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Communications

Exchange Couplings in Lewis Acid Adducts of Substituted Niobiocene Trihydrides

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Exchange couplings in transition metal polyhydrides are presently attracting considerable interest[1-3] even if they were observed 20 years ago on Cp_2NbH_3 and alkylaluminium adducts of it.[4] Several trihydrides have been shown to display this behaviour, namely Ru,[1a-d,2c] Ir,[2a,b] Nb,[1e,2e,6] Os,[2c] and Mo[2e] compounds, all adopting the same geometry implying a planar array for the three hydrides and the metal. Exchange couplings between two hydrogen atoms only have been first observed by reacting a Lewis acid (Cu^+) with $Cp^*RuH_3PCy_3$[1b,d] and more recently in tantalum dihydrides.[5]

The quantum mechanical nature of this phenomenon was first recognized by Zilm et al.[6] and Weitekamp et al.,[7] but the physical processes responsible for it remains more obscure. We have addressed this problem using (i) theoretical calculations which demonstrated that niobium trihydrides possess a thermally accessible dihydrogen state whereas the tantalum ones do not,[8] (ii) NMR calculations which suggest that the phenomenon occurs because of rotational tunneling of H_2 in a slightly higher in energy dihydrogen state,[9] and (iii) an experimental approach in which we looked for the modification of exchange couplings induced by the modulation of the electronic density on the complex and by the chemical environment of the hydrides. We report in this communication a series of new adducts of substituted niobiocene trihydrides with Cu^+ and Ag^+, their spectroscopic properties, and a proposal for explaining them.

The niobiocene trihydrides[1e,4] $Cp^{\dagger}_2NbH_3$ ($Cp^{\dagger} = C_5H_5$(Cp), **1**, $C_5H_4SiMe_3$(Cp′), **2**, or $C_5H_3(SiMe_3)_2$(Cp″), **3**) react very rapidly with $[Cu(MeCN)_4]PF_6$ at room temperature in THF to give, after recrystallization from dichloromethane/hexane, the white crystalline complexes $\{(Cp^{\dagger}_2NbH_3)_2Cu\}PF_6$ ($Cp^{\dagger}$ = Cp (**4**), Cp′ (**5**), or Cp″ (**6**)) in high yield (>90%). A similar procedure, viz. reaction of **2** and **3** with $AgBF_4$ in THF and recrystallization from dichloromethane/hexane, led to the preparation of $\{(Cp^{\dagger}_2NbH_3)_2Ag\}BF_4$ ($Cp^{\dagger}$ = Cp′ (**7**) or Cp″ (**8**)) as white or light brown crystalline material in yields superior to 95%. This reaction was unsuccessful with **1** because of extensive decomposition of the product. Compounds **4**–**8** were characterized by classical microanalytical infrared and ^1H NMR methods.[10] Their proposed structure consists of two niobiocene trihydride units linked by the Lewis acid bonded to two hydrides of each unit (Figure 1). The most interesting data concern the hydride region in the high-field ^1H NMR spectra, which will be discussed hereafter as a function of the Lewis acid used.

The spectrum of any Nb–Cu complex is AB_2 at room temperature. It becomes ABC at low temperature in the case of **5** (coalescence near 235 K, $\Delta G^{\ddagger} = 43.5 \pm 0.5$ kJ·mol^{-1}) and **6** (coalescence near 220 K, $\Delta G^{\ddagger} = 40.5 \pm 0.5$ kJ·mol^{-1}). Compounds **5** and **6** show no H–H coupling despite a fairly narrow half-height width (7 Hz for **5** at room temperature). However, compound **4**, $\{(Cp_2NbH_3)_2Cu\}PF_6$, shows sharp signals for the hydrides (typical AB_2 pattern; J_{AB} = 15.8 Hz) and *no* variation of the spectrum as a function of temperature. This observation definitely rules out any influence of the niobium nucleus on the line width of the NMR signals and demonstrates for the first

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[10] NMR were on a WM250 Bruker at 250 MHz. For all compounds, satisfactory microanalyses were obtained. ^1H NMR in $(CD_3)_2CO$ at room temperature (ppm): **4**, 5.91 (s, 20H, C_5H_5), –4.26 (d, 4H), –6.20 (t, 2H, J_{HH} 16 Hz), **5**, 5.99, 5.35 (AA′BB′, 16H, C_5H_4, J_{app} 2.4 Hz), 0.43 (s, 36H, $SiMe_3$), –3.88 (s, 4H), –4.63 (s, 2H); **6**, 5.59 (d, 8H), 4.94 (t, 4H, J_{HH} 1.6 Hz, C_5H_3), 0.48 (s, 72H, $SiMe_3$), –4.13 (s, 4H), –5.1 (s, 2H); **7**, 5.99 (s, 4H), 5.33 (s, 4H), 0.36 (s, 36H), –3.67 (br s, 6H); **8**, 5.60 (s, 8H), 4.86 (s, 4H), C_5H_3), 0.48 (s, 72H, $SiMe_3$), –3 to –4 (m, 6H; see text).

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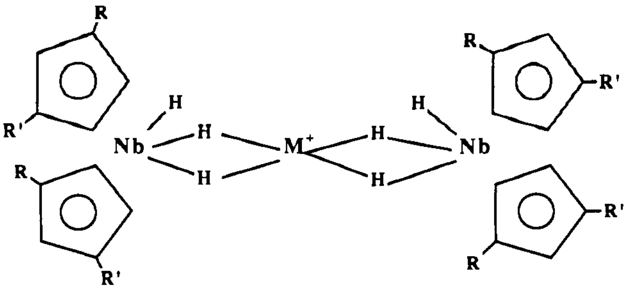


R = H, SiMe$_3$; R' = SiMe$_3$; M = Cu, Ag

Figure 1. Proposed structure for compounds **4**–**8** (M = Cu, R = R' = H (**4**); M = Cu, R = H, R' = SiMe$_3$ (**5**); M = Cu, R = R' = SiMe$_3$ (**6**); M = Ag, R = H, R' = SiMe$_3$ (**7**); M = Ag, R = R' = SiMe$_3$ (**8**).

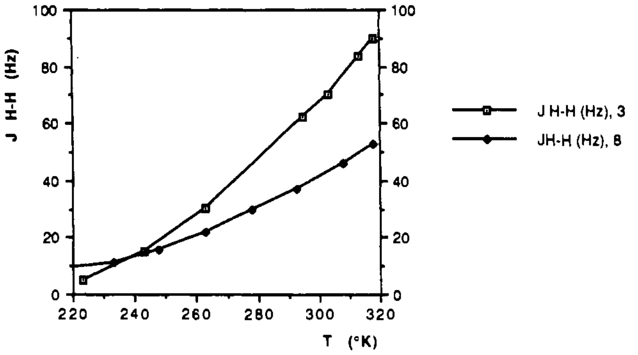


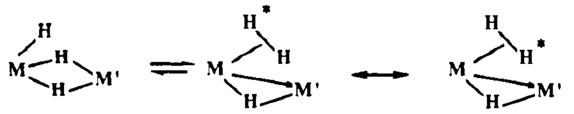
Figure 2. Variation of J_{H-H} $f(T)$ for complexes **3** and **8**.

time that exchange couplings can be suppressed, hence rendering apparent the magnetic coupling.

In the niobium–silver complex **7** the chemical shift difference between the hydrides, $\Delta\nu$, is too small to allow a clear visualization of the phenomenon. Compound **8** also shows an AB$_2$ spectrum and broadens at 188 K, but the low-temperature spectrum was not reached. The observed exchange-coupling constants are of the same order of magnitude as the starting niobium complex (**3**) itself but larger at low temperature and smaller at high temperature (see Figure 2). Ag is linked to two hydrides of each niobium moiety (J_{H_A-Ag} = 85.5 Hz; J_{H_B-Ag} = 37.5 Hz). It is noteworthy that J_{H_B-Ag} is not half of J_{H_A-Ag}, thus suggesting some asymmetry in the bonding of silver to these two kinds of hydrides.

Discussion. The presence of exchange couplings is very clear in the case of **8** and possible in the case of **5** and **6**. In the latter compounds, as in similar ruthenium ones,[1d] the presence of copper leads to an important reduction of the magnitude of the observed H–H couplings. In the case of **4** addition of Cu$^+$ on the long-studied complex **1** leads to the observation of usual magnetic couplings as for Cp$_2$TaH$_3$. This gives further evidence for the proposal of Heinekey, who suggests that in metallocene trihydrides the magnetic and exchange coupling constants are opposite in sign.[2e] Furthermore, in all copper cation adducts of metal trihydrides the variation with temperature of the H–H coupling constants is much less important than in the starting compound. This may explain the behavior observed for **5** and **6**, i.e. a spectrum resulting from the superposition of two coupling constants opposite in sign and showing a very small variation as a function of temperature.

Scheme I. Proposed Model for the Appearance of Exchange Couplings in Lewis Acid Adducts of Niobium Trihydrides



To account for these observations, we propose an alternative structure to the one shown in Figure 1 which could show a direct interaction between the niobium lone pair (in a thermally accessible dihydrogen state) and the Lewis acid (see Scheme I). This structure would be favored by reduction of electron density on niobium induced by the presence of the Lewis acid. A similar electron donation has been previously observed in a niobium–gold raft cluster.[11] The differences observed between copper and silver coordination could result from both a better overlap of the silver orbitals with the niobium ones and a stronger interaction between copper and the hydrides. The latter effect can be deduced from the observation that niobium–silver compounds are more fluxional and less stable than niobium–copper ones.

To conclude, this communication demonstrates that, as already observed, Lewis acid coordination influences but does not generally impede exchange couplings in trihydrides. This surprising fact could be due to a competition between coordination of the Lewis acid to two hydrides and coordination to one hydride and to the metal lone pair in a thermally accessible dihydrogen complex. Attempts to isolate such a complex with a metal leading to a stronger interaction with niobium are presently underway. Finally, it is worth noting the disappearance of exchange couplings in the copper adduct of Cp$_2$NbH$_3$, which definitely confirms that niobium is not responsible for the broad lines observed for the hydrides, and new evidence for the proposal that in these trihydrides magnetic and exchange couplings are opposite in sign.

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