A New Mechanism for Exchange Processes observed in the Compounds [M(η-C_5H_5)$_2$(*exo*-η-RCH=CH_2)H], M = Nb and Ta

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Dynamic n.m.r. studies of the exchange processes in the complexes [M(η-C_5H_5)(*exo*-η-RCH=CH_2)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-C_5H_5)$_2$(*exo*-η-RCH=CH_2)H] (**1**).[1] For these *exo*-complexes it was found that exchange between the Nb–H and the vinylic CH_2 hydrogens was much *faster* (by *ca.* 2 orders of magnitude) than the exchange between the chemically inequivalent C_5 rings. For the *exo*-propene-hydride complex (**1**, R = Me), an approximate analysis† showed the rates of exchange of the Nb–H and the two inequivalent methylene hydrogens [k(H ⟷ CH_2)],

† The exchange of the *exo* methyl group with the Nb–H and the methylene hydrogens was treated as a two-site exchange process.

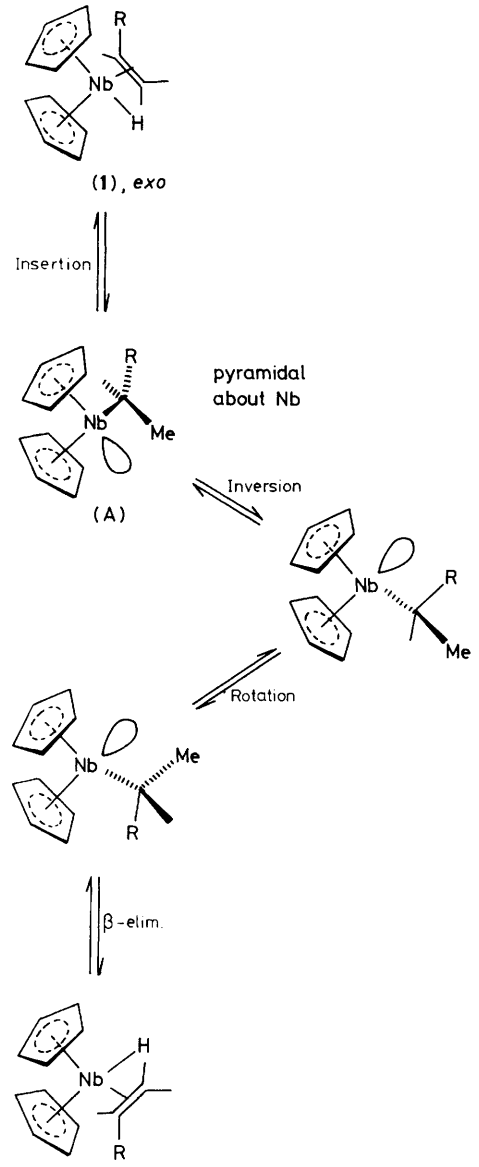

Figure 1. Previous proposed mechanism I[1] showing the pyramidal intermediate and the inversion process.

and the *exo*-methyl group [k(Me ⟷ H)], to be *similar*, and as for R ≠ 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 σ-alkyl species (A), in which the metal centre adopts a 'pyramidal' structure. Rotation about the C_α–C_β 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 σ-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,[2,3] we propose an alternative mechanism (mechanism

Table 1. Rate constants[a] of hydrogen scrambling in [M(η-C_5H_5)$_2$(*exo*-η-MeCH=CH_2)H] (M = Nb, Ta).

M = Nb			M = Ta		
T/K	k(Me ⟷ H)	k(H ⟷ CH_2)	T/K	k(Me ⟷ H)	k(H ⟷ CH_2)
293	0.12(4)	0.39(6)	337	0.14(1)	0.15(2)
298	0.24(4)	0.81(6)	347	0.32(2)	0.27(4)
303	0.36(4)	1.47(12)	357	0.95(13)	0.79(11)
313	1.32(16)	4.02(39)	412[b]	53.5[c]	
348[d]	40.8[c]	125.0[c]			

[a] Reported in s^{-1}, standard deviations ($n \geq 6$) are in parentheses. [b] The reported coalescence temperature for the resonances due to the η-C_5H_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 η-C_5H_5 ligands of the niobium compound. k(Cp) = 10.4 s^{-1}.

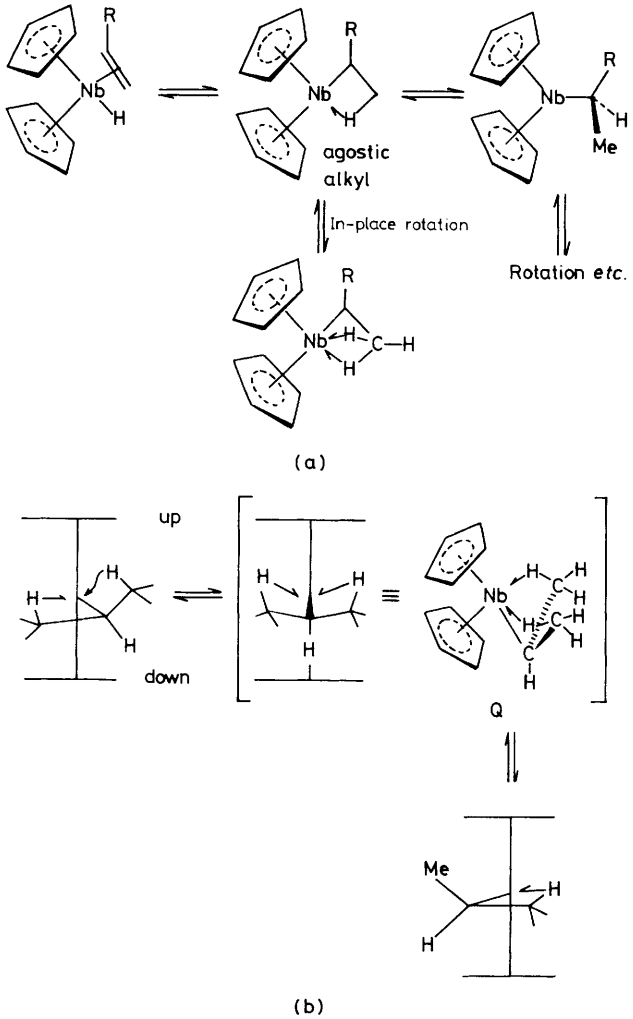

Figure 2. Proposed new mechanism II for hydrogen scrambling in (**1**, R = Me). (a) The process of rotation about the M–C_α bond, and β-elimination are assumed to be fast compared to the cleavage of the agostic interaction, which is proposed to be rate limiting. (b) The new pathway for exchange of the propene methyl group with the metal hydride *via* the species Q.

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 C_5 rings occurs *via* the rate-limiting dissociation of the agostic hydrogen in the η^2-alkyl intermediate to form a *symmetrical* 16-electron σ-alkyl intermediate, in which the σ-alkyl group undergoes *rapid* rotation about the Nb–C_α bond. We propose a symmetrical intermediate, *i.e.* with the M–C_α bond aligned with the C_2 axis, since there are no obvious reasons, steric or electronic,[4] for a 16-electron σ-alkyl species such as (A) to be pyramidal. Indeed, such a structure is found in the crystallographically characterised isoelectronic compound [V(η-$C_5H_5)_2$Cl].[5] If the 16-electron σ-alkyl species is symmetrical, then the relatively slower rates of exchange between the C_5 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 σ-isopropyl group in the intermediate followed by β-elimination results in exchange of the C_5 rings. Rotation by 60° about the M–C_α bond (isopropyl rock), followed by β-elimination, results in exchange of the M–H with the *exo*-methyl group *without* scrambling of the C_5 rings. In mechanism II, the hydride to methyl exchange proceeds *via* the intermediate Q (Figure 2b). A 16-electron σ-isopropyl 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 $k(H \longleftrightarrow CH_2) = k(Me \longleftrightarrow H)$, whereas $k(H \longleftrightarrow CH_2) > k(Me \longleftrightarrow H)$ 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(η-$C_5H_5)_2$(η-MeCH=CH_2)H], M = Nb, Ta,[1,6] were determined by variable temperature multisite spin saturation transfer (SST)‡ n.m.r. experiments.[7,8] The results are shown in Table 1. The data show that for both the niobium and tantalum complexes $k(Me \longleftrightarrow H) > k(Cp)$, and for the Nb compound $k(H \longleftrightarrow CH_2) \approx 3\,k(Me \longleftrightarrow H)$, but within experimental error $k(H \longleftrightarrow CH_2) = k(Me \longleftrightarrow H)$ for the tantalum compound.

The observation for the tantalum compound that $k(H) \longleftrightarrow CH_2) = k(Me \longleftrightarrow H)$ 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 $k(H \longleftrightarrow CH_2) > k(Me \longleftrightarrow H)$. 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,[2,3] and agostic η^2-isopropyl compounds have been characterised.[9,10] 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-C_6H_8–H)$(CO)_3$],[1] *viz.* C–H → M H–C ⇌ C–H M ← H–C. Indeed the η^3-isopropyl system in Q clearly is similar to the η^3-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.

We thank NATO (research grant 287-84) for support, and the Gas Research Institute for partial support, of this work. We thank D. O'Hare, C. M. Dobson, and S. J. Heyes for helpful discussion.

Received, 20th December 1988; Com. 8/04965C

‡ 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.

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