Hydrogen Scrambling Processes in $[Ta(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)\{(\mu\text{-}H)_2BH_2\}]$: A Surprising Observation

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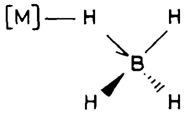
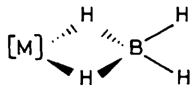
Quantitative phase-sensitive two-dimensional exchange n.m.r. spectra of $[Ta(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)\{(\mu\text{-}H)_2BH_2\}]$ show that the observed scrambling of the terminal and bridging hydrogens of the $(\mu\text{-}H)_2BH_2$ ligand proceeds by a dominant mechanism in which there is no direct exchange between the two terminal hydrogens. This has been interpreted in terms of an associative mechanism proceeding *via* an $Ta\{(\mu\text{-}H)_3BH\}$ intermediate accompanied by $\eta^5 \longleftrightarrow \eta^3$ shifts of the C_5 rings.

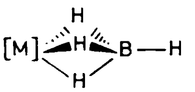
In the numerous tetrahydroborate derivatives of the *d*- and *f*-block metals [1-3] three modes of bonding of the BH_4 ligand are found, (**A**)—(**C**). Examples of the relatively rare mode (**A**) are the 18-electron compounds $[Cu(BH_4)(PMePh_2)_3]$,[4] $[Fe(BH_4)H(dmpe)_2]$,[5] and the 15-electron d^3 complex $[V(BH_4)_2(dmpe)_2]$ (dmpe = $Me_2PCH_2CH_2PMe_2$).[6] Mode (**B**) is the most commonly found, and recent examples include $[V(BH_4)_3(PMe_3)_2]$[6] and $[Ti(BH_4)_2(dmpe)_2]$.[7] The crystal structure of the hafnium compound $[Hf(\eta\text{-}C_5H_4Me)_2(BH_4)_2]$[8] determined by neutron diffraction showed that there are two bidentate tetrahydroborate ligands. The tridentate mode (**C**) has also been structurally characterised, for example in $[Al(BH_4)_3]$[9] and $[M(BH_4)_4]$, M = Zr or Hf.[10]



(A)



(B)



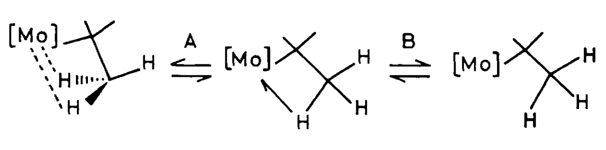
(C)

Transition-metal tetrahydroborate complexes are often fluxional, and commonly a single resonance is observed for all four B–H hydrogens in the ^1H n.m.r. spectrum at ambient temperatures. In the tridentate BH_4 complexes, rapid exchange of the three bridging hydrogens has been proposed to occur by rotation about the local three-fold axis of the ligand, *i.e.* the M–B vector.[11] Exchange of the single terminal hydrogen with the bridging ones can be envisaged to proceed *via* reversible dissociation of one of the bridging hydrogens to form a bidentate intermediate species (**B**).

The exchange of the terminal and bridging hydrogens in bidentate tetrahydroborate complexes has been studied in detail, and the mechanisms proposed are shown in Figure 1. The dissociative mechanism proceeds *via* an unidentate intermediate which undergoes rotation about the H_b–B bond (a local three-fold axis of the ligand), whereas the associative mechanism proceeds *via* a tridentate BH_4 followed by rotation about the M–B vector (a local three-fold axis). The pseudo-rotation mechanism is a dissociative pathway, rather akin to a Berry pseudo-rotation, which scrambles the hydrogens by inversion at the boron atom but with an additional 90° rotation about the M–B axis. The in-place rotation mechanism is a concerted, associative mechanism with a terminal hydrogen becoming co-ordinated to the metal centre and displacing one of the bridging hydrogens. At the transition state there is a tridentate BH_4 species.

Of the mechanisms outlined in Figure 1, the pseudo-rotation pathway, with an intermediate in which the boron atom has square pyramidal co-ordination, is the most speculative.[12] There is no evidence to support this mechanism and it may therefore be discarded. Of the remaining three mechanisms there is no direct evidence to discriminate between them, although the dissociative mechanism is normally proposed. Marks and co-workers[8] preferred the in-place rotation mechanism for hydrogen scrambling within each of the bidentate BH_4 ligands in $[Hf(\eta\text{-}C_5H_4Me)_2(BH_4)_2]$ on the basis of structural evidence. Thus it was observed that the thermal ellipsoid of one of the bridging hydrogens was substantially smaller than those of the other three hydrogens on the bidentate BH_4 ligand, and the direction of maximum displacement corresponds to the reaction co-ordinate for an in-place rotation mechanism. It was inferred that this may be associated with a low activation barrier for hydrogen scrambling in solution *via* in-place rotation and it was found that the terminal–bridging hydrogen exchange process is fast on the 90 MHz ^1H n.m.r. time-scale even at −155 °C.

Our recent reinvestigation of the fluxional processes in the complex $[\{Mo(dppen)_2(\eta\text{-}C_2H_4)_2H\}^+CF_3CO_2^-]$,[13] dppen = *cis*-$Ph_2PCH{=}CHPPh_2$, using detailed dynamic n.m.r. techniques led us to propose a new mechanism for the exchange between the hydride and ethylene hydrogens. In this new mechanism, ethylene insertion gives an unobserved 18-electron agostic ethyl intermediate in which scrambling of the β-hydrogens occurs *via* a formally *associative* process (A) involving an in-place rotation about the C_α–C_β bond without, as normally proposed, dissociation of the agostic hydrogen to form a 16-electron σ-ethyl species (process B).[14] The transition state of the in-place rotation process has a tridentate ethyl ligand.



We were interested in investigating whether associative mechanisms occur more frequently than hitherto suspected. We noted that the bidentate BH_4 ligand is similar to an agostic bidentate ethyl group: both are formally three-electron donors and their frontier orbitals are identical in their symmetry. We therefore decided to study the kinetics of hydrogen scrambling in the tantalum complex $[Ta(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)\{(\mu\text{-}H)_2BH_2\}]$, (**1**), as described below. This bent-metallocene bidentate borohydride was chosen since by analogy with closely related compounds[15] it was reasonable to expect that the $\Delta G^\ddagger$ of the borohydride exchange process would be compatible with achieving both rapid and slow exchange conditions on the n.m.r. time-scale at accessible temperatures. The purpose of the

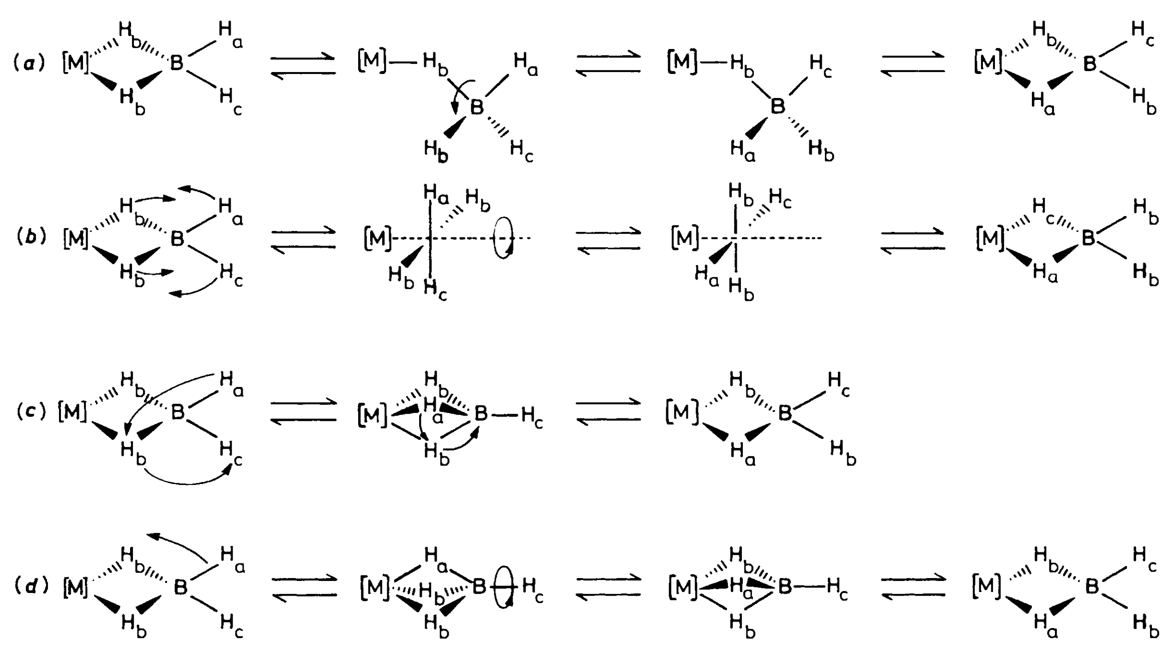


Figure 1. Some previously proposed mechanisms for hydrogen scrambling in bidentate borohydride complexes: (*a*) the dissociative mechanism *via* a unidentate BH_4 intermediate, (*b*) the pseudo-rotation mechanism *via* a square pyramidal intermediate which undergoes a 90° rotation about the M–B vector, (*c*) the in-place rotation mechanism by rotation about the H_b–B bond and *via* the tridentate BH_4 transition state, and (*d*) the associative rotation mechanism *via* a tridentate BH_4 intermediate in which there is rotation about the M–B vector

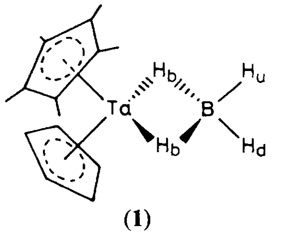
mixed-ring system was to allow differentiation of the terminal B–H hydrogens.

Concerning the probable mechanisms of hydrogen scrambling in complex (**1**) and their kinetic implications, we assumed that the mechanisms would proceed by either dissociative or associative activation. In the dissociative mechanism proceeding *via* a 16-electron unidentate BH_4 intermediate the rates of exchange between the inequivalent terminal hydrogens and the bridging hydrogens should be the same. For the associative mechanisms proceeding *via* tridentate BH_4 intermediate or transition states the stereoelectronic factors giving rise to the inequivalence of the terminal hydrogens *may* result in different activation barriers to their exchange with the equivalent bridging hydrogens. Hence, if differential broadening of, for example, one of the terminal B–H hydrogen resonances in the intermediate exchange region can be observed, it would allow us to distinguish between the dissociative and associative pathways. A preliminary communication of this work has been published.[16]

Results and Discussion

Synthesis of Complex (**1**).—The mixed-ring dichloride complex $[Ta(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)Cl_2]$, (**2**), was prepared as described.[17] Reduction of (**2**) with magnesium amalgam in tetrahydrofuran (thf) under an atmosphere of carbon monoxide[18] gave the carbonyl chloride complex $[Ta(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)(CO)Cl]$, (**3**), in good yield. Photolysis of (**3**) with a suspension of $LiBH_4$ in thf gave the desired borohydride complex $[Ta(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)\{(\mu\text{-}H)_2BH_2\}]$, (**1**), which was isolated in good yield as an air- and moisture-sensitive crystalline solid. Complex (**1**) is thermally unstable, light petroleum solutions decomposing in *ca.* 12 h at 50 °C, and no pure decomposition product could be isolated. Curiously when (**2**) or (**3**) was heated with $LiBH_4$ in thf or 1,2-dimethoxyethane there was no evidence for the formation of (**1**). This is in marked contrast to the niobium system where treatment of $[Nb(\eta\text{-}C_5H_5)_2Cl_2]$ with $NaBH_4$ at room temperature in thf gives $[Nb(\eta\text{-}C_5H_5)_2\{(\mu\text{-}H)_2BH_2\}]$ in high yield.

The exchange system in complex (**1**) is at the slow-exchange limit on the ^1H n.m.r. time-scale at room temperature. Thus in the $^1H\text{-}\{^{11}B\}$ n.m.r. spectrum at 298 K the bridging hydrogens H_b were observed as a triplet [*J*(H–H) 8 Hz] at δ −15.44 while the inequivalent terminal hydrogens were observed as quartets [*J*(H–H) 8 Hz] at δ 6.27 and 5.91. We tentatively assign the higher field resonance, at δ 5.91, to H_u by assuming that the diamagnetic shielding effects due to the methyl groups of the $\eta\text{-}C_5Me_5$ ligand on H_u are greater than that of the $\eta\text{-}C_5H_5$ ligand on H_d. The ^{11}B n.m.r. spectrum of (**1**) showed a triplet of triplets centred at δ 47.2 p.p.m., consistent with splitting of the boron resonance by coupling to two terminal hydrogens [*J*(B–H) 117 Hz] and two bridging hydrogens [*J*(B–H) 60 Hz]. Heteronuclear decoupling of the resonance due to the terminal B–H hydrogens confirmed this assignment. These double resonance experiments were necessary definitively to establish the bidentate BH_4 structure of (**1**) because it has been shown that reaction of monoborane precursors such as BH_4^- with transition-metal complexes can result in homologation to form higher borane species.[19]



(**1**)

Determination of Rate Constants.—Attempts to observe differential broadening of the boron hydrogens, and the fast-exchange limit in the $^1H\text{-}\{^{11}B\}$ n.m.r. spectrum of complex (**1**) at high temperatures, were prevented by its thermal instability. Determination of the rate constants of exchange by n.m.r. multisite spin saturation transfer techniques[20,21] were hampered by difficulties in selective saturation of one of the terminal hydrogen resonances. However, the exchange rate

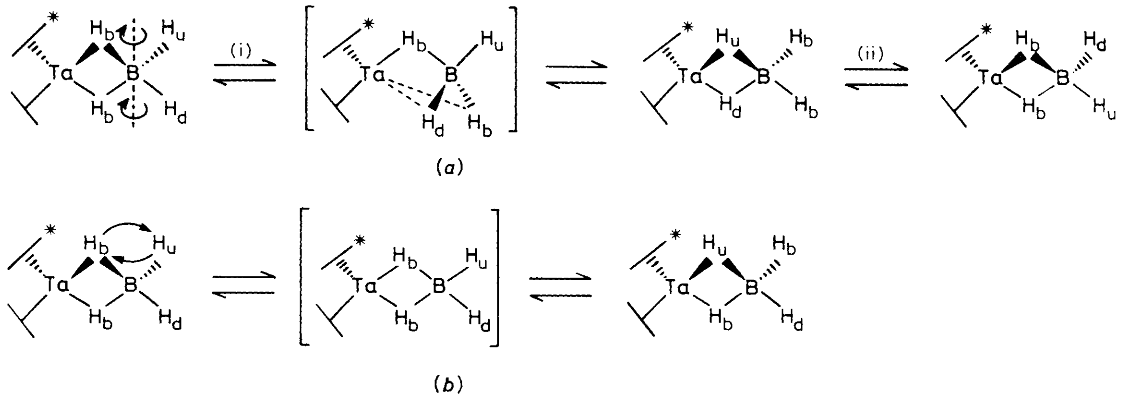


Figure 2. (*a*) The bridge–terminal hydrogen-exchange mechanism by rotation about the local two-fold axes in the planes containing a bridging and a terminal hydrogen and the boron atom and which bisect the $H_{bridging}$–B–$H_{terminal}$ angle. Step (i): rotation about the local C_2 axis in the plane of the paper and bisecting the H_b–B–H_d angle. Step (ii): rotation about the local C_2 axis which goes into the plane of the paper and bisects H_b–B–H_u. This mechanism exchanges the terminal hydrogens if there is rotation about all the possible two-fold axes described above. (*b*) The bridge–terminal exchange mechanism *via* a pairwise rotation of the exchanging hydrogens. At the transition state the boron atom has a planar co-ordination arrangement and the BH_4 ligand is in an orientation which does not overlap effectively with the tantalum centre. The C_5 rings are represented by lines; the asterisks denote the η-C_5Me_5 ligands

Table. Rate constants (s^{-1}) for hydrogen scrambling in complex (**1**)*

T/K	k_{ud}	k_{db}	k_{ub}
273	0.25 ± 0.1	0.36 ± 0.05	0.38 ± 0.04
303	1.06 ± 0.8	8.5 ± 0.7	9.3 ± 0.8
313	2.4 ± 2.2	23.8 ± 3.1	24.4 ± 3.2

* The mean and standard error of the mean are reported. See Experimental section for details.

constants between the borohydride hydrogens could be obtained, for example, by using volume integrals of the diagonal and off-diagonal peaks from ^{11}B-decoupled phase-sensitive ^1H–^1H two-dimensional exchange n.m.r. spectroscopy (EXSY) as inputs to the D2DNMR program developed by Abel and co-workers,[22,23] which gives all the rate constants from one experiment. In the phase-sensitive EXSY experiment, if the diagonal peaks are phased to have negative intensities, transient nuclear Overhauser effects give rise to pure absorption off-diagonal peaks of negative intensity. Using this method at 253 K, where hydrogen scrambling was slow, it was demonstrated that transient nuclear Overhauser effects were negligible. The rate constants thus obtained are shown in the Table, from which an Eyring plot gave $\Delta G^\ddagger$ (298 K) = 68.7 kJ mol^{-1} for the bridge–terminal hydrogen-exchange process $H_d \longleftrightarrow H_b$.

The data clearly show that, within experimental error, the exchange rate constant between H_u and the bridging hydrogens H_b (k_{ub}), and that between H_d and H_b, *i.e.* k_{db}, are the same, and, surprisingly, $k_{ud} \approx 0$. Thus although a cross-peak is observed between the terminal hydrogens in the two-dimensional EXSY n.m.r. spectrum, the quantitative analysis shows that there is in fact negligible direct exchange between the two sites. These second-order cross-peaks, which arise as a result of transfer of magnetisation from one site to another *via* chemical exchange with a *third* site, have been noted previously,[23,24] and illustrate the point that qualitative two-dimensional exchange n.m.r. experiments should be interpreted with caution.

Mechanism of Hydrogen Scrambling in Complex (**1**).—Although crossover experiments were not carried out, the observation that the rate constants for hydrogen scrambling in complex (**1**) obtained from samples of different concentrations were identical within experimental error clearly suggests that the fluxional mechanism is intramolecular.

As can be seen from Figure 1, the dissociative and in-place rotation mechanisms, in which there is rotation about a local three-fold axis, namely a H_b–B bond, result in cyclical exchange of the hydrogens, *i.e.* $H_u \longleftrightarrow H_b$, $H_b \longleftrightarrow H_d$, and $H_d \longleftrightarrow H_u$ in complex (**1**). Both mechanisms will therefore predict $2K_{ud} = k_{ub} = k_{db}$. The observation $k_{ub} = k_{db}$ and $k_{ud} \approx 0$ therefore immediately rules out both mechanisms. Further, since $k_{ud} \approx 0$, there is no observable direct exchange of the terminal hydrogens even at the highest temperature studied (313 K). This implies that the dominant mechanism of hydrogen scrambling up to the highest temperature studied involves *different* intermediates for the exchange processes $H_u \longleftrightarrow H_b$ and $H_d \longleftrightarrow H_b$, and that these intermediate species do not interconvert on the time-scale of the exchange process.

In view of the surprising observation that there is negligible direct exchange between the terminal hydrogens in (**1**), we have, for the purpose of completeness, considered a number of possible hydrogen-scrambling mechanisms including those which we disfavour because they are inconsistent with the normal stereochemical and bonding requirements of the tantalum and boron centres. For example, it is possible to envisage a bridge–terminal hydrogen-exchange mechanism proceeding *via* rotation about the local two-fold axes which bisect the H_u–B–H_b and H_d–B–H_b angles of the bidentate BH_4 ligand [see Figure 2(*a*)]. Both terminal hydrogens become bridging ones in a single rotation. During this rotation there is reduced interaction between the frontier orbitals of the BH_4 ligand and the tantalum centre. More importantly, this mechanism leads to exchange of the terminal hydrogens if there is, as it is likely, rotation about all such two-fold axes. It may thus be discarded. Alternatively a terminal and a bridging hydrogen may simply rotate as a pair and undergo a concerted exchange reaction without significant movement of the other B–H hydrogens [see Figure 2(*b*)]. There is no exchange between the terminal hydrogens. However the transition state for this pathway has a boron atom with square-planar co-ordination. This is expected to be of high energy and such a concerted mechanism is highly unlikely.

The associative mechanism proceeding *via* tridentate BH_4 intermediates is shown in Figure 3. The first steps are co-ordination of the terminal hydrogens to the metal centre to form the tridentate BH_4 intermediates. These intermediates would then undergo rotations in 60° steps about the Ta–B vector and interconvert between the six rotamers. This rotation process

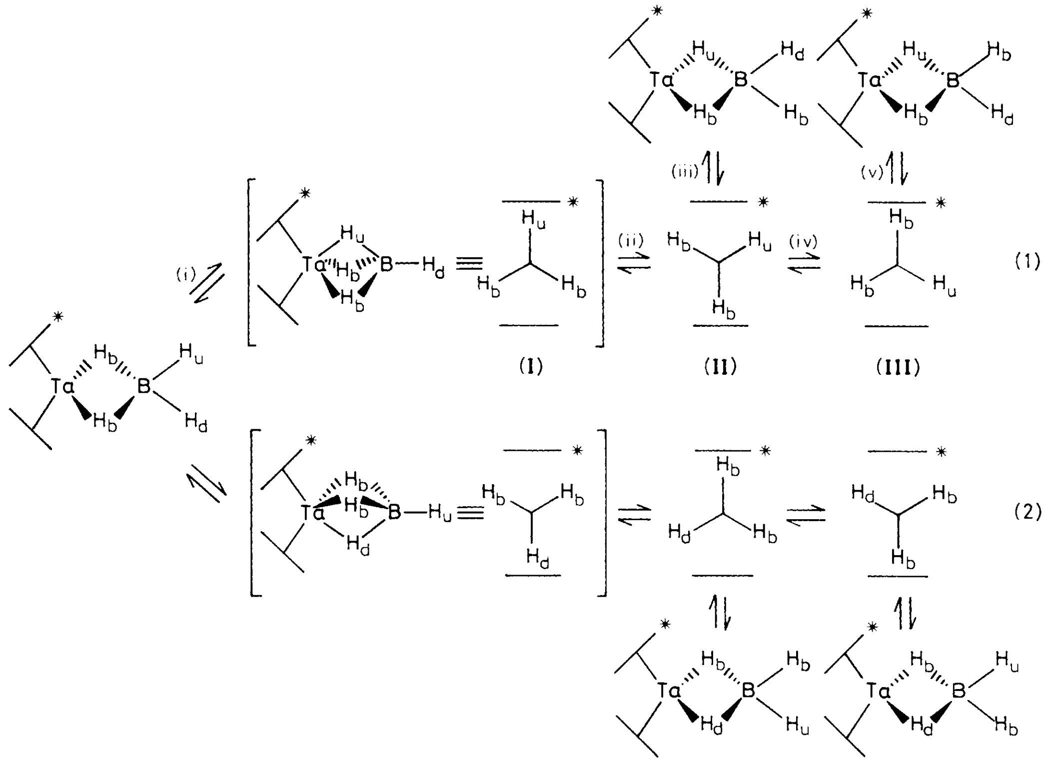


Figure 3. The associative mechanism for hydrogen scrambling in complex (**1**) proceeding *via* tridentate BH_4 intermediates. The Newmann projections are views down the $H_{terminal}$–B–Ta vectors of these intermediate species. Pathway (1): (i) co-ordination of H_u to the tantalum centre forming the tridentate BH_4 intermediate, (**I**); (ii) a 60° rotation in the clockwise direction about the B–Ta vector giving the rotamer (**II**); (iii) dissociation of a bridging hydrogen in (**II**) to reform (**1**), H_d is now in the *up* position, *i.e.* there is exchange between the terminal hydrogens; (iv) a 60° rotation about the B–Ta vector in (**II**) giving the rotamer (**III**), which can be formed from (**I**) by a 120° rotation; (v) dissociation of a bridging hydrogen in (**III**) to reform (**1**), note that H_d is still in the *down* position, *i.e.* no exchange between the terminal hydrogens. Pathway (2), starting with the co-ordination of H_d to the tantalum centre, is similar. There is exchange between the terminal hydrogens if the rotations about the B–Ta vector proceed by 60° steps, but no such exchange if they are in 120° steps. This mechanism assumes that the potential-energy surface for these rotations is not flat, *i.e.* the rotamers are distinct species at the bottom of a potential energy well

scrambles the three hydrogens of the bridge. The implicit assumption is that the potential-energy surface for the rotation processes is not flat, *i.e.* the rotamers are at the bottom of sizeable potential wells. For the last step of the exchange mechanism, that of dissociation of one of the three bridging hydrogens to reform the bidentate BH_4 structure, the principle of microscopic reversibility dictates that it is the hydrogen which lies in the plane containing the ring centroids and the metal centre which dissociates. It is evident from Figure 3 that this mechanism gives rise to exchange of the terminal hydrogens *unless* the rotation process proceeds by 120° *rather than* 60° steps. Rotation by 120° steps can occur if the rotamers formed by a 60° rotation about the Ta–B vector are of high energy, *i.e.* they become transition states for the 120° rotations. However, the 60° rotamer for the intermediate formed by the co-ordination of H_U is the intermediate formed by the co-ordination of H_d to the tantalum centre. Hence, if this assumption is correct we will predict, for example, that k_{ub} is much larger than k_{db}. This is at variance with the experimental data.

The associative mechanism can be modified to account for the rate data by invoking some specific, concerted motion of another ligand in the molecule when, for example, H_u becomes co-ordinated to the metal centre to form the tridentate BH_4 intermediate. The principle of microscopic reversibility will then dictate that when one of the bridging hydrogens of this intermediate dissociates from the metal centre the concerted motion in the other part of the molecule will force this hydrogen into the terminal position previously occupied by H_u. This mechanism is shown in Figure 4. In this new mechanism, co-ordination of H_u is accompanied by selective ring slippage of one of the η-C_5 ligands, for example the η-C_5H_5 ring, to form the tridentate BH_4 complex (**IV**). Similarly H_d co-ordination is accompanied by ring slippage of the η-C_5Me_5 ring to form (**V**). Hydrogen scrambling occurs by rotation of the tridentate BH_4 fragment about the Ta–B vector and this is followed by dissociation of one of the original bridging hydrogens in (**IV**) *specifically* to the H_u site and the concerted re-co-ordination of the 'free' olefinic double bond of the η^3-C_5H_5 ligand to reform (**1**). The exchange of the inequivalent terminal hydrogens with the bridging ones thus involves the two intermediates (**IV**) and (**V**), and it is implicit that they do not rapidly interconvert on the time-scale of the exchange. Thus direct exchange of the terminal hydrogens does not occur. Reversible $\eta^5 \longleftrightarrow \eta^3$ ring slippage has been invoked in a variety of reactions.[25]

There are a number of questions concerning the new mechanism which the rate data obtained in this work do not answer. Thus the data do not indicate, *a priori*, which of the η-C_5 ligands will undergo ring slippage when H_u or H_d is co-ordinated, nor whether formation of the tridentate BH_4 complexes involves ring slippage before or after co-ordination of the terminal hydrogens. The nature of the rate-limiting step for the exchange process is more problematical. The most likely candidates are the co-ordination of the terminal hydrogens and the ring slippage, or these processes may be concerted. Since it is generally observed that slippage of a η-C_5Me_5 ligand is slower than that of its unsubstituted analogue,[25] one might have expected the rate constants k_{ub} and k_{db} to be significantly different. The data in the Table show these rate constants to be

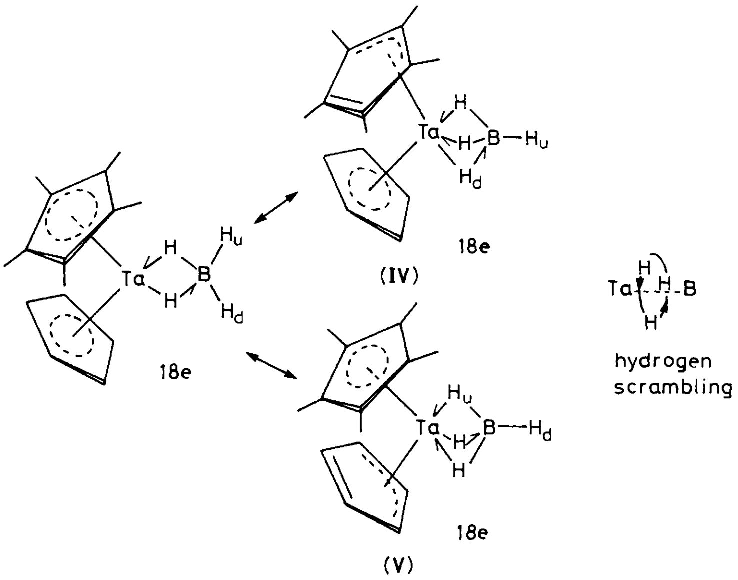


Figure 4. The proposed new mechanism for scrambling of the bridging and terminal hydrogens in complex (**1**) showing the different intermediates (**IV**) and (**V**) for the exchange of the terminal hydrogens H_u and H_d with the bridging hydrogens H_b showing the simultaneous $\eta^5 \longleftrightarrow \eta^3$ shifts of the C_5 rings upon co-ordination of the terminal hydrogens to the tantalum centre. The interconversion between (**IV**) and (**V**) must be relatively slow on the time-scale of this mechanism

identical within experimental error. One possible explanation is that the rate-limiting step is the co-ordination of the terminal hydrogens to the metal centre. Alternatively it may be argued that previous studies on ring-slippage reactions are intermolecular in nature, mainly substitution reactions at transition-metal centres, and the intramolecular slippage reactions proposed in this work are not subject to complicating factors such as steric interactions inherent in intermolecular reactions.

In conclusion, we have demonstrated that evaluation of the rate constants for the exchange processes for *all* the hydrogens of the bidentate BH_4 ligand show that there is negligible direct exchange between the terminal hydrogens. This observation eliminates the intuitively expected mechanisms for hydrogen scrambling in complex (**1**), and leads to the proposal of a new mechanism.

Experimental

All preparations, manipulations, and reactions were carried out under an inert atmosphere of dinitrogen (<10 p.p.m. oxygen, <20 p.p.m. water) using standard Schlenk-tube and vacuum-line techniques, or in a dry-box. Dinitrogen was purified by passage through a column containing BASF catalyst and 5-Å molecular sieves.

All solvents were thoroughly deoxygenated before use by repeated evacuation followed by admission of dinitrogen. Solvents were pre-dried over activated molecular sieves and then distilled from potassium (tetrahydrofuran, thf), sodium (toluene), or sodium–potassium alloy [light petroleum (b.p. 40—60 °C throughout), diethyl ether] under an inert atmosphere of dinitrogen before use. [$^2H_6$]Benzene for n.m.r. samples was stored in glass ampoules equipped with a Teflon stopcock over sodium–potassium alloy and transferred using pipettes in the dry-box. The solutions were then filtered through a plug of glass wool. Celite 545 filtration aid (Koch-Light) was pre-dried at 80 °C before use. The mixed-ring dichloride complex [$Ta(\eta-C_5Me_5)(\eta-C_5H_5)Cl_2$] was prepared as described.[17]

Infrared spectra were recorded as Nujol mulls between CsI plates on a Perkin-Elmer 1510 FT interferometer. Proton n.m.r. spectra were determined at 250 or 500 MHz using Bruker AM-250 or AM-500 spectrometers, ^{13}C and ^{11}B n.m.r. spectra at 62.9 and 80.2 MHz, respectively, using a Bruker AM-250 spectrometer. Spectra were referenced internally using the residual solvent (^1H) and solvent (^{13}C) resonances relative to tetramethylsilane ($\delta = 0$ p.p.m.), or externally using $BF_3{\cdot}OEt_2$ in [^2H]chloroform (^{11}B). All chemical shifts are quoted in δ (p.p.m.) and coupling constants are in Hertz (Hz). Two-dimensional n.m.r. experiments were acquired using the Bruker AM-250 spectrometer using standard Bruker software, and processed using the array processor coupled to an ASPECT 3000 computer.

Elemental analyses for air-stable compounds were performed by the Analysis Department in this laboratory. Elemental analyses for air-sensitive materials were performed by Analytische Laboratorien, Elbach, W. Germany.

Synthesis of [$Ta(\eta-C_5Me_5)(\eta-C_5H_5)(CO)Cl$], (**3**).—A glass ampoule equipped with a Teflon stopcock was charged with [$Ta(\eta-C_5Me_5)(\eta-C_5H_5)Cl_2$] (0.9 g, 2 mmol) and magnesium amalgam (*ca.* 0.6% w/w, 150 g). Toluene (30 cm^3) was added at *ca.* -20 °C to give a pale green solution. The vessel was evacuated briefly to remove the dinitrogen and then charged with carbon monoxide (2 atm, 202 650 Pa). The mixture was stirred vigorously at room temperature for 36 h giving an olive green solution. Volatiles were removed *in vacuo* leaving a green solid which was extracted with toluene and filtered through Celite. The combined filtrates were concentrated to *ca.* 10 cm^3 and light petroleum was added until a green crystalline solid appeared. Cooling at -80 °C gave green crystals of [$Ta(\eta-C_5Me_5)(\eta-C_5H_5)(CO)Cl$]. Concentration and cooling of the supernatant liquor gave a second crop of crystals. Total yield, 700 mg, 79% (Found: C, 43.6; H, 4.5. Calc. for $C_{16}H_{20}ClOTa$: Cl, 43.2; H, 4.5%). I.r. data: 1 884 cm^{-1} [ν(CO)].

Synthesis of [$Ta(\eta-C_5Me_5)(\eta-C_5H_5)\{(\mu-H)_2BH_2\}$] (**1**).—A Pyrex glass ampoule equipped with a Teflon stopcock was charged with [$Ta(\eta-C_5Me_5)(\eta-C_5H_5)(CO)Cl$] (500 mg, 1.1 mmol) and $LiBH_4$ (50 mg, 2.5 mmol). Tetrahydrofuran (20 cm^3) was added giving an olive green solution. The mixture was photolysed with a 500-W medium-pressure mercury vapour lamp under a stream of dinitrogen for 24 h giving a pale green solution. Volatiles were removed *in vacuo* leaving a green solid which was extracted with light petroleum (2 × 20 cm^3) and filtered. The combined filtrates were concentrated to *ca.* 15 cm^3 and cooled at $-80\,°C$ giving a green crystalline solid. Recrystallisation from light petroleum gave analytically pure complex (**1**). Yield 370 mg, 83%. The ^1H n.m.r. spectrum of the reaction mixture showed the presence of traces (< 5%) of $[Ta(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)H_3]$ and $[Ta(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)(CO)H]$ (Found: C, 45.1; H, 5.9. Calc. for $C_{15}H_{24}BTa$: C, 45.5; H, 6.1%). N.m.r. data: all in $[^2H_6]$benzene at 298 K, chemical shifts in δ and coupling constants in Hz; $^1H\text{-}\{^{11}B\}$, 6.27 [q, 1 H, $J(H_u\text{–}H_d)$, $J(H_u\text{–}H_b)$ 8, H_d], 5.91 [q, 1 H, $J(H_d\text{–}H_u)$, $J(H_d\text{–}H_b)$ 8, H_u], 4.76 (s, 5 H, $\eta\text{-}C_5H_5$), 1.83 (s, 15 H, $\eta\text{-}C_5Me_5$), and -15.44 [t, 2 H, $J(H_b\text{–}H_u)$, $J(H_b\text{–}H_d)$ 8, 2 H_b]; ^{11}B, 47.2 [tt, $J(B\text{–}H_u)$, $J(B\text{–}H_d)$ 117, $J(B\text{–}H_b)$ 60]. I.r. data: 2 478, 2 437, 1 747, 1 621, and 1 160 cm^{-1}.

Determination of Rate Constants for Hydrogen Scrambling in Complex (**1**).—The standard pulse sequence D1–90–D0–90–D9–90–FID for phase-sensitive NOESY experiments was used with a recycling time D1 = 3 s. The mixing time D9 was varied randomly by ±15% between scans by the computer to remove scalar *J*-coupling effects. The number of transients acquired for each increment was greater than 16 to ensure that this variation was sufficiently random. A typical experiment required 12 h. The ^{11}B nucleus was continuously decoupled during the acquisition of 256 increments of 1 K words each, thus giving a two-dimensional data matrix of 256 K words. The F1 dimensions were zero-filled but no zero-filling was applied in the F2 dimensions resulting a symmetrised transformed matrix of size 1 028 K words. Rate constants obtained from the volume integrals of a larger data matrix of 4 096 K by zero-filling in both the F1 and F2 dimensions were not significantly different.

The diagonal peaks were phased to have negative intensities with the result that transient nuclear Overhauser effects (n.O.e.s) should give cross-peaks of *positive* intensities and chemical exchange cross-peaks with *negative* intensities. The EXSY spectrum at 253 K where exchange is slow, shows no readily detectable cross-peaks of positive intensity suggesting that transient n.O.e.s can be ignored. Scalar coupling gives cross-peaks of both positive and negative intensities in the two-dimensional n.m.r. spectrum depending on the magnitude and sign. Since there were no cross-peaks of unusual lineshape in the spectrum it was concluded that scalar coupling effects were removed very effectively by random variation of the mixing time D9.

The values of the rate constants given in the Table are the mean and standard errors of the mean from at least eight calculations. The EXSY experiments were repeated at each temperature using different mixing times D9; typical values are 0.5 s at 273 K, 0.2 s at 303 K, and 0.1 s at 313 K. The FIDs in the two-dimensional data files were either Fourier-transformed directly (natural linewidths), or pre-multiplied with shifted sine-bell-squared or Gaussian apodization functions (mild signal-to-noise enhancement) before the two-dimensional Fourier transform. Volume integrals of the diagonal and cross-peaks in the spectrum were used as inputs for the D2DNMR program.[22] The sum of the integrals of each peak in the three slices of highest intensities (the slice of highest intensity and the ones immediately before and after) in the two-dimensional n.m.r. spectrum were also used as inputs, giving rate constants in good agreement with those from volume integrals. The rate constants obtained from the sum of the heights of each peak in the three slices of highest intensities gave rate constants which deviate significantly from those obtained from volume integrals. All these values of the rate constants were used in calculations of the mean and the associated errors.

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