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Hydrogen Scrambling in $[(C_5R_5)(L)M(H)(C_2H_4)]^+$ (M = Co, Rh). Relation of Experimental Kinetic Data to the Barriers of the Elementary Reaction Steps

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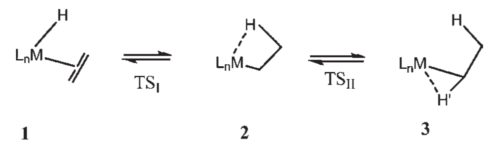
The energetics of hydrogen scrambling in the ethylene hydride complexes of two late transition metals $[(C_5R_5)(L)M(H)(C_2H_4)]^+$ (R = H, Me; L = $P(OMe)_3$, PMe_3; M = Co, Rh) were studied using density functional theory. Four potential nuclear (C/H) scrambling processes in these complexes are discussed; the computed energy barriers for three of them compare very well with activation energies from previous NMR studies, while the fourth process appears to be inactive for energetic reasons. The observed trends for the different metals M, ligands L, and substituents R are reproduced; the activation barriers are insensitive toward L, but somewhat higher for R = H than R = Me. The connection of these elementary processes (or lack thereof) to the β-migratory insertion reaction in these complexes is discussed; the reported data from NMR experiments are not directly related to the elementary steps of the insertion/elimination reaction. Furthermore, for rhodium complexes with L = C_2H_4, the observed shift of the global energy minimum is correctly reproduced by our calculations.

Introduction

Catalytic ethylene homo- and copolymerization has been largely dominated by early transition metal (TM) catalysts (mainly based on titanium, zirconium and chromium).[1] However, these catalysts are generally very oxophilic and do not tolerate many functionalized olefins. This drawback has spurred considerable interest in polymerization catalysts derived from late TMs with presumed greater functional group tolerance. However, in addition to reduced polymerization activities, late metal catalysts generally show a strong tendency to form oligomers because of β-hydrogen elimination being competitive with chain growth. In recent years, these disadvantages have been overcome by a new generation of late TM polymerization catalysts, which are capable of producing a wide range of products ranging from oligomers to high polymer and strictly linear to highly branched, giving access to polymers with novel and highly interesting properties.[2] It is obvious that in these catalysts control of chain termination and chain transfer reactions is of paramount importance.

Scheme 1



The isomerization of TM ethylene hydrides **1** to β/α-agostic ethyl compounds **2** and **3** via transition states TS_I and TS_{II} has been the subject of extensive experimental and theoretical work[3] (Scheme 1). In many catalytic processes, the ethylene insertion step associated with the TS_I barrier is frequently assumed to play an important if not rate-determining role.[3] While β-hydrogen elimination can be followed directly starting from a coordinatively unsatured ethyl complex (which itself may be generated as a transient species from a suitable precursor),[4] the insertion reaction is more difficult to address. In several experimental studies attempts were made to deduce the height of the insertion barrier from kinetic data resulting from the scrambling of the metal hydride atom in **1** with the olefinic hydrogens, which is often accessible by NMR methods and has been studied for

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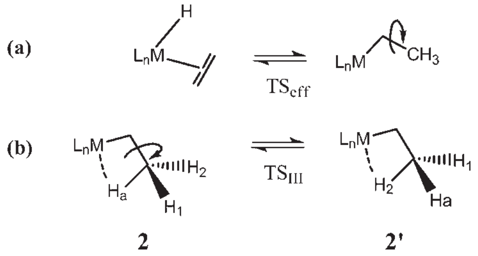
(4) The best-studied system appears to be $[(C_5R_5)(CO)_2M(C_2H_5)]$ (M = Mo, W; R = H, Me): (a) Johnson, F. P. A.; Gordon, C. M.; Hodges, P. M.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1991**, 833–839. (b) Yang, G. K.; Peters, K. S.; Vaida, V. *J. Am. Chem. Soc.* **1986**, *108*, 2511–2513. (c) Kazlauskas, R. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 6005–6015.

Scheme 2



complexes of Co,[5,6] Rh,[6,7] Pd,[8−12] and Ni.[13] Classically, this so-called "three-hydrogen (3H) scrambling" process is viewed as a migratory insertion via a transition state TS$_{eff}$ to form an unsaturated species, followed by rotation around the C−C bond and β-elimination of a different hydrogen atom to the metal (Scheme 2a). Over the years evidence has emerged, however, that at least in some cases the experimentally obtained activation parameters corresponding to TS$_{eff}$ result in fact from the "in-place rotation"[14] of an agostic ethyl group only, with its own barrier TS$_{III}$, and that the originally postulated 16e intermediates are probably never formed (Scheme 2b).[15]

In the complexes where insertion was studied experimentally, several atom scrambling processes occur concurrently and/or sequentially. This obviously greatly complicates the quantitative interpretation of the experimental data. We thus decided to embark on a theoretical study of these exchange processes in eight model complexes $[(C_5R_5)(L)M(H)(C_2H_4)]^+$ (R = H, Me; L = P(OMe)$_3$, PMe$_3$; M = Co, Rh); these complexes have been well studied experimentally, and kinetic data relevant to a number of scrambling processes are available in the literature.[5−7,16] Moreover, the cobalt species are well-defined ethylene polymerization catalysts.[17] Several computational studies on $[(C_5R_5)(L)M(H)(C_2H_4)]^+$ with M = Ir,[3a,18] Co,[3a,19] and Rh[3a,19] have appeared. As a first step toward a more detailed understanding of the reaction on a quantal level, a multidimensional quantum dynamical study of the migratory insertion/β-elimination process in the model complex $[(C_5H_5)(PH_3)Rh(H)(C_2H_4)]^+$ was recently reported by some of us.[20] The aim of the present paper is to demonstrate how effectively theory can guide and inform the experimentalist in the interpretation of kinetic data, for example, from dynamic NMR measurements. We shall also discuss the difficulties that arise from a seemingly so simple a reaction as migratory insertion turning out to actually be part of a sequence of mutually coupled steps with comparable changes in energy. While theoretical studies of hydrogen scrambling in organic compounds have appeared in the literature,[21] this is to our knowledge the first computational study including both hydrogen and carbon scrambling in TM complexes.

Computational Details

All calculations were carried out using the Gaussian 03 software package.[22] Geometry and energy optimizations were performed at the BP86/6-31G**/SDD(Co,Rh) level of theory for all calculated species. In this basis, active hydrogens (i.e., terminal hydrogen atoms at the β-carbon in the ethylene moiety, as well as the migrating hydrogen atom) are treated with the 6-31G** basis set, and the spectator hydrogen atoms are treated with 6-31G*. This combination of basis set and level of theory has been used successfully in our earlier work.[23] All stationary points involved were fully optimized. Frequency calculations were undertaken to confirm the nature of the stationary points, yielding one imaginary frequency for transition states (TS) and zero for minima. Transition states were obtained by either a combined scanning and transit-guided quasi-Newton (STQN) method or a combination of the two STQN approaches LST [24] and QST3,[25] as implemented in Gaussian 03. Zero point energy (ZPE) corrections were carried out for all computed energies. Free energies were calculated for selected isomers using the harmonic approximation and standard textbook procedures. A natural population analysis (NPA) [26] and resulting Wiberg

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Table 1. Relative Free Energies $\Delta G_{298.15}$ and Selected ZPE-Corrected Electronic Energies ΔE (in Parentheses) of Stationary Points for $[(C_5R_5)(L)M(H)(C_2H_4)]^+$ (R = H, Me; L = $P(OMe)_3$, PMe_3; M = Co, Rh)[a]

M	L	R	**1**	TS_I	**2**	TS_{II}	**3**
Co	PMe_3	H	0	0.9(0.5)[c]	−0.9(−1.0)[c]	14.0(13.4)[c]	10.9(11.5)[c]
		Me	0	0.8(1.0)	−0.8(−0.6)	8.9(10.0)	8.0(9.5)
	$P(OMe)_3$	H	0	0.8(0.3)[c]	−0.6(−1.3)[c]	17.5(18.9)[c]	10.1(10.7)[c]
		Me	0	1.8(1.0)	−1.1(−0.8)	11.9(12.8)	8.5(9.5)
Rh	PMe_3	H	0	5.3(5.0)[c]	5.4(5.1)[b,c]	18.6(18.4)[c]	16.5(17.3)[c]
		Me	0	5.6(5.8)	5.4(5.5)	10.9(12.2)	10.9(12.0)
	$P(OMe)_3$	H	0	3.7(3.8)[c]	3.7(3.4)[c]	21.4(22.4)[c]	15.5(16.3)[c]
		Me	0	5.5(4.9)	3.9(4.0)	13.7(13.9)	10.7(12.9)

[a] **1**, **2**, **3** correspond to the ethylene hydride and β/α-agostic isomers, respectively. TS_I and TS_{II} represent the interconnecting transition states. **1** were chosen as the isomers of zero energy. [b] After ZPE correction the structure ceases to be a potential energy minimum. [c] ΔE values taken from ref 23.

bond indices (WBIs) [27] were used for a detailed study of the electronic structure and bonding in some cases. Instead of the distances, WBIs describe the bond strengths, allowing the limitation of looking only at bond lengths to be overcome.

Results and Discussion

Our search for stationary points of the $[(C_5R_5)(L)M(H)(C_2H_4)]^+$ systems yielded ethylene hydride and β-agostic conformers **1** and **2** similar to those that had been found for the simple L = PH_3 system,[3a,23] as well as ethyl minima **3**. We compared these minima with those reported in our previous work[23] and found that, in general, the distances between the metal center and one of the α-hydrogen atoms in **3** are rather small; for example, in the Cp-$P(OMe)_3$-complexes of Co and Rh they are calculated as 1.76 Å and 2.03 Å, respectively. This is within the typical range reported for agostic interactions;[14] in contrast to our earlier work, we therefore now prefer the term "α-agostic" over "ethyl" for these structures (Scheme 1).

The relative free energies $\Delta G_{298.15}$ are given in Table 1 in relation to **1**. In accordance with experimental observations[5,7] and previous computational work[19] we identify for Co complexes the β-agostic structure **2** as the global energy minimum, while for the rhodium complexes the ethylene hydride structure **1** is invariably more stable. However, our results deviate from the findings of Ziegler et al., who established the β-agostic isomer **2** as the global minimum for the rhodium complex with L = PH_3 and R = H.[3a] To clarify the issue we proceeded to calculate the energies of **1** and **2** for this complex using different density functional theory (DFT) methods, as well as MP2-MP4, CCSD, and CCSD(T), and obtained the ethylene hydride structure **1** as the global minimum in every case except for the MP3 calculation; the results are presented in Table 3 of ref 19. We discard the MP3 energies because of the well-known unbalanced weight of the terms in the perturbation expansion[28] and believe our result to be accurate in the light of these additional calculations as well as the available experimental data.[29] The structures corresponding to the global minima for the Rh and Co complexes are given in Figure 1.

Frequently, agostic interactions like that in **2** have been interpreted as arising from a donation of two electrons of the C−H bond into an empty TM d-orbital.[30] Since the 4d orbitals of Rh are destabilized compared to cobalt's 3d shell, the interaction energy decreases; the more suitable acceptor orbital of Co results in a stronger agostic bond.[3a] Table 1 also lists the relative ZPE-corrected electronic energies ΔE; their values for R = H have been reported earlier and are included here for comparison.[23]

Looking at the ΔE values for the $CpRhPMe_3$ system, it is noted that **2** is not a minimum of the ZPE-corrected energy surface. We found the ZPE-*uncorrected* energy for **2** to be lower by only 1.3 kcal/mol than that for the TS_I structure, which is due to the shallowness of the energy surface in this region. Since the ZPE for **2** is obtained as 161.9 kcal/mol, whereas the corresponding TS_I value is only 160.5 kcal/mol, the β-agostic minimum is lost after ZPE-correction. It is not surprising that the transition state's ZPE should be lower by 1.4 kcal/mol, which is likely a consequence of the loss of the vibrational degree of freedom associated with the reaction coordinate.

Furthermore, it is seen that ΔG and ΔE differ by less than 3 kcal/mol in all cases, that is, $\Delta S \approx 0$ for the isomerization as expected, since the number of free particles remains constant. This also holds for the other isomerizations considered here, and we will therefore compare ΔG and ΔE directly in the remainder of this work.

In the following we define the insertion process proper as the **1**→**2** conversion; this choice will be justified and discussed in more detail in the Conclusion of the present paper. The insertion barriers TS_I are very low for the Co complexes and amount to typically 5−6 kcal/mol for the Rh complexes. The reverse reaction we accordingly term β-elimination, and its barrier heights are lower, and sometimes even non-existent, for the complexes with M = Rh. For example, after applying ZPE and thermal corrections the isomer **2** of the complex $[CpRh\,(P(OMe)_3)(C_2H_5)]^+$ no longer represents a local free energy minimum on these profiles; this is a consequence of the very shallow potential in the vicinity of **2** because of the comparatively weak β-agostic interaction. This is a theoretical justification of Brookhart's early suggestion that systems with a β-agostic ground state generally are better polymerization catalysts, that is, less prone to chain termination [16]. In their experimental study of the migratory insertion reaction in $Cp^*CoP(OMe)_3$ Brookhart et al. estimated the free energy difference between **1** and **2** as 3−5 kcal/mol,[6] while our calculations suggest a value of 1.1 kcal/mol. In the light of the fact that **1** cannot be directly observed in this system and the necessarily crude assumptions made to estimate its relative energy, we believe that the above estimates bracket the true value.

The transition states TS_I connecting **1** and **2** are also β-agostic, with structural parameters roughly intermediate between **1** and **2** (see Table 2). The α-agostic structures **3** with a three-membered MHC ring are characterized by increased ring strain compared to the β-agostic structures **2** (four-membered MHCC rings); their energies are substantially higher than for the other minima. For one of the studied complexes the formation of **3** can be inferred from NMR data (see discussion of the inversion process below). **3** is connected

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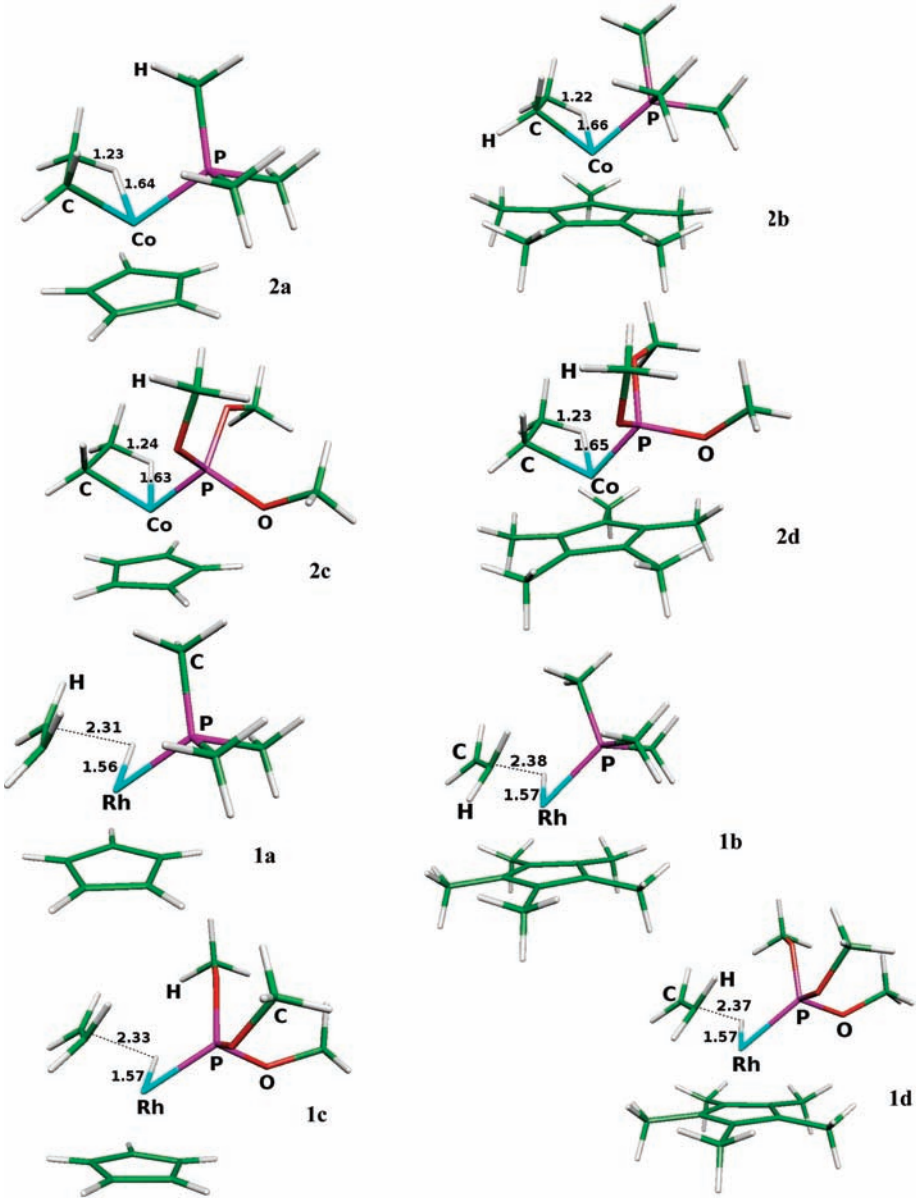


Figure 1. Global minimum energy structures for the complexes $[(C_5R_5)(L)M(H)(C_2H_4)]^+$ with M = Rh (**1**) and Co (**2**), and R = H; L = PMe_3 (**a**), R = Me; L = PMe_3 (**b**), R = H; L = $P(OMe)_3$, (**c**), R = Me; L = $P(OMe)_3$, (**d**) . The key interatomic distances $d(M-H_\beta)$ and $d(C_\beta-H_\beta)$ are indicated in angstrom.

to **2** via TS_{II}; this barrier is substantially lowered (by typically 6−7 kcal/mol) if the Cp ligand is replaced by Cp*. This is probably due to the larger *trans* effect that can be expected for this stronger donor ligand (see discussion of the in-place rotation below). The stabilization also extends to the α-agostic structures themselves.

As already mentioned, the short $C-H_\alpha$ distances in **3** as given in Table 2 are indicative of an α-agostic interaction in these structures. The distances $M-H_\beta$ for structures **2** are elongated by 0.02 Å (Co) or 0.05 Å (Rh) by the presence of a Cp* ligand, while the associated distances $C_\beta-H_\beta$ are slightly shortened (0.01 or 0.03 Å). This is another example for the trans-influence observable in these complexes. Commonly, the agostic interaction is pictured as a population transfer from the C−H bonding orbital to a metal d-orbital; strong agostic interactions are therefore characterized by a short M−H bond and an elongated C−H bond. Cp* is a better donor ligand than Cp; substituting it for the latter is expected to result in enhanced interaction of the (pentamethyl-)cyclopentadienyl fragment orbitals with metal d-orbitals, and therefore their increased contribution to the bonding molecular orbitals (MOs), while the orbitals of the agostically bound C−H fragment should contribute correspondingly less, weakening the agostic interaction and shortening the C−H distance.

Conversely, the influence of the *cis*-standing phosphine ligand L is much less pronounced; indeed, for structures **1**, **2**, and TS_I the influence of L on the geometric parameters under investigation is very slight and does not exceed 0.01 Å. Likewise, the $M-H_\alpha$ distances in **3** also increase upon substitution of Cp by Cp*. It is seen that for Structures **3** all $M-H_\alpha$ distances conform to the agostic definition given in ref 14, except in the case of the Cp^*RhPMe_3 complex. Upon examining its structure we noted two close contacts of hydrogen atoms of the ethyl moiety: first, a contact between a β-hydrogen and a PMe_3-hydrogen (2.34 Å), and second a

Table 2. Selected Geometry Parameters for Stationary Points of $[(C_5R_5)(L)M(H)(C_2H_4)]^+$ (R = H, Me; L = $P(OMe)_3$, PMe_3; M = Co, Rh)[a]

parameter	M	L	R	**1**	TS_I	**2**	TS_{II}	**3**
$d(M-H_\alpha)$[Å]	Co	PMe_3	H	2.72	2.70	2.67	1.80	1.78
			Me	2.73	2.71	2.69	2.25	2.00
		$P(OMe)_3$	H	2.70	2.66	2.69	2.45	1.76
			Me	2.72	2.69	2.67	2.44	1.83
	Rh	PMe_3	H	2.83	2.80	2.79	2.24	2.21
			Me	2.84	2.82	2.80	2.64	2.59
		$P(OMe)_3$	H	2.82	2.77	2.76	2.54	2.03
			Me	2.83	2.78	2.76	2.52	2.25
$d(M-H_\beta)$[Å]	Co	PMe_3	H	1.46	1.48	1.64	3.36	3.38
			Me	1.46	1.48	1.66	3.44	3.44
		$P(OMe)_3$	H	1.46	1.47	1.63	3.23	3.35
			Me	1.46	1.48	1.65	3.27	3.36
	Rh	PMe_3	H	1.56	1.63	1.77	3.47	3.50
			Me	1.57	1.63	1.82	3.35	3.43
		$P(OMe)_3$	H	1.57	1.62	1.76	3.35	3.45
			Me	1.57	1.62	1.81	3.47	3.48
$d(C_\beta-H_\beta)$[Å]	Co	PMe_3	H	2.11	1.66	1.23	1.10	1.10
			Me	2.16	1.64	1.22	1.10	1.10
		$P(OMe)_3$	H	2.08	1.71	1.24	1.10	1.10
			Me	2.11	1.69	1.23	1.10	1.10
	Rh	PMe_3	H	2.31	1.51	1.24	1.10	1.10
			Me	2.38	1.53	1.21	1.10	1.10
		$P(OMe)_3$	H	2.33	1.55	1.25	1.10	1.11
			Me	2.37	1.56	1.22	1.10	1.10
$\angle(M-C_\alpha-C_\beta)$[deg]	Co	PMe_3	H	69.8	70.7	74.6	126.4	137.0
			Me	69.8	70.7	75.2	129.2	135.3
		$P(OMe)_3$	H	70.0	70.8	74.3	120.8	135.6
			Me	69.9	71.0	75.1	118.7	135.8
	Rh	PMe_3	H	70.9	73.5	77.2	126.6	132.7
			Me	70.8	73.4	78.5	115.6	120.1
		$P(OMe)_3$	H	70.9	73.6	76.7	122.0	133.4
			Me	70.8	73.6	78.1	128.7	130.9

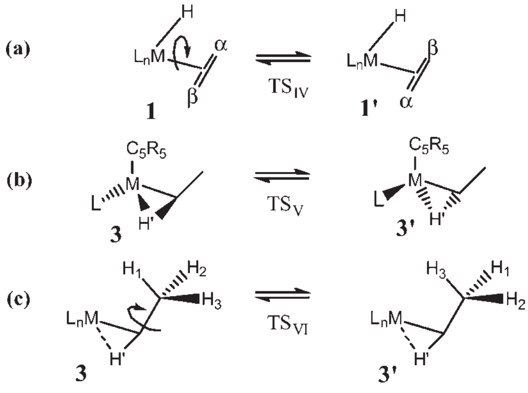
[a] **1**, **2**, **3** correspond to the ethylene hydride and β/α-agostic isomers, respectively. TS_I and TS_{II} represent the interconnecting transition states.

contact between an α-hydrogen and a Cp*-hydrogen (2.50 Å). The steric hindrance hereby imposed on the ethyl ligand is likely to prevent the α-agostic interaction from being formed. This structure is therefore best termed a "forced" 16e ethyl complex. The angle $\angle(MC_\alpha C_\beta)$ increases monotonically in the course of the isomerization; this applies particularly to the second reaction step **2** → **3**. It is therefore a suitable parameter to describe the progress of the reaction.[19] No clear influence of either L or R on this parameter is discernible. Finally, we note that the distance $M-H_\beta$ between the metal center and the agostic hydrogen is larger for M = Rh, which is a consequence of the larger atomic radius.

As already mentioned in the Introduction, experimental studies of the migratory insertion of the ethylene ligand into the M−H bond in the title complexes met with some fundamental difficulties. The species studied in detail all exhibit a number of dynamic processes which are accessible to NMR methods. As has been pointed out by Brookhart et al.,[5,7] exchange processes observable in the NMR spectra may or may not be directly related to the elementary reaction steps, depending on the particular situation and the relative magnitudes of the rates of these processes. In the system ranging from **1** to **3** the following dynamic processes are considered in this work:

– Process I: the migratory insertion proper [In the literature, the term "migratory insertion" is most often used in a generic sense, spanning the range **1** to **3**. We propose a somewhat more restricted and concise usage, namely, for the reaction step **1** to **2** only (see discussion in conclusions)], which converts **1** to **2** via TS_I (see Scheme 1).
– Process II: the conversion of the β-agostic **2** to the α-agostic isomer **3** via TS_{II}.
– Process III: "in place" rotation[31] of the methyl group in **2** via TS_{III} (see Scheme 2b).
– Process IV: ethylene rotation in **1** via TS_{IV}. This interchanges the CH_2 termini of this ligand (Scheme 3a).
– Process V: inversion of the chiral pseudo-tetrahedral isomer **3** via TS_V (Scheme 3b).
– Process VI: rotation of the methyl group in **3** via TS_{VI} (Scheme 3c).

Scheme 3



Processes I and II have been discussed above (Scheme 1/Table 1). Process III causes the well-known 3H-scrambling visible in the NMR and sometimes mistakenly identified with the migratory insertion process (see Scheme 2). The remaining Processes IV−VI are additional H respectively C scrambling reactions that may be experimentally accessible, depending on the respective ground state and the relative magnitudes of the barriers; Scheme 3 provides an overview of them.

While most of these processes cannot be observed independently, they are accessible by theoretical calculations. Table 3 gives a compilation of our calculated barriers for Processes III to VI, along with some literature data from experimental NMR kinetic measurements under various assumptions (discussed in more detail below).

Experimental kinetic data were derived for three scrambling processes. We shall first focus on the three-hydrogen scrambling (Process III), which causes the exchange of the hydride and the olefinic methylene protons. As discussed above, we assume $\Delta S \approx 0$, facilitating a comparison of the experimental $\Delta G^\ddagger$ values with our calculated energies. In the most general case the experimental data arise from a combination of Processes I to V above. Hydrogen scambling occurs when the initially formed ethyl group rotates; we shall therefore first compare our TS_{III} energies to the experimental $\Delta G^\ddagger$ values for 3H-scrambling in Table 3. We find that these calculated barriers are consistently lowered (by up to 3.1 kcal/mol) when Cp is replaced by Cp*. The cis-standing phosphine ligand L, on the other hand, appears to have a smaller effect (below 2 kcal/mol in all cases). Experimental activation parameters were indeed found to depend on the substitution

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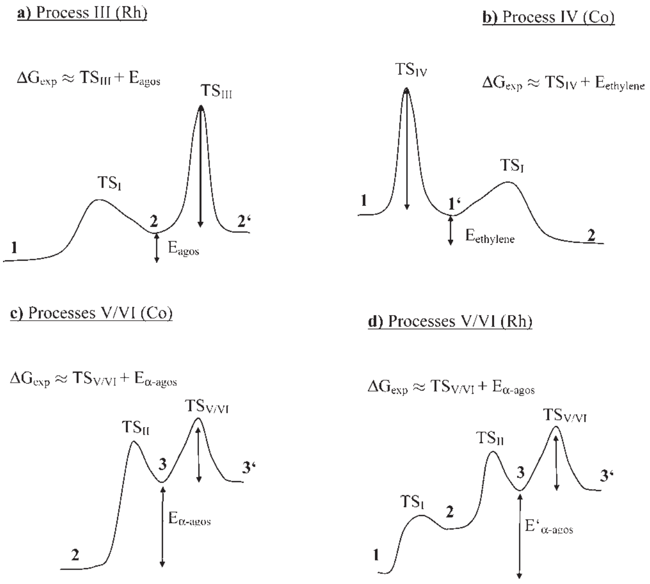
(31) Green, M. L. H.; Wong, L. L. *J. Chem. Soc., Chem. Commun.* **1988**, 677–679.

Table 3. Calculated Energy Barriers TS_x and Experimental Free Energies of Activation $\Delta G^‡$ [kcal·mol^{-1}] for Processes III–VI in $[(C_5R_5)(L)M(H)(C_2H_4)]^+$ (R = H, Me; L = $P(OMe)_3$, PMe_3; M = Co, Rh)[a]

			Process III		Process IV		Process V		Process VI
M	L	R	TS_{III}	$\Delta G^‡$(expt.)	TS_{IV}	$\Delta G^‡$ (expt.)	TS_V	$\Delta G^‡$ (expt.)	TS_{VI}
Co	PMe_3	H	11.1	12.5	12.3(13.4)	13.4	7.0(19.5)		2.7(15.3)
		Me	9.0	10.9	15.8(16.4)	< 15.6	2.6(12.7)	13.4	2.5(12.6)
	$P(OMe)_3$	H	11.3	12.5	10.5(11.8)	12.7	8.2(20.3)		1.9(14.0)
		Me	10.0	11.1	13.0(13.8)	13.4	3.2(13.3)		2.2(12.5)
Rh	PMe_3	H	9.5(14.6)	15.0	9.9	8.8	3.6(20.8)		2.1(19.4)
		Me	6.0(11.5)	12.1	12.2	11.3	2.9(14.9)		2.1(18.4)
	$P(OMe)_3$	H	10.7(13.8)	15.0	8.4	7.8	3.2(19.5)		2.4(14.4)
		Me	6.7(10.7)	12.2	10.0	10.2	1.9(14.8)		2.4(15.3)

[a] Experimental data from ref 5 for Co and ref 7 for Rh. The TS energies are given in relation to the minima connected by them; barrier heights with respect to the global minimum (**1** for Rh and **2** for Co) were added in parentheses for cases where these differ from the global minimum (for details see Scheme 4).

Scheme 4



of the cyclopentadienyl ligand, but were essentially independent of the nature of the phosphine ligand.[7] These findings can be attributed to the trans effect of the C_5R_5 ligand, which is in a trans position with respect to the rotating methyl group. This effect is expected to be stronger for the more electron-donating Cp* ligand. The "pure" TS_{III} barriers are lower for M = Rh (by 1–3 kcal/mol compared to Co), which is a consequence of the larger $d(M-H_\beta)$ distances (Table 2) and therefore weaker agostic interaction, which facilitates the methyl rotation process (Scheme 2b). The experimental results appear to contradict this. However, it must be kept in mind that $\Delta G^‡_{expt}$ is measured in reference to the global minimum, which for M = Rh differs from the interconnected agostic structures **2** and **2′**; the experimental activation energies for Process III are therefore higher for the rhodium complexes. Once the relative energies of the agostic structures E_{agos} are added to the computed TS_{III} values, the correct energy ordering is obtained. The issue is illustrated in Scheme 4a. Our energy barriers are in excellent agreement and correctly reproduce the trends seen in experiment, while the insertion barriers associated with TS_I and previously associated with 3H-scrambling (given in Table 1) are much lower (0.8–1.8 kcal/mol for Co complexes and 3.7–5.6 kcal/mol for Rh complexes). The insertion (Process I) is therefore much faster and not experimentally accessible with equilibrium NMR methods.

Comparing the energy barriers TS_{IV} (i.e., olefin rotation) for the substituted versus unsubstituted cyclopentadiene, the opposite result as for TS_{III} is obtained. For Process IV the barriers are consistently higher (by 1.6–3.5 kcal/mol) in the case of R = Me, which is attributed to the repulsive interaction of the methyl groups with the rotating ethylene in the transition state. For example, the distances of two ethylene hydrogens from the closest Cp* hydrogens in the $Cp^*CoP(OMe)_3$ complex are merely 2.31 Å, as opposed to 2.34/2.61 Å for the unsubstituted Cp ligand. Comparing the rhodium and cobalt complexes we obtain an increase of the above-mentioned distances for $Cp^*MP(OMe)_3$ to 2.38/2.39 Å for M = Rh, which is reflected in a decrease in barrier height by 2–3 kcal/mol when measured from the interconnected ethylene minima **1** and **1′**; these trends are corroborated by the experimental data.[7] In contrast to Process III, it is now the Co complexes for which these minima do not correspond to the global minimum; to obtain energy values comparable with $\Delta G^‡_{expt}$, the energy difference $E_{ethylene}$ must for them now be added to the TS_{IV} energy (Scheme 4b).

Likewise, the barriers are higher for L = PMe_3 than L = $P(OMe)_3$, which is also due to steric factors. For example, the distances of the two ethylene hydrogens facing the ligand L in the transition state from the closest hydrogen atoms in these ligands are 2.26 and 2.67 Å in the case of Cp^*CoPMe_3, which increases to 2.98 and 3.43 Å for $Cp^*CoP(OMe)_3$. Evidently, the oxygen bridges present in the methoxy ligand afford greater steric flexibility.

A thorough assessment of the inversion barriers TS_V (i.e., inversion of the chiral metal center) is hampered by the near complete absence of experimental data; from the averaging of the diastereotopic α-hydrogen atoms in the $Cp^*(PMe_3)Co$ system this barrier has been determined to be 13.4 kcal/mol,[5] which matches the value determined from the interconversion of the diastereotopic methyl groups of a $P(Me)_2Ph$ ligand.[32] Our computed TS energies indicate lower inversion barriers for Cp* than Cp, in particular for the cobalt complexes (4–5 kcal/mol), probably because of the aforementioned *trans* effect of the cyclopentadienyl ligand. Furthermore, the barriers for CpRh are significantly lower than for CpCo (3.4 and 5.0 kcal/mol); this no longer applies once the

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(32) Cracknell, R. B.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1005–1006.

Table 4. Relative ZPE-Corrected Electronic Energies of Stationary Points for $[(C_5R_5)Rh(H)(C_2H_4)_2]^+$ (R = H, Me)[a]

R	**1**	TS_I	**2**	TS_{II}	**3**
H	0	0.6	−1.2	16.8	10.7
Me	0	1.0	−1.8	10.1	7.3

[a] **1**, **2**, **3** correspond to the ethylene hydride and β/α-agostic isomers, respectively. TS_I and TS_{II} represent the interconnecting transition states. **1** were chosen as the isomers of zero energy.

Table 5. Selected Wiberg Bond Indices (WBIs) for the Ethylene Hydride **1** and β-Agostic Structures **2** of $[(C_5H_5)Rh(H)(C_2H_4)L]^+$ ($L = PH_3$, C_2H_4)[a]

	1, $L = PH_3$	**1**, $L = C_2H_4$	
$Rh-C_\alpha$	0.37	0.37	0.35
$Rh-C_\beta$	0.37	0.34	0.35
$Rh-P$	0.54		
$C_\alpha-C_\beta$	1.42	1.43	1.44
$Rh-H_{ag}$	0.53	0.49	
	2, $L = PH_3$	**2**, $L = C_2H_4$	
$Rh-C_\alpha$	0.56	0.54	0.37
$Rh-C_\beta$	0.17	0.16	0.38
$Rh-P$	0.53		
$C_\alpha-C_\beta$	1.13	1.14	1.43
$Rh-H_{ag}$	0.15	0.14	

[a] C_α and C_β are the α and β carbons of the ethylene **1**,**2** or β-agostic ethyl **2** moieties, and H_{ag} is the hydride **1** or β-agostic hydrogen **2**.

corresponding Cp*-complexes are compared. No clear trends for the influence of the phosphine ligands on the inversion are discernible. TS_V connects the α-agostic minima **3** and **3′**, which differ from the global minima of both Rh- and Co-complexes (Scheme 4c/d). Therefore, the TS energy must be corrected by $E_{\alpha\text{-agos}}$ (Co) or $E'_{\alpha\text{-agos}}$ (Rh) to arrive at the values in parentheses in Table 3 that may be compared to experiment.

We also looked into the possibility of three-hydrogen scrambling occurring via a rotation of the uncoordinated methyl group in **3** via Process VI. The calculated TS_{VI} barriers are low (1.9 to 2.7 kcal/mol) in relation to the interconnected α-agostic minima **3** and **3′**, but the total energies consist of the same contributions as for TS_V (Scheme 4c/d) and are significantly higher. In every case they surpass the energy required for "in place" rotation (by 0.6 to 6.9 kcal/mol). We conclude that "in place" rotation is energetically favored with respect to the alternative loss of the agostic interaction to give **3** (Process II) and rotation of the non-coordinating methyl group. Substantial experimental evidence also suggests that "in place" rotation is generally a lower energy pathway than decoordination of an agostic ethyl group, followed by methyl rotation in the η^1-ethyl complex.[15]

Experimental work has shown that, for $L = C_2H_4$ (i.e., the *bis* ethylene complex), the β-agostic isomer **2** becomes more stable than **1** even for M = Rh [6]. We therefore carried out a series of additional calculations for this system to establish whether this situation is accurately modeled by our approach; the resulting ZPE-corrected energies are presented in Table 4. The data show that the shift of the global minimum is indeed correctly reproduced by our calculations, despite the fact that ΔE is calculated to be less than 2 kcal/mol. Our findings are in accordance with the experimental observation that the barrier for an isomerization of **2** via **1** is < 3.7 kcal/mol.[6] As seen before, the Cp* ligand exerts a stabilizing influence on the α/β-agostic isomers and the interconnecting TS_{II}.

To shed light on this ligand-induced shift of the global minimum we calculated the Wiberg bond indices (WBIs) for **1** and **2** with $L = PH_3$ and $L = C_2H_4$ (Table 5). In the ethylene hydride complex **1** with the PH_3 ligand one notices higher WBIs for the bonds of Rh to its neighboring atoms, signifying better orbital overlap and thus stronger bonds than for a complex with two η^2-coordinated ethylene ligands, in addition to the η^5-coordinated Cp* moiety. Clearly, the bonding of three π-ligands to the same metal center implies additional steric repulsion, requiring a simultaneous overlap of their π-orbitals with empty metal d-orbitals *and* of their π*-orbitals with filled metal d-orbitals according to the Chatt−Dewar−Duncanson picture. Looking at the β-agostic ethyl isomer **2** we note that the bonds of Rh to the atoms C_α, C_β, and H_{ag} are also stronger for the phosphine complex; however, it is seen that the Rh−P bond is slightly weakened in the insertion reaction **1** → **2**, while for the *bis*-ethylene complex a strengthening of the bonds to the "spectator ethylene" is observed in this step. This is consistent with the notion that a reduction of the number of π-ligands from three to two in this reaction step facilitates a better overlap of their π-systems with the d-orbitals at the metal center. This isomer therefore becomes the global energy minimum.

Conclusions

Our calculations support the earlier conclusion, derived from experimental findings, that unsaturated 16e ethyl complexes are probably never formed in the migratory insertion process. This suggests a correction of the classical textbook description of the insertion process as given by the sequence "ethylene hydride → β-agostic → ethyl".[33] Instead of an ethyl complex, formation of an α-agostic species is normally preferred [On the basis of the occurrence of α-agostic interactions throughout the TM series, we consider it likely for this statement to also hold for many other systems, even quite different from the ones studied here.] according to our calculations. It remains doubtful, however, whether even such α-agostic isomers are relevant to the kinetics of the insertion process in late TM complexes, since they are of relatively high energy; they may nevertheless become relevant for complexes of early or intermediate TMs, such as Cr.[34] Hence, for olefin insertion in TM hydride complexes we propose that the term "migratory insertion" be used in a more restrictive way, denoting only the formation of the *initial* agostic isomer from the olefin complex, that is, our Process I.

The migratory hydride insertion process, a single elementary step, has sometimes been confused with the two-step process of insertion followed by three-hydrogen scrambling.[5,7] The present work confirms the notion put forward by Ziegler et al. that the experimental barriers derived from 3H-scrambling are unrelated to the insertion barriers TS_I.[3a] However, contrary to the proposition made by these authors, the measured barrier is not due to the formation of an unsaturated ethyl complex, but rather to the rotation of the β-agostic methyl group. The alternative 3H scrambling

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(33) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, U.S.A., 1987; Chapter 6.3.

(34) Döhring, A.; Jensen, V. R.; Jolly, P. W.; Thiel, W.; Weber, J. C. *Organometallics* **2001**, *20*, 2234–2245.

process via formation of **3** and rotation of the free methyl group appears to be higher in energy. Furthermore, the importance of using the correct reference point, that is, measuring theoretical barriers from the global minimum of energy when comparing them against experimental NMR data, is confirmed; incorrect numbers may be obtained if individual scrambling processes are considered in isolation. For one particular case this was pointed out earlier by Brookhart et al.[7] However, in this experimental study the necessary corrections could only be roughly estimated.

We have also studied the influence of the TM atom, as well as the phosphine and cyclopentadienyl ligand, on these dynamical processes. The rise in d-level energy going from first to second row TMs has a strong impact, shifting the global minimum and affecting barrier heights. The *trans*-effect results in a stronger influence of the Cp ligand in comparison to the phosphine ligand; however, a replacement of PX_3 by strongly π-coordinating ligands such as ethylene may also have a strong impact, that is, shifting the global minimum of the Rh complexes from **1** to **2**. We hope that the excellent agreement between computation and NMR results (where available) of this work provides encouragement for future studies to comprehensively examine the various dynamic H respectively C-scrambling processes in TM complexes by theoretical methods.

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Supporting Information Available: Additional detailed structural information on the stationary points for $[(C_5R_5)(L)M(H)(C_2H_4)]^+$ (R = H, Me; L = $P(OMe)_3$, PMe_3, C_2H_4; M = Co, Rh). This material is available free of charge via the Internet at http://pubs.acs.org.