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Transition metal polyhydride complexes. 5. Complexes with a cyclopentadienyl ligand

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contain bridging thiolato ligands serving as three-electron donors. Although edge-bridging thiolato ligands are commonly found in osmium cluster complexes,[1-4,18] these may be the first examples of these ligands in trirhenium complexes.[14] The tertiary phosphine, PMe_2Ph, did not add at the thietane carbon atom but instead displaced the thietane ligand and added two PMe_2Ph ligands to the cluster.

Unlike the previously studied osmium complexes, we were unable to protonate the anionic clusters in this study. In the osmium clusters the protonation reactions led to the formation of complexes with bridging hydride ligands. In these rhenium complexes each rhenium–rhenium interaction already contains one bridging hydride ligand; thus, the addition of another hydrogen atom would require the placement of two hydride ligands across one metal–metal bond or the formation of a terminal hydride ligand. Although complexes with two hydride ligands bridging one Re–Re bond are known,[19] they are not commonly found in electron-saturated complexes such as these.

Complex 8 was not characterized crystallographically but is believed to contain a thietane ligand coordinated in a terminal fashion by using only one of the lone pairs of electrons on the sulfur atom as found in the related osmium complex $Os_3(CO)_{11}(\overline{SCH_2CH_2CH_2})$, **12**. An attempt was also made to induce the terminal 3,3-DMT ligand in 8 to open by reaction with I^-, but this reaction led only to the formation of $[Re_3(CO)_{11}I(\mu\text{-}H)_3]^-$, **9**, by ligand substitution. In this and all previous cases, we have observed nucleophilic ring-opening addition reactions only for bridging thietane ligands.[1]

We have proposed previously that the activation of *bridging* thietane ligands to ring opening by nucleophiles can be explained by the withdrawl of electron density from the sulfur atom via the σ-donation of the *two* lone pairs of electrons to the metal atoms. This will in turn lead to some withdrawl of electron density from the carbon atoms bonded to the sulfur atom, thus making them more susceptible to attack by nucleophiles. Similar mechanisms have been proposed to explain the cleavage of C–S bonds in other sulfur-containing ligands.[20]

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Supplementary Material Available: Tables of hydrogen atom and phenyl ring carbon atom positional parameters and anisotropic thermal parameters for the structural analyses of compounds **2a**, **4a**, and **7b** (12 pages). Ordering information is given on any current masthead page.

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Transition Metal Polyhydride Complexes. 5. Complexes with a Cyclopentadienyl Ligand

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Ab initio calculations with effective core potentials have been used to study the relative stabilities of classical and nonclassical isomers of 18-electron polyhydride transition metal complexes with an η^5-C_5H_5 ligand. Systematic calculations on $MH_nL_{4-n}Cp$ (n = 1–4), where M = Ru, Rh, Os, and Ir and L = PH_3 and CO, indicate that most polyhydrides with a cyclopentadienyl ligand adopt classical isomers. The strong "σ"- and "π"-donating ability of the Cp ligand increases the transfer of metal d electrons to hydrides and stabilizes the classical isomers. Although the nonclassical form is stabilized by replacing phosphine ligand(s) with π-accepting CO ligand(s), the classical form is still preferred for most complexes.

Introduction

Extensive studies of transition metal polyhydride complexes have led to the conclusion that polyhydrides may adopt both classical structures having terminal hydride ligands and nonclassical structures containing η^2-H_2 ligands.[1-25] In a series of papers, we suggested the use of the second-order Møller–Plesset (MP2)[26] perturbation calculations as a mean of obtaining reliable results on deter-

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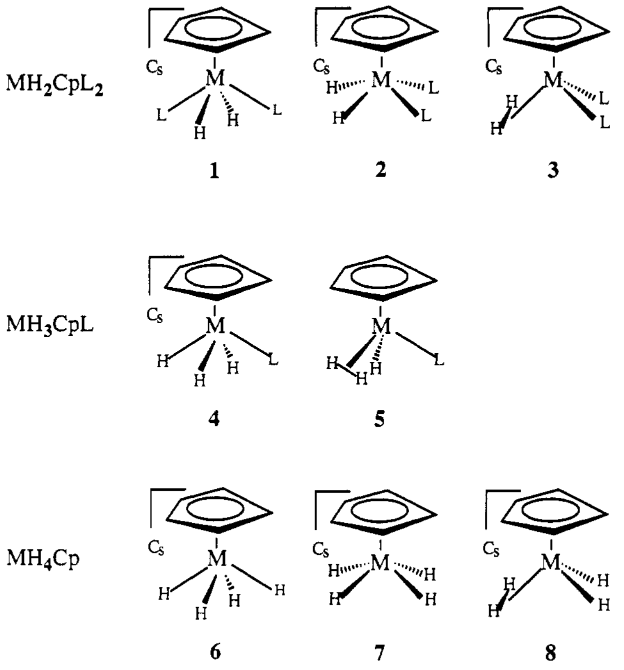
mining the relative stability of classical and nonclassical isomers.[25b] We also examined the factors that contribute to stabilizing one isomer over the other, provided some qualitative rules governing their stabilities,[25c] and proposed a model to explain the high stability of the six-coordinate octahedral structure for those transition metal polyhydride complexes which prefer a nonclassical isomer.[25d]

Table I. Selected Examples of Polyhydride Transition Metal Complexes with η^5-C_5R_5 Ligand(s)

complex[a]	means of structural characterization	geometry of metal–ligand core determined or proposed	ref
$MH_3(Cp)_2$ (M = Ta, Nb)	X-ray, neutron	classical hydride	13b
$MoH_2(Cp)_2$	X-ray, neutron	classical hydride	13a
$ReH_2Cp(PPh_3)$	X-ray	1	13c
$RuH_3Cp(PPh_3)$	X-ray	4	14
$OsH_3Cp(PR_3)$	NMR	4	15a
$OsH_3(CO)$	IR	4	15b
$[RuH_2Cp^*(PR_3)_2]^+$	NMR, X-ray	1–3	16
$[RuH_2Cp(PR_3)(CO)]^+$	NMR	3	16b
$[RuH_2Cp^*(CO)_2]^+$	NMR	3	16d
$RhH_2Cp^*(SiEt_3)_2$	X-ray, neutron	1	17
$[IrH_3Cp(PR_3)]^+$	NMR, X-ray, neutron	4	18
$IrH_3Cp(SnPh_3)$	X-ray	4	19
IrH_4Cp	NMR	6, 7	19

[a] Cp = η^5-C_5H_5 and Cp* = η^5-C_5Me_5.

Chart I



In systematic quantum-mechanical calculations on neutral $MH_n(PH_3)_{7-n}$ and $MH_n(PH_3)_{8-n}$ (n = 2–7) polyhydride model complexes,[25c] where M ranges from group 6 to group 9 of second and third row transition metal atoms, we found that a diagonal line in the periodic table through Ru and Ir atoms divides the classical (left side of the line) and nonclassical (right side of the line) forms. For monocationic hydride complexes the corresponding diagonal line shifts slightly toward the early transition metals and crosses between the Tc/Ru and Os/Ir atoms. In this paper, we will investigate how the corresponding diagonal line shifts in the transition metal polyhydride complexes with an η^5-C_5R_5 ligand. Following a strategy similar to that used in previous papers, we will focus our discussion on

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Table II. Neutral and Cationic Model Cp Complexes and Their Relative Energies of Classical and Nonclassical Isomers (MP2 Results)

neutral model complexes	$RuH_3Cp(PH_3)$	RhH_4Cp		
		0.0 (6 → 7)		
	15.5 (4 → 5)	11.8 (6 → 8)		
	$OsH_3Cp(PH_3)$	IrH_4Cp	$OsH_3Cp(CO)$	
		0.7 (6 → 7)		
	21.9 (4 → 5)	23.1 (6 → 8)	17.8 (4 → 5)	
cationic model complexes	$RuH_2Cp(PH_3)_2{}^+$	$RhH_3Cp(PH_3)^+$	$RuH_2Cp(CO)_2{}^+$	
	5.7 (1 → 2)		3.0 (1 → 2)	
	12.5 (1 → 3)	−0.5 (4 → 5)	3.2 (1 → 3)	
	$OsH_2Cp(PH_3)_2{}^+$	$IrH_3Cp(PH_3)^+$	$OsH_2Cp(CO)_2{}^+$	$IrH_3Cp(CO)^+$
	5.8 (1 → 2)		3.6 (1 → 2)	
	17.8 (1 → 3)	11.7 (4 → 5)	8.7 (1 → 3)	8.7 (4 → 5)

$MH_nL_{4-n}Cp$ (n = 1–4) polyhydride complexes with a closed-shell configuration of 18 valence electrons, where M = Ru, Rh, Os, and Ir and L = PH_3 and CO.

Theoretical Details

Ab initio effective core potentials[27] were employed in all calculations. All geometries were optimized at the restricted Hartree–Fock (HF) level. When energies were to be compared, they were recalculated with electron correlation included at the MP2 level. In this study, all aryl and alkyl groups were replaced by H atoms; i.e., PR_3 was replaced by PH_3. The H–P–H angle was fixed at 103.4°, and the P–H bond distance was fixed at 1.44 Å. The C_5H_5 unit is also fixed as planar with C–C and C–H bond lengths of 1.41 and 1.08 Å, respectively.

In the effective core potentials (ECPs) for the transition metals, the outermost core orbitals, which correspond to a ns^2np^6 configuration, were treated explicitly on an equal footing with the nd, (n + 1)s, and (n + 1)p valence orbitals. The basis sets of the second and third transition series atoms were described with (541/41/211) and (541/41/111), respectively, which correspond to a double-ζ representation of the (n + 1)s/np electrons and a triple-ζ representation of the nd electrons.[27] For ligand atoms, the ECPs and double-ζ basis sets of Stevens, Basch, and Krauss were used.[28] [He] and [Ne] configurations were taken as cores for the first- and second-row main group atoms. The Dunning–Huzinaga double-ζ basis set (31) was used for the H atom.[29]

All HF calculations were performed with the GAMESS package,[30] while all MP2 calculations were completed using the Gaussian 90 program.[31] All GAMESS calculations were made at the Cornell National Supercomputer Facility (CNSF) on an IBM 3090-600VF, at the Supercomputer Center of Texas A&M University on a Cray Y-MP2/116, and at the Chemistry Department on a FPS Model 522. Gaussian 90 was run at the CNSF.

Results

A large number of polyhydride transition metal complexes with η^5-C_5R_5 ligand(s) have been structurally characterized and identified either in the solid state or in solution.[13-19] Selected examples of this class of polyhydrides are listed in Table I. We systematically calculated the model complexes listed in Table II. Geometries for these model complexes with different isomers are illustrated in Chart I. All complexes in Table II with different isomers (see Chart I) were optimized at the restricted Hartree–Fock (HF) level, and energies for optimized geometries were recalculated with MP2 method. In certain cases of the geometry optimizations, we fixed the distance of one pair of hydrogens and then performed partial geometry optimizations for those isomers which could not be found by full geometry optimizations. We fixed a separation of 1.70 Å between the two hydrogens which are involved in the isomerization to the nonclassical form for the isomers

$$RuH_2Cp(PH_3)_2{}^+\ (2) \qquad RhH_3Cp(PH_3)^+\ (4)$$
$$OsH_2Cp(CO)_2{}^+\ (2)$$

and fixed η^2-H_2 unit(s) at a separation of 0.82 Å between the two hydrogens which are involved in the isomerization to the classical form for the complexes

$$OsH_3CpPH_3\ (5) \qquad IrH_4Cp\ (8) \qquad OsH_3Cp(CO)\ (5)$$

At the MP2 level, if these partially optimized isomers have lower energy than their isomerizing counterparts, they should be close to minima on the potential surface with respect to the H⋯H separation. If they have higher energy than their isomerizing counterparts, they may not be local minima. However, we are interested primarily in the structures of more stable species, so the actual characterization of the high-energy species is not very important. The fixed structural parameters are derived from a variety of compounds which show comparable H⋯H separations, and the error caused by fixing these parameters is estimated to be about ±1.0 kcal/mol.

The relative MP2 energy differences (ΔE) for different model complexes are also given in Table II. The bold numbers in Table II indicate the isomerizing pair for the energy difference (Chart I). For most model complexes, two ΔE's are presented in Table II. The first one indicates the energy difference between two different classical isomers, while the second one denotes the energy difference between a classical isomer and a nonclassical isomer with one (η^2-H_2) ligand. In some complexes, the first number is omitted from the table because either no comparison can be made or no calculation was done.

Discussion

Neutral and Cationic Complexes without Strong π-Accepting Ligands. Surprisingly, results in Table II show that the classical hydrides, with "four-legged piano stool" structures, are preferred for most complexes. A nonclassical isomer is calculated to be slightly more stable (only by −0.50 kcal/mol) for the $RhH_3Cp(PH_3)^+$ complex. The energy difference between two classical isomers for each complex is relatively small, and the one with two hydrogen atoms trans to each other (with respect to the four legs) is always found to be more stable. The relative energies listed in Table II show that no nonclassical isomer is found to be more stable for the neutral complexes and only one [$RhH_3Cp(PH_3)^+$ (5)] is found to be slightly more stable for cationic complexes without strong π-accepting

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ligand(s). This result implies that the Cp ligand is a very strong "σ" and "π" donor. The strong σ- and π-donating ability of 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 nonclassical isomers (observed in MH_nL_{7-n} and MH_nL_{8-n} (n = 2-7, L = PH_3) complexes) is shifted toward late transition metals in the periodic table when three phosphine ligands are replaced by a Cp ligand.

The experimental results in Table I indicate that most polyhydrides with η^5-C_5R_5 ligand(s) adopt classical isomers. In general, this is in agreement with our calculations (see Table II). An exception is seen for cationic Ru complexes. Most experimental studies[16] suggest that they are nonclassical, but our calculations suggest that the classical isomers are more stable (see Table II). The $RuH_2Cp(PH_3)_2$ complex prefers the classical isomer **1** over the nonclassical isomer **3** by 12.5 kcal/mol, a significant energy difference. Recently, the X-ray crystal structure of the $[RuH_2(\eta^5\text{-}C_5Me_5)(PPh_2CH_2PPh_2)]^+$ complex suggested a nonclassical form **3**.[16a] Because of the bidentate ligand, the geometry of the Ru complex is forced to adopt either **2** or **3**. The energy difference between **2** and **3** for the $[RuH_2Cp(PH_3)_2]^+$ complex is 6.8 kcal/mol (see Table II) with a preference for the classical form **2**. Even on the basis of the X-ray crystal structure for the heavy-atom positions, our calculation still has the classical isomer **2** 5.4 kcal/mol more stable than isomer **3**.

We do not have an explanation for this discrepancy between our theoretical calculations and NMR experimental results. However, in view of the periodically diagonal similarity in transition metals as discussed in our previous papers, we would expect that $RuH_2Cp(PR_3)_2^+$ adopts a classical isomer from the fact that the $IrH_3Cp(PR_3)^+$ complex is characterized by neutron diffraction as a classical isomer. A final structural determination by neutron diffraction will provide a test of the accuracy of our prediction.

Neutral and Cationic Complexes with Strong π-Accepting Ligands. We have shown[25c] that strong π-accepting ligands stabilize the nonclassical isomers and shift the diagonal line which divides the classical (left side of the line) and nonclassical (right side of the line) isomers toward early transition metals in the periodic table. The stabilizing effect of carbonyl ligand(s) on nonclassical isomers is clearly seen from Table I. For example, the energy difference between classical **4** and nonclassical **5** isomers is greater (21.9 kcal/mol) for $OsH_3Cp(PH_3)$ than that (17.8 kcal/mol) for $OsH_3Cp(CO)$. We can see from Table II that the energy difference between classical and nonclassical isomers decreases by about 3.0–4.6 kcal/mol with each replacement of PH_3 by CO ligand.

In general the σ- and π-donating ability of the Cp ligand is so strong that in most transition metal cyclopentadienyl polyhydride complexes the classical hydrides are still preferred even in the presence of strong π-accepting ligands such as carbonyls. For the $RuH_2Cp(CO)_2^+$ complex with two carbonyls, the classical isomer **1** is 3.2 kcal/mol more stable than the nonclassical isomer **3** although NMR experiments suggested a dihydrogen complex for the $[RuH_2(\eta^5\text{-}C_5Me_5)(CO)_2]^+$ complex.[16d]

The stabilizing effect of carbonyl on nonclassical isomers allows us to predict a more stable nonclassical isomer **5** (ca. −4.5 kcal/mol) for the $[RhH_3Cp(CO)]^+$ complex (from the result of $[RhH_3Cp(PH_3)]^+$). However, this estimated energy difference is not significant enough for us to conclude the existence of the Rh nonclassical isomer, particularly if a η^5-C_5Me_5 ligand instead of η^5-C_5H_5 is present since the Me groups enhance the donating ability of the Cp ligand.

Conclusion

The relative stabilities of classical and nonclassical polyhydride cyclopentadienyl transition metal complexes have been studied. Our calculations indicate that most of these polyhydrides adopt classical isomers. We have reclassified the $[RuH_2Cp(L)_2]^+$ (L = phosphine, CO) complexes as classical isomers. The strong σ- and π-donating ability of the Cp ligand stabilizes the classical isomers by increasing the transfer of metal d electrons to the hydrides. Although the nonclassical form is stabilized by replacing phosphine ligand(s) with π-accepting CO ligand(s), the classical form is still preferred in most complexes.

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Supplementary Material Available: Tables of coordinates of optimized model complexes (12 pages). Ordering information is given on any current masthead page.

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