_2$. Isomer **9** is 17.6 kcal mol^{-1} higher than isomer **10** for the Rh complex and 11.4 kcal mol^{-1} higher for the Ir complex (see Table 1). Other examples can be seen in the isomeric pair **56** and **57**.

For the $IrH_5(PH_3)_2$ complex, isomers **8** and **10** are almost of equal energy (see Table 1). Only isomer **8** is found in the crystal structure of $IrH_5[P(i\text{-}Pr)_3]_2$ [28]. This result is probably due to the steric effect of two bulky phosphine ligands in isomer **10**. This steric effect forces all five H atoms to occupy the equatorial plane, and therefore a pentagonal-bipyramidal structure is favored because it avoids a pair of trans H ligands. Together, these results show that the destabilization of two H ligands trans to each other is significant and should be borne in mind when proposing a structure for a polyhydride complex. No trans pair exists in the dodecahedral geometry and only one occurs along the axial positions in the pentagonal-bipyramidal geometry. The trans influence is particularly important for pseudo-octahedral complexes since all ligands are trans to each other.

5.2. *The orientations of the η^2-H_2 in non-classical structures*

Theoretical and experimental studies show that the rotation of the η^2-H_2 ligand around the metal–(η^2-H_2) axis in most non-classical complexes usually has a barrier of about 2.5 kcal mol^{-1} [19b,55]. This small barrier is large enough to lock the η^2-H_2 ligand into the preferred orientation observed in the crystal structures [2,6–9]. A schematic illustration of the η^2-H_2 orientations is shown in Chart VII for the five firmly known d^6 octahedral non-classical complexes.



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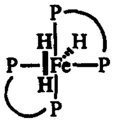

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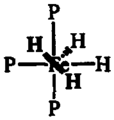

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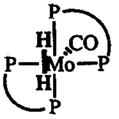

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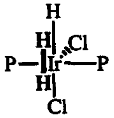

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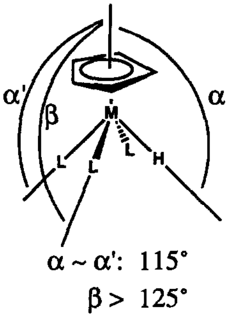
A large number of theoretical studies [9,19,24,55,56] have been performed to study the factors determining the η^2-H_2 orientation in some of the five firmly established non-classical complexes. Two factors are identified, i.e. the metal (d)–$H_2(\sigma^*)$ back donation and the "cis effect" of the hydride ligand. The cis effect is the attractive two-electron interaction between cis σ(M–H) and σ^*(H–H). In the absence of a cis hydride ligand (**58**, **59** and **61**), back donation determines the η^2-H_2 orientation and the optimal back donation is obtained when the H–H eclipses one P–M–P axis. In **58**, the d orbital in the $W(CO)_3$ plane is stabilized by the CO ligands and becomes unavailable to back donate to the σ^*(H–H) oribtal. In **59** and **61**, the η^2-H_2 ligand eclipses one P–M–P axis because the two phosphine ligands along this axis can distort away from the η^2-H_2 unit so that the d orbital in the $M(\eta^2$-$H_2)$ plane becomes slightly antibonding and more reactive towards the η^2-H_2 ligand. The conformation of **60** is apparently a result of balancing the two factors. In **62**, both factors favor the eclipsing of the η^2-H_2 ligand with the H–Ir–Cl axis because of the π-donating nature of the chloride ligands.

5.3. Four-legged piano-stool structures

5.3.1. Structural features

In this section, we focus on the complexes with molecular formulae of MHL_3Cp, MH_2L_2Cp and MH_3LCp ($L \equiv PH_3$ or CO). These complexes are usually described as "four-legged piano-stool", and may also be viewed as pseudo-square-pyramidal (see **63**–**65**, Chart VIII) [43,57]. Theoretical calculations [58] reveal that when the four L ligands are not identical, a unique structural feature is observed in which the arrangement of the four legs distorts from an ideal pseudo-square-pyramidal geometry (as measured by the angle Cp–M–L, α). The ligands distort in a pairwise fashion; the two larger α angles correspond to one pair of trans ligands and the two smaller ones correspond to the other pair. Illustrations **63**–**65** summarize the observation for the three types of hydride complex [58]. The two smaller Cp–M–L angles (about 115°) are always associated with the two trans hydrogens, while the two larger ones (126°–133°) are associated with the two L ligands or with one L ligand and the



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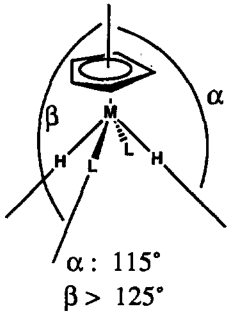

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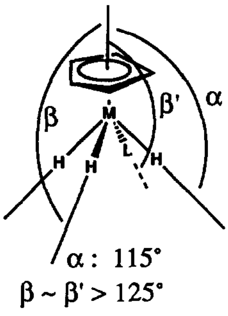

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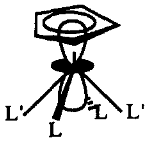
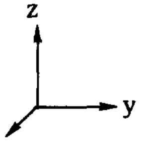
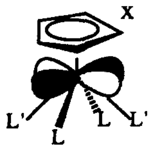






66 **67**

hydrogen trans to it. We can see from **65** that the Cp–M–H angle for the H ligands that are trans to each other is quite different from the angle for the H ligand that is trans to another ligand. This distortion feature will be explained in the next section in terms of a second-order Jahn–Teller effect [59].

5.3.2. *Molecular orbital model*

The distortions discussed in Section 5.3.1 were previously named the "angular trans influence" [43], and to understand such distortions a molecular orbital argument was developed [58]. A schematic molecular orbital diagram for the interaction between the central metal atom and the σ-donor orbitals of the ligands for a psuedo-C_{4v} ML$_4$Cp complex is presented in Fig. 3. The $d_{x^2-y^2}$ orbital interacts with the four L ligands in a σ fashion. This σ interaction results in one bonding orbital (b_1) with more ligand character and one antibonding orbital (b_1^*) with more metal $d_{x^2-y^2}$ character. The d_{xz} and d_{yz} orbitals are involved with both the Cp and L ligands. For an 18-electron complex, the two non-bonding orbitals (d_{z^2} (a_1) (**66**) and d_{xy} (b_2) (**67**)) are fully occupied with a d^4 configuration. Recently, Poli [43] explained the distortions in the "legs" of non-hydride four-legged piano-stool complexes in terms of the different π-bonding ability of the four L ligands with the two metal non-bonding d orbitals. He assumed that the d_{z^2} orbital is a better base than the d_{xy} orbital. Therefore he concluded that larger Cp–M–L angles are associated with stronger π-

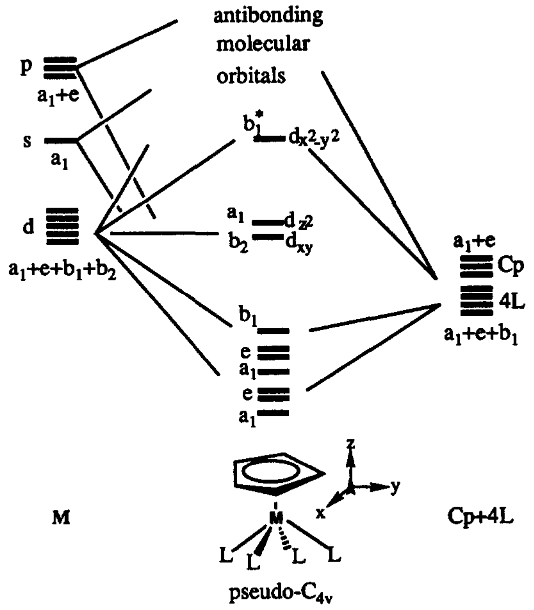
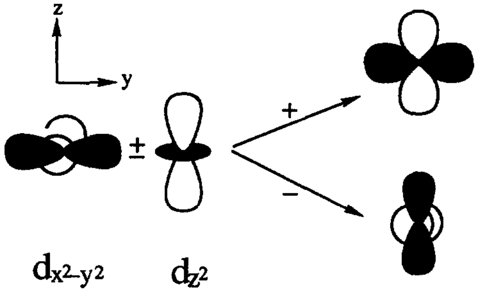


Fig. 3. Molecular orbital interaction scheme for a pseudo-C_{4v} $CpML_4$ transition metal complex. (Reproduced with permission from Z. Lin and M.B. Hall, Organometallics, 12 (1993) 19.)

accepting ligands, because maximizing the π interaction between the d_{z^2} and ligand π-accepting orbitals will stabilize d_{z^2} more strongly than it will destabilize d_{xy}. Smaller Cp–M–L angles will be favored by π-donating ligands, because minimizing the corresponding repulsive π interaction dominates the energy. This conclusion can be used to explain the distortions observed for MH_2L_2Cp ($L \equiv CO$ and PH_3) complexes (with larger Cp–M–L angles, see **64**) as long as we assume that the phosphine ligands are π-accepting ligands. However, the distortions found in MHL_3Cp and MH_3LCp complexes (see **63** and **65**) cannot be explained by this π model. For example, MH_3LCp ($L \equiv PH_3$ or CO) has a larger Cp–M–H angle, in which the H atom is trans to the L ligand, although the H ligand is neutral rather than a π acceptor.

A σ model, different from the π model above, was developed to explain the pairwise distortion. This σ model emphasizes the importance of the relevant σ interactions. A distortion from C_{4v} to C_{2v} allows a significant mixing (rehybridization) of $d_{z^2}(a_1)$ and $d_{x^2-y^2}(b_1^*)$ orbitals which are both of a_1 type in point group C_{2v}. The $d_{xy}(b_2)$ orbital does not change, and remains non-bonding because the four L ligands are always located on nodal planes. The extent of mixing depends on the type of L ligands. The complete mixing of d_{z^2} and $d_{x^2-y^2}$, which results in the formation of two new hybrid orbitals (hy+ and hy−), is illustrated in Scheme III. Since the d_{xy} orbital remains non-bonding in the distortion from C_{4v} to C_{2v} and is occupied with two d electrons, the remaining two d electrons will occupy one of the two hybridized



Scheme III

orbitals (hy±). When hy+ is occupied with two d electrons, the two L ligands in the *yz* plane will locate themselves in the hy+ nodal planes with α angles of 135° to minimize the repulsive interaction, while the other two L ligands in the *xz* plane will occupy the $\pm x$ directions with α angles of 90° to maximize the σ interaction with the empty hy− orbital. A similar consequence can be seen when the hy− orbital is occupied with two d electrons. The distortion in a four-legged piano-stool structure from the C_{4v} to C_{2v} geometry with two larger α angles (maximum of 135°) and two smaller α angles (minimum of 90°) leads to $d_{z^2} \pm d_{x^2-y^2}$ rehybridization. This rehybridization results in the formation of two hybridized orbitals in which the amplitude of each is maximized in a particular plane, either *xz* or *yz*. In other words, the two hybridized orbitals become more localized, and therefore interact more effectively with different pairs of ligands.

As a consequence of this rehybridization, strong covalent σ-bonding ligands tend to coordinate to the central metal atom with smaller α angles, since the small angle maximizes the covalent σ-interaction. Therefore all complexes with the formula MH_2L_2Cp ($L \equiv PH_3$ or CO) have small H–M–Cp angles and large Cp–M–L angles. Because the $d_{z^2} \pm d_{x^2-y^2}$ rehybridization, which occurs in the distortion from C_{4v} to C_{2v}, produces two pairs of high-symmetry hybridized orbitals (see Scheme III), each trans pair of L ligands in the four legs tend to move symmetrically inwards (increasing α angles) or outwards (decreasing α angles). This pairwise movement explains why the Cp–M–H angle associated with the H trans to L increases simultaneously with the Cp–M–L angle associated with the L ligand in MH_3LCp complexes. The two smaller α angles result from the maximization of the covalent M–H σ interaction. Therefore the "angular trans influence" in MH_3LCp complexes can be well explained in terms of this symmetrical $d_{z^2} \pm d_{x^2-y^2}$ rehybridization.

5.4. Significant distortion in the pseudo-pentagonal-bipyramidal MH_6Cp and MH_5LCp complexes

In a systematic study [26f] of the relative stabilities of different isomers (classical or non-classical) of the complex ReH_6Cp, a pseudo-pentagonal-bipyramidal structure (classical) (**33**), which was also characterized by the X-ray technique, has been shown to be the most stable. Surprisingly, the Cp–Re–H_e angle is calculated to be about 112° at both HF and MP2 levels [26f]. This result is consistent with the X-ray crystal structure [45]. In the $WH_5(PH_3)Cp$ complex (**37**), the Cp–W–H_e angle is calculated to be about 107°, again significantly larger than 90°.

This significant deviation from 90° could be due to the repulsive Cp–H interaction, an M–H electronic factor or the combination of both. Detailed theoretical studies [26f] have shown that the ligand–ligand repulsion is not responsible for the observation [26f] and it is an electronic "driving force" behind the distortion which plays an important role.

In order to explain this "driving force", a simple molecular orbital model was developed [26f]. A schematic molecular orbital diagram is shown in Fig. 4 for the interaction between the metal atom and ligand σ-donor orbitals for an MH_6Cp complex (C_{5v}) with Cp–M–H_e angles of 90°. The metal has only one $e_2(d_{x^2-y^2}, d_{xy})$ set of orbitals, which only interact with the e_2 set derived from the five equatorial hydrogens. However, the metal has two e_1 sets of orbitals [(p_x, p_y) and (d_{xz}, d_{yz})] which by symmetry could interact with the e_1 combinations from both Cp and the five equatorial hydrogens. In a regular pentagonal-bipyramid where Cp–M–H_e = 90.0°, the metal $e_1(d_{xz},d_{yz})$ orbitals maximize their overlap with the Cp e_1 combina-

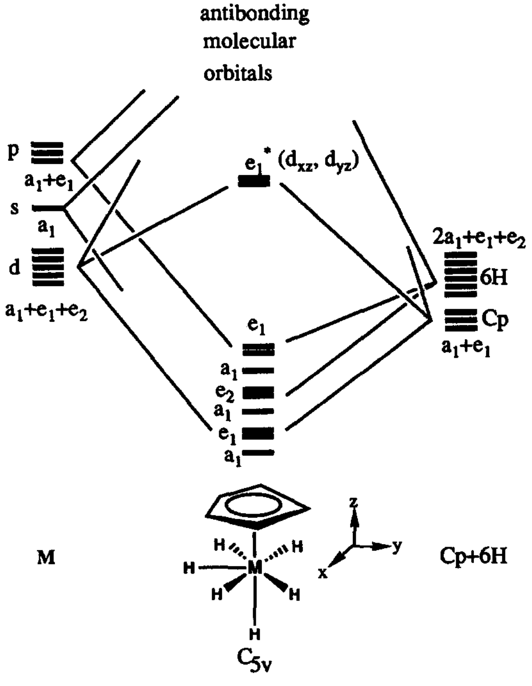


Fig. 4. Molecular orbital interaction scheme for a C_{5v} $CpMH_6$ transition metal complex. (Reproduced with permission from Z. Lin and M.B. Hall, Organometallics, 12 (1993) 4046.)

tions and minimize it (zero overlap) with the equatorial hydrogen orbitals. Thus the equatorial hydrogen e_1 orbitals can exhibit net overlap only with the metal $e_1(p_x,p_y)$ orbitals.

Consequently, a regular pentagonal-bipyramidal structure provides a geometry with minimal metal–hydrogen e_1 bonding interaction because only metal p orbitals are available for the hydrogen e_1 orbitals. Thus a distortion from the regular pentagonal-bipyramidal structure is likely to occur if these e_1 orbitals can be stabilized by interaction with the metal d orbitals. Since the e_1^* LUMO contain significant d_{xz} and d_{yz} character, this molecular structure exhibits a strong pseudo-SOJT effect [59], which is driven by the mixing between the occupied and unoccupied molecular orbitals, usually, as in this case, the HOMO and LUMO. Bending the equatorial hydrogens away from the Cp ligand allows a stronger interaction between the equatorial hydrogen e_1 set of orbitals and metal d_{xz} and d_{yz} orbitals, and therefore stabilizes the HOMO (e_1) bonding orbitals and destabilizes the LUMO (e_1^*). Because of the small size of hydrogen and the short covalent metal–hydrogen bond, the SOJT distortion is particularly noticeable [58,60]. Calculations on a model ReF_6Cp complex (C_{5v}) gave an angle of only about 98°.

6. SUMMARY

The stabilities of classical and non-classical polyhydride transition metal complexes have been reviewed. (1) For neutral complexes without strong π-accepting ligands, a diagonal line in the Periodic Table through Ru and Ir divides the classical (left side of the line) and non-classical (right side of the line) forms. Those complexes on the line may adopt either or both structures. (2) For monocationic and monochloride hydride complexes without strong π-accepting ligands, the corresponding diagonal line shifts slightly towards early transition metals and crosses between Tc/Ru and Os/Ir (see Scheme II for the illustration of these two conclusions). (3) Most polyhydrides with Cp ligand(s) adopt classical structures. The strong σ- and π-donating ability of the Cp ligand stabilizes the classical isomer by increasing the transfer of metal d electrons to the hydrides. (4) The stability of non-classical complexes with strong π-accepting ligands depends on the number of strong π-accepting ligands and the diffuse nature of the transition metal d orbitals. The non-classical isomers are more likely to exist in complexes with a larger number of strong π-accepting ligands. (5) Most non-classical isomers adopt a six-coordinate octahedral structure. This is because the octahedral structure provides a situation with the maximum number of metal d electrons occupying pure metal d orbitals. In other words, the metal orbitals accommodating d electrons do not have significant d–p mixing in an octahedral structure.

We also discussed some unique structural features in certain types of polyhydride complex. (1) The influence of two H ligands trans to each other is significantly destablizing. Thus suggestions on the stability and structure of a polyhydride complex, particularly in those complexes with an octahedral structure, must account for this influence. (2) The orientation of the η^2-H_2 ligand in the non-classical structures is attributed to the stabilization of metal(d)–$H_2(\sigma^*)$ back donation and the "cis effect" of the hydride ligand. (3) The pairwise distortion in the "four-legged piano-stool" polyhydride structures can be explained in terms of a σ model and is a result of symmetrical $d_{z^2} \pm d_{x^2-y^2}$ rehybridization arising from the distortion of an ideal pseudo-C_{4v} geometry to pseudo-C_{2v}. It was concluded that the more covalent σ-bonding pair of the trans ligands tends to be coordinated to the transition metal with the smaller α (L–M–Cp) angle. (4) Significant distortion [in which Cp–M–H (equatorial) is larger than 110°] is found in the pseudo-pentagonal-bipyramidal MH_6Cp and MH_5LCp complexes. This distortion allows a stronger interaction between the metal and equatorial hydrogens.

In this review, discrepancies between theoretical predictions and experimental results were also noted. In terms of theoretical calculations, we predict that $TcH_2Cl(dppe)_2$ [51], $ReH_2Cl(PMePh_2)_4$ [12c], $[RuH_2(PR_3)_2Cp]^+$ [5,39] and $[OsH_5L_3]^+$ ($L \equiv PPh_3$ and PMe_2Ph) [32] should be reclassified as classical isomers. We also predict the complexes $[ReH_6PP_2]^+$ to be classical structures, although X-ray diffraction and ^1H NMR T_1 studies suggest that they contain an elongated η^2-H_2 ligand [35a,b].

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