Bonding Interactions Between Three Adjacent Hydrogen Ligands. Preparation and Spectroscopic Properties of the Tantalum and Niobium Complexes $[Ta(H)_3(C_5H_{5-n}R_n)_2]$ ($R = SiMe_3$, $n = 1$ or 2) and $[Nb(H_3)(C_5H_{5-n}R_n)_2]$ ($n = 1$, $R = Me$ or $SiMe_3$; $n = 2$, $R = SiMe_3$)

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The new title complexes of tantalum are true hydrides whereas the niobium complexes have bonding interactions among the three hydrogen atoms, as evidenced by short n.m.r. T_1 values and unusual couplings $^1J(H,H)$ which vary with temperature from less than 3 to about 100 Hz.

The properties of the niobiocene trihydride $[NbH_3(C_5H_5)_2]$ have been of much interest ever since Parshall and Tebbe[1] demonstrated its activation of carbon–hydrogen bonds. In particular, its ^1H n.m.r. properties have been found to be anomalous in many respects. The first study reported that the hydride gave two separate broad resonances at room temperature which sharpened at low temperature.[2] More recently, Curtis *et al.* observed a small temperature-dependence of the coupling constant $J(H,H)$ of the hydrido hydrogen which was not explained.[3] Similarly, the adduct of $[NbH_3(C_5H_5)_2]$ with $AlEt_3$ exhibits an unexplained, large value for $J(H,H)$.[2] We describe here the simple preparation, in high yield, of a series of niobium and tantalum trihydrides containing silylated cyclopentadienyl groups. If the tantalum complexes are regarded as 'classical' trihydrides, then the niobium ones are 'non-classical,' as judged from the anomalous ^1H n.m.r. properties, *viz.* short relaxation times (T_1) and large, temperature-dependent couplings [$^1J(H,H)$]. We suggest that this is evidence for the existence of a co-ordinated H_3 ligand (probably H_3^-). This is the second observation of such a phenomenon, the first being for $[RuH_3(C_5Me_5)(PR_3)]$[4] (R = Ph, Pr^i, or cyclo-C_6H_{11}), where the magnitude of $^1J(H,H)$ increased with temperature from 60 Hz at 170 K to 130 Hz at 203 K.[4b]† In the present case, the steric demands and the electron-withdrawing effect of the silylated cyclopentadienyl groups[7] play an important role in encouraging H–H bonding interactions. Studies of this type with substituted cyclopentadienyl ligands are rare.[7—10]

The reactions of the lithium derivatives LLi [$L = C_5H_4Me$, $C_5H_4SiMe_3$, or $C_5H_3(SiMe_3)_2$] with $NbCl_4(thf)_2$ (thf=tetrahydrofuran) leads to the paramagnetic Nb^{IV} complexes $NbCl_2L_2$. These complexes and those of tantalum[11] both react like $[NbCl_2(C_5H_5)_2]$[12] itself with $NaAlH_2(OCH_2CH_2OMe)_2$ in toluene to give, after hydrolysis and appropriate work-up, white to yellow complexes (**1**)—(**5**) analysing for MH_3L_2, in 60—70% yield.

$[NbH_3(C_5H_4Me)_2]$ (**1**)
$[NbH_3(C_5H_4SiMe_3)_2]$ (**2**)
$[NbH_3\{C_5H_3(SiMe_3)_2\}_2]$ (**3**)
$[TaH_3(C_5H_4SiMe_3)_2]$ (**4**)
$[TaH_3\{C_5H_3(SiMe_3)_2\}_2]$ (**5**)

The tantalum derivatives show AB_2 patterns with $^2J(A,B)$ *ca.* 10 Hz for the hydrido hydrogen in the ^1H n.m.r. spectra (Table 1), and this coupling does not change when the temperature is varied. This is consistent with a solution structure with three separate hydride ligands similar to the solid state one determined by neutron diffraction for $[TaH_3(C_5H_5)_2]$.[13] However, unusually large values for $^1J(H,H)$ of 36.5 and 70.0 Hz are observed for the niobium derivatives (**2**) and (**3**), respectively, which led us to study in detail the spectra and their temperature dependence. The results are shown in Figure 1.

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† Large H–H coupling constants in the ruthenium complex $[RuH_3(C_5Me_5)PMe_3]$ have been observed by Paciello and Bercaw;[5] Heynekey *et al.* have recently observed a similar effect in iridium compounds.[6]

Table 1. I.r. and ^{1}H n.m.r. data at room temperature for some niobium and tantalum trihydrides.[a]

		^{1}H N.m.r.				
Complex	ν(H–H)/cm^{-1}	δ_A	δ_B	J(A,B)/Hz	Solvent	Ref.
$[Ta(C_5Me_5)_2H_3]$	1745, 1695	+1.11	−0.91	13	C_6D_6	8
$[Ta(C_5Me_5)(C_5H_5)H_3]$	1750, 1720	+0.07	−1.53	11.8	C_6D_6	8
$[Ta(C_5H_4Me)_2H_3]$	1740	−0.69	−2.20	12.2	C_6D_6	1b
$[Ta(C_5H_4SiMe_3)_2H_3]$(**4**)	1760, 1710	−2.13	−3.29	8.8	C_6D_6	[b]
$[Ta\{C_5H_3(SiMe_3)_2\}_2H_3]$(**5**)	1760	−2.83	−3.73	7.3	C_6D_6	[b]
$[Nb(C_5Me_5)H_3]$	1745, 1695	−1.23	−2.31	4	C_6D_6	7
$[Nb(C_5H_4Me)_2H_3]$(**1**)	1705	−1.86	−2.89	10.4	C_6D_6	[b]
$[Nb(C_5H_5)_2H_3]$	1710	−2.75	−3.75	11.2	C_7D_8	3
$[Nb(C_5H_4SiMe_3)_2H_3]$(**2**)	1740	−2.85	−3.78	36.5	C_6D_6	[b]
$[Nb\{C_5H_3(SiMe_3)_2\}_2H_3]$(**3**)	1720	−3.57	−4.20	70.0	C_6D_6	[b]

[a] Note that, in the classical tantalum complexes, reducing the electron density on the metal causes a decrease in the chemical shift and coupling constant values, whereas the inverse occurs for the coupling constants in the niobium derivatives as a result of H–H bond formation.
[b] This work.

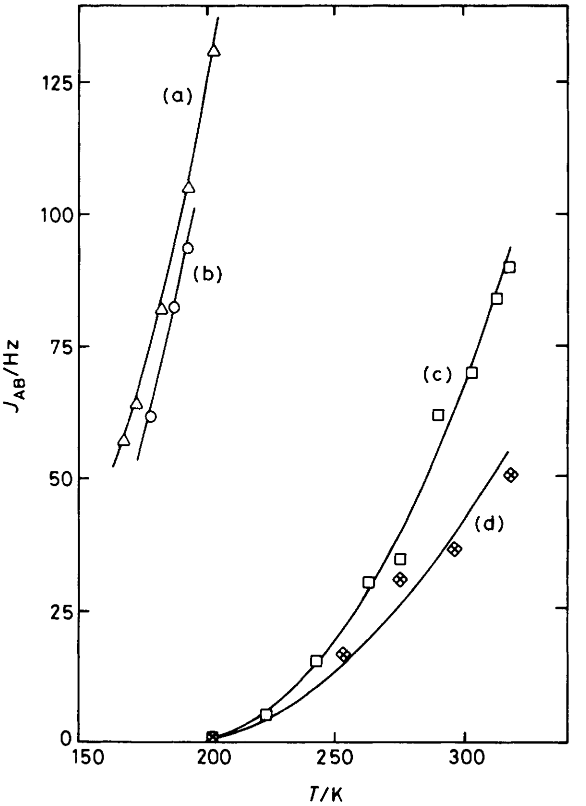

Figure 1. Variation of J(H,H) as a function of temperature in some non-classical 'trihydrides'; the ruthenium complexes are included for comparison: (a) $[RuH_3C_5Me_5PPr^i_3]$, (b) $[RuH_3C_5Me_5PCy_3]$, (c) $[NbH_3\{C_5H_5(SiMe_3)_2\}_2]$, (d) $[NbH_3(C_5H_4SiMe_3)_2]$.

The ^{1}H n.m.r. spectra show some features in common with those of the previously studied complexes $[RuH_3(C_5Me_5)(PR_3)]$: (a) the rapid exchange of the three hydrogen atom ligands at a 'high' temperature limit which varies with the ligand; (b) the observation at lower temperatures of AB_2 patterns where the coupling J(A,B) varies dramatically with temperature but the chemical shifts δ_A and δ_B do not. The size of these couplings suggest that they involve direct H–H bonding interactions.

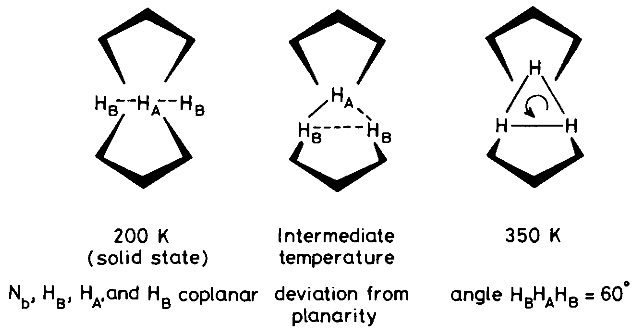

Figure 2. Proposed model for explaining the non-classical n.m.r. properties of the 'trihydrides'.

Curtis *et al.* have observed a small temperature dependence of the ^{1}H n.m.r. spectrum of $[NbH_3(C_5H_5)_2]$,[3] and also what was thought to be a field dependence of the spectra. We observed no field dependence in the room temperature spectra of (**2**) and (**3**). The variations of coupling constants could perhaps be explained by a change in the sign of J(A,B). However this is not the case since J(A,B) for (**2**) does not increase again after passing through zero at 223 K.

Variable-temperature i.r. studies have not yet proved informative. However the measurements of proton relaxation times, T_1, as a function of temperature for (**2**)—(**4**) were revealing. The value of T_1 for (**3**) in [$^2H_8$]toluene passes through a minimum of 40 ms at 205 K (at 200 MHz); minima for the smaller molecules (**2**) and (**4**) occur at a lower temperature, as expected [55 ± 5 ms for H_A and H_B of (**2**); 127 ± 15 ms for H_A and 196 ± 15 H_B of (**4**) at 223 K and 250 MHz]. The tantalum complex shows distinct T_1 values for H_A and H_B indicating a lack of exchange at all temperatures. A fit of standard equations for dipolar relaxation to the data gives an H_A–H_B distance of 1.77 Å, in good agreement with that of $[TaH_3(C_5H_5)_2]$ which was determined to be 1.85 Å.[13] The distance for the former is expected to be less as a result of steric congestion due to the $SiMe_3$ groups. In the calculation it was assumed that H_A has twice the relaxation rate of H_B. The different hydrido hydrogens of (**2**) and (**3**) show the same relaxation time at every temperature. The much shorter T_1 values than those of (**4**) are consistent with shorter H–H distances and H–H bonding. An analysis of the T_1 data is in progress. It is clear that the phenomenon described here for niobium cannot be explained in terms of a classical trihydride structure.

A hydrido dihydrogen structure could at first sight be invoked to explain the phenomenon. However some bonding must be present between the hydride and the dihydrogen in order to explain the large coupling constants (> 200 Hz) obtained in other related systems. We proposed in the ruthenium case the existence of a non-classical interation between a hydride and co-ordinated η^2-dihydrogen, in fact an open form of H_3 [Figure 2, structure (b)].[4b] Another possibility is that the structure starts from a trihydride at low temperature or in the solid state $H_BH_AH_B$ and Nb coplanar, as observed in the structure of $[TaH_3(C_5H_5)_2]$. This progresses through a static, angular array of H atoms deviating from the plane, with the H_B–H_B distance decreasing as the temperature increases until a triangular trihydrogen ligand is formed which begins to rotate to make all the H atoms equivalent at the 'high' temperature limit (see Figure 2). The angular structure might be the reason for the large coupling constants, and might explain the fact that the relaxation times of H_A and H_B are so similar while the chemical shifts remain distinct.

Finally it is interesting to note the similarity between these systems and the 'usual' molecular hydrogen derivatives. When transition metals with 5d electrons form polyhydrides with little or no H–H bonding {*e.g.* $[OsH_4(PPh_3)_3]$, or $[Os(H_2)(H)(depe)_2]^+$}, the corresponding 4d complex often contains strong H–H bonding interactions {*e.g.* $[Ru(H)_2(\eta^2\text{-}H_2)(PPh_3)_3]$ and $[Ru(H_2)(H)(depe)_2]^+$}[14,15] Furthermore the presence of the electron-withdrawing $SiMe_3$ groups in our niobium complexes favours further H–H interactions by reducing back donation into the antibonding orbital of the trihydrogen ligand.

It is not possible at present to distinguish between an open and a closed form of trihydrogen.‡ It is however clear from the data presented that a bonding interaction must be present between the three hydrogen atoms; the same conclusions have been reached recently by Heynekey *et al.* for the related $[CpIrH_3(PR_3)]^+$ complexes.[6] We are at present trying to obtain more information on the structure of these peculiar niobium complexes.

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‡ Recent calculations have suggested the existence of both species, the open form being the most stable.[16]