Table II. Calculated Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km mol^{-1}) of Isomeric NSO^- Anions

NSO^-	freq	574 (515)[a]	1139 (990)[a]	1443 (1270)[a]
	intens	56	201	156
SNO^-	freq	547	811	1765
	intens	6	146	493
SON^-	freq	447	647	1619
	intens	4	3	42
cy-NSO^-	freq	380	764	1060
	intens	67	6	35

[a] Observed values.

Table III. Mulliken Charge Distributions (q_A), Total Atomic Overlap Populations (q_{AB}), and Charge Separations (Δq_{AB}) for Isomeric NSO^- Anions

ion	property	6-31G*	6-31+G*
NSO^-	q_N	−0.722	−0.736
	q_S	+0.542	+0.467
	q_O	−0.820	−0.730
	q_{SN}	+0.797	+0.342
	q_{SO}	+0.194	−1.086
	Δq_{SN}	1.264	1.203
	Δq_{SO}	1.362	1.197
SNO^-	q_S	−0.523	−0.612
	q_N	−0.037	−0.124
	q_O	−0.440	−0.264
	q_{SN}	+0.327	+0.006
	q_{NO}	+0.399	+0.207
	Δq_{SN}	0.486	0.488
	Δq_{NO}	0.403	0.140
SON^-	q_S	−0.466	−0.586
	q_O	−0.385	−0.048
	q_N	−0.149	−0.366
	q_{SO}	+0.065	−0.185
	q_{NO}	+0.313	−0.230
	Δq_{SO}	0.081	0.538
	Δq_{NO}	0.236	0.318
cy-NSO^-	q_N	−0.430	−0.572
	q_S	−0.007	−0.056
	q_O	−0.563	−0.373
	q_{SN}	+0.097	−0.292
	q_{SO}	+0.086	−0.129
	q_{NO}	−0.004	−0.252
	Δq_{SN}	0.423	0.516
	Δq_{SO}	0.556	0.317
	Δq_{NO}	0.133	0.199

atoms vary, from slightly to substantially, according to the basis sets used. On the other hand, the basis-set dependences of the total atomic overlap populations are more dramatic, the inclusion of diffuse functions changing half of the values of the total atomic overlap populations from positive to negative. Nevertheless, their relative values obtained with both the 6-31G* and the 6-31+G* basis sets correlate well with the calculated bond distances (Tables II and III) except for the SO bond of NSO^-. It is interesting to note that the bonds of NSO^- are most ionic in comparison to the bonds of the other three anions.

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Synthesis and Structural Characterization of a Mixed-Ring Rhenocene Hydride Complex, $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)ReH$

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Rhenocene hydride, Cp_2ReH (Cp = $\eta^5\text{-}C_5H_5$), the first carbonyl-free hydride,[2] the first hydride characterized by ^1H NMR spectroscopy, and the first bent metallocene,[3] has been quite important in the development of modern organometallic concepts since first reported in 1955. Despite this, the chemistry of this complex has remained relatively unexplored;[4] this neglect can perhaps be attributed to difficulties with its synthesis. Permethylrhenocene hydride, $Cp^*{}_2ReH$ (Cp^* = $\eta^5\text{-}C_5Me_5$), has only recently been reported,[5] and has been shown to exhibit reactivity significantly different from that observed for the cyclopentadienyl species. For example, the Re(II) species $Cp^*{}_2Re$ produced upon UV photolysis has been isolated and fully characterized.[6] The required metal vapor synthesis, however, of permethylrhenocene hydride is not amenable to general use. A solution synthesis of rhenocene derivatives based on the easily available Cp^*ReCl_4[7] (**1**) would afford an opportunity to explore the chemistry of this class of complexes. We now wish to report the synthesis, structural characterization, and some reactivity data of the new mixed-ring rhenocene hydride $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)ReH$ (**2**).

Experimental Section

All manipulations were undertaken with use of standard Schlenk techniques under N_2. $NaBH_4$ (Aldrich) was used as received. Solvents were dried by refluxing over sodium wire under N_2 and stored over Davison 4-Å molecular sieves. Infrared spectra were recorded as Nujol mulls between NaCl plates with a Nicolet FT-5DX instrument. A JEOL-GLX400 spectrometer was used for ^1H and ^{13}C NMR measurements, and C_6D_6 was employed as a solvent (all spectra referenced to $SiMe_4$). Mass spectra were recorded with a Varian MAT A 311 instrument. Microanalyses were obtained from our microanalytical laboratory. Cp^*ReCl_4[8] (**1**) and NaCp[9] were prepared according to literature methods, with some modifications. In particular, yields of the reaction of $Cp^*Re(CO)_3$, available in 95% yield from $Re_2(CO)_{10}$,[10] with aqueous H_2O_2 (30%) in a two-phase benzene/water system can be improved by careful temperature control, i.e., a bath temperature not more than 80 °C, by addition of the H_2O_2 solution in two aliquots, one at the start of the reaction and one after the reaction mixture has turned deep red (ca. 3 h), by use of smaller amounts of H_2SO_4, ca. 0.1 mL for 10 g of the starting material, and by prompt termination of the reaction. It can be observed that the reaction solution first goes from clear to yellow, then to a deep red, and then back to a bright yellow. After the reaction is stopped at this point, the organic phase should be washed with a 5% aqueous $NaHCO_3$ solution before drying with $MgSO_4$ and solvent removal. Yields of 80–85% from $Cp^*Re(CO)_3$ have been consistently achieved on a 10-g scale. The raw product can be recrystallized from toluene/pentane or can be directly treated with 1 equiv of PPh_3 and excess $ClSiMe_3$ in toluene to yield >90% yields of Cp^*ReCl_4. Careful washing of the microcrystalline product from this reaction with toluene and ether directly yields Cp^*ReCl_4 of sufficient purity for further reactions. An alternative direct oxidation of $Cp^*Re(CO)_3$ to Cp^*ReO_3 in CCl_4 at −78 °C by slow addition of Mn_2O_7[11] (yield ca. 90%) has also recently been developed in this laboratory.[12] Preparation of the tetramethylethylcyclopentadienyl rhenocene hydride $(\eta^5\text{-}C_5Me_4Et)(\eta^5\text{-}$

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Table I. Crystallographic Data for (η^5-C_5Me_4Et)(η^5-C_5H_5)ReH

formula: $C_{16}H_{23}Re$	$M_r = 401.6$
space group: $P\bar{1}$ (No. 2)	$T = -60 \pm 3$ °C
$a = 859.3$ (2) pm	$\alpha = 80.00$ (2)°
$b = 832.6$ (1) pm	$\beta = 74.62$ (2)°
$c = 1168.1$ (4) pm	$\gamma = 61.60$ (2)°
$V = 708 \times 10^6$ pm^3	$Z = 2$
ρ(calcd) = 1.884 g cm^{-3}	Mo Kα radiation (λ = 71.073 pm)
$R = 0.031^a$	μ(Mo Kα) = 86.8 cm^{-1}
$R_w = 0.040^b$	transmissn coeff: 0.8126–1.000

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

C5H$_5$)ReH (**2′**) was carried out in precisely the same manner as that for the parent complex **2**, which is detailed below.

Preparation of (η^5-Pentamethylcyclopentadienyl)(η^5-cyclopentadienyl)hydridorhenium(III) (2). To a mixture of Cp*ReCl (**1**) (610 mg, 1.3 mmol) and $NaBH_4$ (199 mg, 5.3 mmol) at liquid-nitrogen temperature was added 20 mL of THF. The mixture was allowed to warm to room temperature and was stirred for 6 h. The solution was again frozen, and NaCp (230 mg, 2.6 mmol) was added. The solution was allowed to warm to room temperature and was stirred overnight. Volatiles were removed under high vacuum from room temperature to 90 °C, at which point cooling of the sublimation finger was begun. The sublimation temperature was slowly raised to 150 °C and held there ca. 4 h. The product on the probe was resublimed under high vacuum at room temperature by utilizing an liquid-nitrogen-cooled probe. The resublimed material was washed into a Schlenk tube with 10 mL of *n*-pentane, the solvent volume was reduced to ca. 2 mL, and crystals were grown at −78 °C overnight. Concentration of the mother liquor yielded a second crop; yield: 220 mg (43%). Anal. Calcd for $C_{15}H_{21}Re$ (M_r 387.2): C, 46.48; H, 5.42. Found: C, 46.67; H, 5.54. IR: ν_{Re-H} 2034 (w) cm^{-1}. ^{1}H NMR: δ 3.95 (d, $^3J_{H-H}$ = 1.2 Hz, 5 H), 2.07 (s, 15 H), −12.34 (s, 1 H). ^{13}C NMR: δ 82.8 (C_5Me_5, complex multiplet), 13.4 ($C_5(CH_3)_5$, q, $^1J_{C-H}$ = 126 Hz), 67.2 (C_5H_5, second-order multiplet, $^1J_{C-H}$ = 178 Hz, $^{2,3}J_{C-H}$ = ca. 7 Hz). EI-MS (20 °C, 70 eV): *m/z* 388 ($^{187}M^+$), 387 ($^{187}M^+ - H$), 386 ($^{185}M^+$, $^{187}M^+ - H_2$), 384 ($^{185}M^+ - H_2$).

Structure Determination. Crystal data for (η^5-C_5Me_4Et)(η^5-C_5H_5)ReH (**2′**) are listed in Table I. The compound, obtained as yellow cubes by cooling of an *n*-pentane solution, crystallizes in the triclinic space group $P\bar{1}$ (No. 2; no systematic absences). Cell constants were obtained from least-squares refinement by using a set of 50 reflections in the range 43.9° ≤ 2θ ≤ 55.1°, and the orientation matrix was found by using a set of 25 reflections in the range 13° ≤ 2θ ≤ 50°.[13] Data collection was performed at low temperature ($T = -60 \pm 3$ °C) on an Enraf-Nonius CAD-4 four-circle diffractometer with graphite-monochromated Mo Kα (λ = 71.073 pm) radiation. An ω-scan mode in the range 2.0° ≤ θ ≤ 25.0° was chosen with variable scan width (1.10 + 0.35 tan θ)° ± 25% before and after each reflection for background determination. The maximum scan time amount, T(max), was 60 s. From 4930 measured reflections ($\pm h,\pm k,\pm l$), 73 reflections with negative intensity were rejected. After merging, all 2448 independent reflections with $I < 0.0\sigma(I)$ were used, and 154 parameters were full-matrix least-squares refined. During data collection, no disorientation was detected. The intensity data were collected for Lorentz and polarization effects and for a small linear decay (78.8 h; −8.1%). As an irregular fragment of a crystal was measured, only an empirical absorption correction based upon nine reflections could be applied. The Re atom positions were determined from the Patterson maps. All remaining non-hydrogen atoms were located by successive structure factor calculations and difference Fourier maps and least-squares full-matrix refined. Refinement minimized the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F_o)$.[14] Hydrogen atoms were calculated in ideal positions (C–H = 95 pm), based on 18 hydrogens found with difference Fourier techniques, and added to the calculations with isotropic temperature factors but not refined, except the hydride, which was refined. Anomalous dispersion corrections were applied to all non-hydrogen atoms.[15] Refinements converged with unweighted and weighted agreement factors $R = 0.031$ and $R_w = 0.040$, respectively. The refinement finished with a shift/error ratio <0.001 in the last cycle, and the residual electron densities yielded +1.99 and −2.62 e/Å^3, respectively, near the heavy atom Re. All calculations were performed on VAX11/730 and VAX8200 computers using the STRUX-II[16] and SDP[17] systems. Positional parameters are given in Table II. Selected bond lengths and angles are given in Table III.

Table II. Positional Parameters and Their Estimated Standard Deviations^a

atom	x	y	z	B_{eq}, Å^2
Re	0.35165 (3)	0.17868 (3)	0.29206 (2)	1.386 (6)
C11	0.1877 (8)	0.4684 (9)	0.2378 (6)	1.9 (2)
C12	0.3016 (8)	0.4632 (9)	0.3104 (6)	1.7 (1)
C13	0.4854 (8)	0.3664 (9)	0.2480 (6)	1.9 (2)
C14	0.4915 (8)	0.3020 (10)	0.1376 (6)	1.9 (2)
C15	0.3042 (8)	0.3683 (9)	0.1322 (6)	1.9 (2)
C20	−0.660 (9)	0.7742 (11)	0.2062 (7)	3.0 (2)
C21	−0.0124 (9	0.5808 (11)	0.2579 (7)	2.7 (2)
C22	0.2410 (10)	0.5666 (10)	0.4198 (6)	2.7 (2)
C23	0.6514 (9)	0.3424 (11)	0.2852 (7)	3.1 (2)
C24	0.6484 (10)	0.2129 (12)	0.0412 (7)	3.0 (2)
C25	0.2419 (10)	0.3461 (12)	0.0278 (6)	3.3 (2)
C31	0.1289 (8)	0.1008 (10)	0.3663 (6)	2.2 (2)
C32	0.2326 (9)	0.0136 (10)	0.2577 (6)	2.4 (2)
C33	0.4126 (10)	−0.1092 (11)	0.2748 (7)	3.0 (2)
C34	0.4151 (10)	−0.0938 (11)	0.3927 (7)	2.6 (2)
C35	0.2405 (10)	0.0324 (11)	0.4498 (7)	2.7 (2)
H	0.560 (14)	0.003 (14)	0.283 (9)	6 (3)*
Cp1	0.3540	0.3936	0.2132	
Cp2	0.2859	−0.0112	0.3482	

^{a}Starred values denote atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta_{11} + ... + ab(\cos\gamma)\beta_{12} + ...]$. Cp denotes the center of the ring.

Table III. Selected Bond Lengths (pm) and Bond Angles (deg)

Re–C11	221.8 (4)	C13–C14	145.9 (5)
Re–C12	223.6 (4)	C14–C15	144.8 (5)
Re–C13	226.8 (5)	C15–C11	145.9 (5)
Re–C14	226.5 (4)	C11–C21	149.0 (6)
Re–C15	221.7 (4)	C12–C22	150.0 (5)
Re–C31	222.3 (5)	C13–C23	151.5 (5)
Re–C32	220.1 (4)	C14–C24	147.3 (5)
Re–C33	223.1 (5)	C15–C25	152.4 (5)
Re–C34	225.0 (5)	C20–C21	150.8 (6)
Re–C35	227.7 (4)	C31–C32	142.7 (5)
Re–H	168 (7)	C32–C33	143.8 (6)
Re–Cp1	187.2	C33–C34	141.2 (6)
Re–Cp2	188.2	C34–C35	141.9 (7)
C11–C12	143.7 (5)	C35–C31	140.7 (6)
C12–C13	143.5 (5)		
H–Re–Cp1	113	C13–C14–C15	105.3 (4)
H–Re–Cp2	81	C13–C14–C24	129.0 (4)
Cp1–Re–Cp2	161.6	C15–C14–C24	125.1 (3)
C12–C11–C15	108.0 (4)	C11–C15–C25	126.3 (3)
C12–C11–C21	125.5 (3)	C14–C15–C25	124.6 (3)
C15–C11–C22	125.8 (3)	C11–C21–C20	112.3 (4)
C11–C12–C13	107.1 (3)	C35–C31–C32	108.4 (4)
C11–C12–C22	126.4 (3)	C31–C32–C33	107.8 (3)
C13–C12–C22	125.7 (3)	C32–C33–C34	106.9 (3)
C12–C13–C14	110.5 (4)	C33–C34–C35	109.3 (4)
C12–C13–C23	125.8 (4)	C34–C35–C31	107.7 (4)
C14–C13–C23	123.7 (4)		

Results

We have been interested in reactions of Cp*ReCl$_4$ (**2**) with Grignard reagents[18] and other reducing reagents, such as metal powders.[19] In the absence of trapping ligands, a unifying theme

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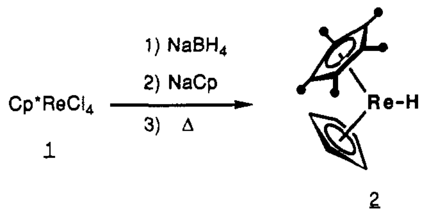
Scheme I



has been initial reduction to Re(IV) and Re(III) species, followed by overreduction and concomitant ring loss. A strategy for limiting such reactions, therefore, has been of general interest in developing the substitution chemistry of these complexes. Such a strategy was suggested by a recently published observation on the use of a titanium(II) borohydride complex, $(DMPE)_2Ti(BH_4)_2$, as a precursor for the previously unobtainable alkyl complex $(DMPE)_2Ti(CH_3)_2$.[20]

The reaction of Cp^*ReCl_4 with 4 equiv of $NaBH_4$ results in reduction and yields a mixture of Re(IV) and Re(III) borohydride complexes of unknown composition. The sensitivity of these complexes to oxygen and moisture has, as yet, precluded their isolation. The oxidation states are proposed on the basis of the previously observed reduction chemistry of Cp^*ReCl_4 (**1**). The aggregation states, i.e., monomer, dimer, or oligomer, are unknown. However, this mixture can be reacted, in situ, with NaCp to yield Cp*CpReH (**2**) upon sublimation (Scheme I). In principle, this synthesis can be thought of as a stepwise version of the original synthesis of Cp_2ReH, i.e., reaction of $ReCl_5$ with $NaBH_4$ and NaCp, followed by sublimation.[21]

We postulate an intermediate complex such as $Cp^*CpRe(BH_4)_x$ (also possibly oligomeric) on the basis of the observation that sublimation of the crude product occurs at ca. 100 °C, while Cp*CpReH itself sublimes at room temperature under the same conditions. Complexes of this type have been previously observed in similar systems; e.g., $Cp^*_2NbBH_4$ has been isolated from the reaction of $NbCl_5$ with LiCp* and $NaBH_4$.[22] As the crude sublimed rhenocene hydride **2** is often contaminated with oily byproducts, this proves a convenient method for obtaining pure product. The reaction mixture is heated to ca. 90 °C under high vacuum; the product is then sublimed to a water-cooled probe with continued heating to ca. 150 °C and then resublimed at room temperature to a liquid-nitrogen-cooled probe (removing the bulk of the contaminants). Crystallization at −78 °C from *n*-pentane then yields analytically pure product in ca. 40% yield (from Cp^*ReCl_4). Unfortunately, the yields obtained with this synthesis are highly dependent on the purity of the starting materials and solvents used. Uncontrolled reduction results in oily byproducts, presumably from Cp* loss and degradation. These interfere with the sublimation and, as the rhenocene hydride is quite pentane soluble, make it very difficult to recrystallize the complex and retain a reasonable yield. Insufficiently dried solvent causes the reaction to fail completely.

The mixed-ring rhenocene hydride Cp*CpReH is obtained as moderately air-sensitive, light yellow crystals. The complex decomposes quickly upon exposure to oxygen in solution but is stable for short periods of time in the solid state. The spectroscopic data are consistent with the assigned structure. In particular, the metal–hydride stretch (Nujol) is observed at 2034 cm^{-1} in the infrared spectrum, and the hydride signal in the ^1H NMR spectrum appears as a broad singlet at δ −12.34 (C_6D_6, 28 °C).

The synthesis outlined above can be easily extended to the derivative $(\eta^5\text{-}C_5Me_4Et)(\eta^5\text{-}C_5H_5)ReH$ (**2′**). It proved possible to obtain good quality crystals of this complex and to obtain a single-crystal X-ray structure (Figure 1).

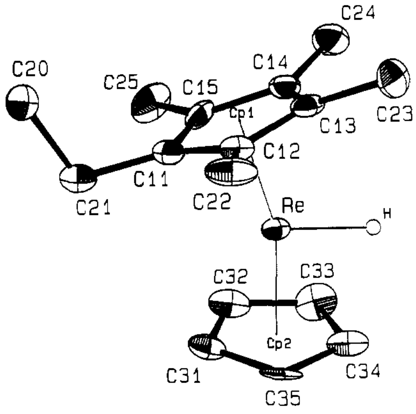


Figure 1. ORTEP plot of $(\eta^5\text{-}C_5Me_4Et)(\eta^5\text{-}C_5H_5)ReH$ (**2′**) with thermal ellipsoids drawn at the 50% level.

Table IV. Selected Crystallographic Parameters for Rhenocene Derivatives[a]

compd	Φ, deg	Re–C (av), Å	C–C (av), Å	ref
$[Cp_2ReBr_2]BF_4$	139.5	2.26	1.39	23
$[Cp_2Re(H)CuI]_2$	158	2.24	1.44	24
$[Cp_2Re]CuCl_2$	150.1	2.275	1.471	25
Cp_2Re				
$[\eta^1\text{-}(E)\text{-}C(CO_2Me){=}CH(CO_2Me)]$	146.8	2.24	1.412	26
$[\eta^1\text{-}(Z)\text{-}C(CO_2Me){=}CH(CO_2Me)]$	146.2	2.23	1.411	26
$Cp_2Re\text{–}CHMe\text{–}O\text{–}ZrCp_2Me$	150.5	2.25	1.37	27
Cp^*_2Re	180	2.23	1.418	28

[a] All compounds have an eclipsed configuration; Me = methyl.

Discussion

The structural parameters for $(\eta^5\text{-}C_5Me_4Et)(\eta^5\text{-}C_5H_5)ReH$ (**2′**) (Table III) can be compared with those of other structurally characterized rhenocene complexes (Table IV). We note that there is *no* difference in the metal-to-carbon bond lengths of the C_5H_5 and the C_5Me_5 ring ligands (Table III).

Cationic bent metallocenes of group VIII transition metals such as protonated ferrocene $[Cp_2FeH]^+$,[29] isoelectronic with the rhenocene hydrides, also form a basis for comparison. Structural parameters for $[Cp_2RuI]I_3$ (Φ = 147.8°, eclipsed)[30] and $[Cp_2Os^+]_2(PF_6)_2$ (Φ = 144.5°, eclipsed)[31] have been reported.

The average rhenium–ring carbon distances for both the cyclopentadienyl and peralkylcyclopentadienyl groups are consistent with those reported for rhenium metallocene complexes. The eclipsed conformation observed could not be predicted from first principles,[32] as has been previously noted during the comparison of the structures of a series of bent metallocenes, but is consistent with the results in previously characterized rhenocene derivatives (Table IV). The position of the ethyl group at the back of the wedge, while unexpected, was also not a priori predictible. What

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is very surprising is the extraordinarily large dihedral angle between the ring planes, Φ, of 161.6° observed in $(\eta^5\text{-}C_5Me_4Et)(\eta^5\text{-}C_5H_5)ReH$ (**2′**). While such large values of Φ have been observed in other rhenocene species (Table IV), they would not be predicted for a neutral bent metallocene.

It is tempting to invoke a steric interaction to explain this result. However, a plot of the metallocene unit as seen from the side shows no significant distortion of the alkyl groups at the back of the wedge, as would be expected if a strong steric interaction were occurring. In addition, a van der Waals plot of the back of the metallocene wedge shows no significant interaction between the ring units. The absence of any significant slippage, i.e., distance between the ring normal and the ring centroid, or tilt of the rings, i.e., an observed difference between the metal–ring centroid vector and the metal–ring normal vector,[33] also implies the lack of a strong steric effect.

As there appears to be no steric reason for the observed rhenocene hydride structure, it is then necessary to invoke an electronic factor. A general theoretical treatment of the structure and chemistry of bent metallocene complexes has been published by Lauher and Hoffmann.[34] In the molecular orbital analysis carried out for Cp_2ReH, at $\Phi = 135°$, the H^- ligand interacts predominantly with the empty $2a_1$ orbital on the bent metallocene fragment. In this model, as the metallocene dihedral angle, Φ, is increased, the metal fragment orbital drops in energy, yielding a smaller energy difference and correspondingly better bonding. This orbital, however, also rehybridizes and does not extend out as far with increasing Φ; therefore, overlap between the orbitals decreases. The effects compete. In the case of the rhenocene hydrides, the small, spherical H^- ligand is apparently still able to achieve good overlap with the metal center.

This model assumes a symmetric structure with the Re–H bond centered in the metallocene wedge. An unsymmetrical structure, with the hydride ligand out of the central position in the wedge plane, is predicted to be highly unfavorable for a d^4 molecule, as the b_2 orbital increases very quickly in energy upon assuming such a geometry. While it is clear that the position of metal hydride ligands cannot be accurately determined by X-ray analysis,[35] an apparently anomalous position for the hydride ligand is obtained for $(\eta^5\text{-}C_5Me_4Et)(\eta^5\text{-}C_5H_5)ReH$ (**2′**). A more exact determination of the position of this ligand has been thwarted by the empirical absorption correction used and the close vicinity of the rhenium atom. We believe, however, that a neutron structure is warranted and are presently attempting to obtain sufficiently large crystals.

In light of the observed structural parameters, electronic and not steric factors appear to predominate in the structure of Cp*CpReH. In the absence of a rigorous calculation and structures of the normal ring and permethyl complexes, the discussion above remains only a qualitative rationalization of the observed structure. However, an increased bending angle, for example, in Cp_2ReH would still be consistent with the photoelectron spectra observed, i.e., two bands at 6.3 and 6.9 eV for the highest occupied metal-centered orbitals.[36]

We point out that a related system, the isoelectronic complex $(\eta^5\text{-}C_5Me_5)ReCl(\eta^5\text{-}(E,E)\text{-}3,4\text{-diphenylhexa-}2,4\text{-diene-}6\text{-yl})$ (**3**), has recently been structurally characterized in our research group and possesses a significantly distorted structure in which the five carbon atoms of the 2,4-pentadienyl skeleton do not define a plane. This ligand can best be described as an allyl/alkene system.[37] The distorted structure of the halide species **3** suggests a rationalization for the observed instability of the rhenocene halide complexes (see below).

We are beginning to explore the chemistry of these mixed-ring rhenocene hydride complexes and have already observed significant reactivity differences from those observed for Cp_2ReH. For example, the pentamethylcyclopentadienyl group, as would be expected, increases the basicity of the metal center. Consequently, initial attempts at deprotonation of the metal center by *n*-BuLi and *t*-BuLi under conditions that yield Cp_2ReLi·(base) have not been successful.[38] We are presently attempting to prepare halide derivatives such as Cp*CpReCl.[39] However, we have found these to be unstable during workup, i.e., clean conversion can be observed by ^1H NMR spectroscopy; however, decomposition occurs upon solvent removal. We are also attempting to isolate some of the proposed intermediate borohydride complexes, either from the reaction mixture itself or by independent synthesis.

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Supplementary Material Available: Listings of bond lengths, bond angles, positional parameters, selected least-squares planes (and distances of atoms from those planes), thermal parameters, and all crystal data and refinement parameters, stereodrawings of the molecule and unit cell, and Schakal plots of **2′** as seen from the side and top and with van der Waals radii (17 pages); a listing of observed and calculated structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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Ground-State Geometries and Inversion Barriers for Simple Complexes of Early Transition Metals

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The electronic and molecular structures of transition-metal hydrides and halides have long been of interest to inorganic and theoretical chemists.[1] A recent report by Zerner and co-workers[2] on the equilibrium geometry of TiH_6^{2-} is a prime example. Crystal and ligand field theories predict the complex to be octahedral. Extended Hückel calculations, however, predict a bicapped tetrahedron of C_{2v} symmetry.[3] Further investigation[2] using more accurate ab initio calculations with large basis sets revealed the ground-state geometry to be octahedral. The addition of electron correlation, however, has been shown to reverse this result; in fact, calculations at the MP2 and MP4 levels of theory predict TiH_6^{2-} to be trigonal prismatic in the ground state.[4]

Many other theoretical studies on simple transition-metal complexes have been performed by various researchers. Schaefer

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