A New Mechanism for Exchange Processes observed in the Compounds 
[M(η-C₅H₅)(exo-η-RCH=CH₂)H], M = Nb and Ta

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Dynamic n.m.r. studies of the exchange processes in the complexes [M(η-C₅H₅)(exo-η-RCH=CH₂)H], M = Nb, Ta, lead to the proposal of a new mechanism involving intermediates with agostic bonding.

We have reported a detailed investigation of the dynamic processes in the exo-niobium complexes [Nb(η-C₅H₅)₂(exo-η-RCH=CH₂)H] (I). For these exo-complexes it was found that exchange between the Nb–H and the vinylic CH₂ hydrogens was much faster (by ca. 2 orders of magnitude) than the exchange between the chemically inequivalent C₅ rings. For the exo-propene-hydride complex (I, R = Me), an approximate analysis† showed the rates of exchange of the Nb–H and the two inequivalent methylene hydrogens [k(H ↔ CH₂)],

† The exchange of the exo methyl group with the Nb–H and the methylene hydrogens was treated as a two-site exchange process.
and the exo-methyl group \([k(\text{Me} \leftrightarrow \text{H})]\), to be similar, and as for \(R \neq \text{Me}\) cases, faster than that for the exchange between the inequivalent \(C_5\) rings \([k(Cp)]\).

The mechanism originally proposed for the exchange processes for the exo isomers is shown in Figure 1. Here, the alkene inserts into the Nb–H bond forming a 16-electron α-alkyl species (A), in which the metal centre adopts a 'pyramidal' structure. Rotation about the \(C_5\) bond followed by β-elimination gives the observed alkene/hydride scrambling. In order to effect exchange between the \(C_5\) rings, it is necessary for the α-alkyl group to undergo a 180° rotation, and the metal centre to invert so as to bring the methyl group to the correct orientation for the β-elimination step. The slower rate of the \(C_5\) ring exchange process was proposed to arise from a non-negligible steric barrier for rotation and/or inversion at the metal centre.

In the light of the recent evidence for an in-place rotation mechanism for hydrogen scrambling in alkene–hydride complexes,\(^2,\) we propose an alternative mechanism (mechanism

Table 1. Rate constants\(^a\) of hydrogen scrambling in [M(\(η\)-C\(_5\)H\(_5\))(exo-\(η\)-\(Me\)CH=CH\(_2\))H] (\(M = \text{Nb, Ta}\)).

<table>
<thead>
<tr>
<th></th>
<th>(M = \text{Nb})</th>
<th>(M = \text{Ta})</th>
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<tbody>
<tr>
<td></td>
<td>(T/K) (k(\text{Me} \leftrightarrow \text{H}))</td>
<td>(k(\text{H} \leftrightarrow \text{CH}_2))</td>
</tr>
<tr>
<td>293</td>
<td>0.12(4)</td>
<td>0.39(6)</td>
</tr>
<tr>
<td>298</td>
<td>0.24(4)</td>
<td>0.81(6)</td>
</tr>
<tr>
<td>303</td>
<td>0.36(4)</td>
<td>1.47(12)</td>
</tr>
<tr>
<td>313</td>
<td>1.32(16)</td>
<td>4.02(39)</td>
</tr>
<tr>
<td>348(^d)</td>
<td>40.8(^e)</td>
<td>(185.0(^e)</td>
</tr>
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\(^a\) Reported in \(s^{-1}\), standard deviations \((n \geq 6)\) are in parentheses.  
\(^b\) The reported coalescence temperature for the resonances due to the \(\eta\)-C\(_5\)H\(_5\) ligands of the tantalum compound, \(k(Cp) = 18.0\ s^{-1}\).  
\(^c\) Extrapolated values.  
\(^d\) The reported coalescence temperature for the resonances due to the \(\eta\)-C\(_5\)H\(_5\) ligands of the niobium compound, \(k(Cp) = 10.4\ s^{-1}\).
II, Figure 2) to account for the exchange processes in the niobium compounds. In mechanism II, the methylene hydrogens/hydride exchange occurs via the in-place rotation of an agostic alkyl intermediate. Exchange of the C₅ rings occurs via the rate-limiting dissociation of the agostic hydrogen in the η²-alkyl intermediate to form a symmetrical 16-electron η-alkyl intermediate, in which the η-alkyl group undergoes rapid rotation about the Nb-C₆ bond. We propose a symmetrical intermediate, i.e. with the M-C₆ bond aligned with the C₅ axis, since there are no obvious reasons, steric or electronic, for a 16-electron η-alkyl species such as (A) to be pyramidal. Indeed, such a structure is found in the crystallographically characterised isoelectronic compound [V(η-C₅H₅)₂Cl]. If the 16-electron η-alkyl species is symmetrical, then the relatively slower rates of exchange between the C₅ rings in mechanism I must be due to slow rotation arising from steric ligand repulsion.

In mechanism I, in order to account for the observed exchange rates in the propene hydride complexes, a full rotation of the η-alkyl group in the intermediate followed by β-elimination results in exchange of the C₅ rings. Rotation by 60° about the M-C₆ bond (isopropyl rock), followed by β-elimination, results in exchange of the M-H with the exo-methyl group without scrambling of the C₅ rings. In mechanism II, the hydride to methyl exchange proceeds via the intermediate Q (Figure 2b). A 16-electron η-alkyl complex is not formed at any time during this formal substitution reaction. If the isopropyl rock or the formation of Q is fast on the time-scale of the β-elimination step, then \( k(H \leftrightarrow CH₃) = k(Me \leftrightarrow H) \), whereas \( k(H \leftrightarrow CH₃) > k(Me \leftrightarrow H) \) if they are slow. It is therefore important to determine these two rate constants accurately.

The rate constants of the four-site exchange system consisting of the exo-methyl group, the inequivalent methylene hydrogens, and the hydride ligand in the complexes \[ M(H\eta-C₅H₅)₂(MeCH=CH₂)H, \] \( M = Nb, Ta \), were determined by variable temperature multisite spin saturation transfer (SST) n.m.r. experiments. The results are shown in Table 1. The data show that for both the niobium and tantalum complexes \( k(Me \leftrightarrow H) > k(Cp) \), and for the Nb compound \( k(H \leftrightarrow CH₃) \approx 3 k(Me \leftrightarrow H) \), but within experimental error \( k(H \leftrightarrow CH₃) = k(Me \leftrightarrow H) \) for the tantalum compound. The observation for the tantalum compound that \( k(H \leftrightarrow CH₃) = k(Me \leftrightarrow H) \) can be explained in both mechanisms in terms of propene insertion being the rate-determining step in both processes. In the case of the niobium compound, the isopropyl rock or the formation of Q must be slow compared to β-elimination, and therefore \( k(H \leftrightarrow CH₃) > k(Me \leftrightarrow H) \). In other words there must be a significant barrier to a 60° ‘rotation’ of the isopropyl group. In mechanism I this barrier is due to steric ligand repulsion whereas in mechanism II it arises from specific agostic interactions. The kinetic data obtained in this work do not definitively distinguish between these two possibilities. However, there are observations in the literature which provide circumstantial evidence which lead us to prefer mechanism II over I. Thus there is already evidence for the in-place rotation mechanism, and agostic η²-isopropyl compounds have been characterised. Concerning the proposal of the participation of the intermediate (or transition state) Q in the exo-methyl to Nb-H exchange process, we note that there are many examples of related agostic-alkyl ≡ alkyl interchanges in complexes such as \[ [Mn(η-C₅H₅-H)(CO)₃] \]. Indeed the η³-isopropyl system in Q clearly is similar to the η³-isopropyl system in the in-place rotation mechanism.

We conclude that for (1; \( R = Me \)) we can account for all the kinetic data if there is some mechanism for a restricted 60° rotation of the isopropyl group and that the proposal of agostic alkyl intermediates (electronic restriction) is a more compelling explanation than that of interligand steric interactions.

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References

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† Multisite irradiation in the SST experiments was carried by sequential irradiation of the desired number of sites for 100—200 ms with a switching time of 5 ms between sites (decoupler gated off). The total irradiation time was varied by recycling through the frequency list the necessary number of times.