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Synthesis, Spectroscopic Properties, and X-ray Crystal Structure of $\{[Nb(C_5H_3[SiMe_3]_2)_2H_3]_2Au\}^+$, a Complex Showing Large Quantum Mechanical Exchange Couplings

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Bis(cyclopentadienyl)niobium trihydrides[1] have been shown to exhibit quantum mechanical exchange couplings.[2] This phenomenon, also observed with other transition metal complexes, is characterized by the presence of large temperature-dependent H−H couplings between the hydrides.[3] Whereas the quantum mechanical nature of this phenomenon has been recognized by both Zilm[4] and Weitekamp,[5] the exact mechanism responsible for these couplings is still open to debate.[4,6] The reactions of such trihydrides with Lewis acidic coinage cations[3a,b] were anticipated to hinder any soft in-plane deformation of the hydrides and therefore, according to model 1, impede the tunneling phenomenon. The result was a strong decrease of the magnitude of exchange couplings in the presence of copper but a small variation in the presence of silver,[3b] which led us to study the gold adducts. We report hereafter the preparation and crystal structure of the complexes $\{[Nb(C_5H_3RR')_2H_3]_2Au\}^+$ (R = R′ = H (**1**); R = H, R′ = $SiMe_3$ (**2**); R = R′ = $SiMe_3$ (**3**)), which display exchange couplings much larger than the starting trihydrides $[Nb(C_5H_3RR')_2H_3]$.

Complexes **1**−**3** were synthesized in high yield upon addition of "$Au(THT)PF_6$" (THT = tetrahydrothiophene), prepared in situ from AuCl(THT) and $TlPF_6$, to $[Nb(C_5H_3RR')_2H_3]$ in THF and recrystallization from THF/Et_2O. Experimental details and full characterization of the complexes are given in the supplementary material. The high-field ^1H NMR spectra of **1**−**3** all show large temperature-dependent couplings. According to the complex and the temperature, the signal shows an AB_2 or an ABC pattern. In the AB_2 case, the observed coupling constant J_{obs} is the sum of the usual magnetic and exchange components (two magnetic and one exchange coupling constants). In these trihydrides, it was found that exchange and magnetic couplings have opposite signs; therefore, $J_{obs} = {}^1/_2(J_{ex} - J_{ab/mag} - J_{bc/mag})$. In the ABC case, if H_b and H_c show exchange couplings, then $J_{bc/obs} = J_{ex} - J_{bc/mag}$.

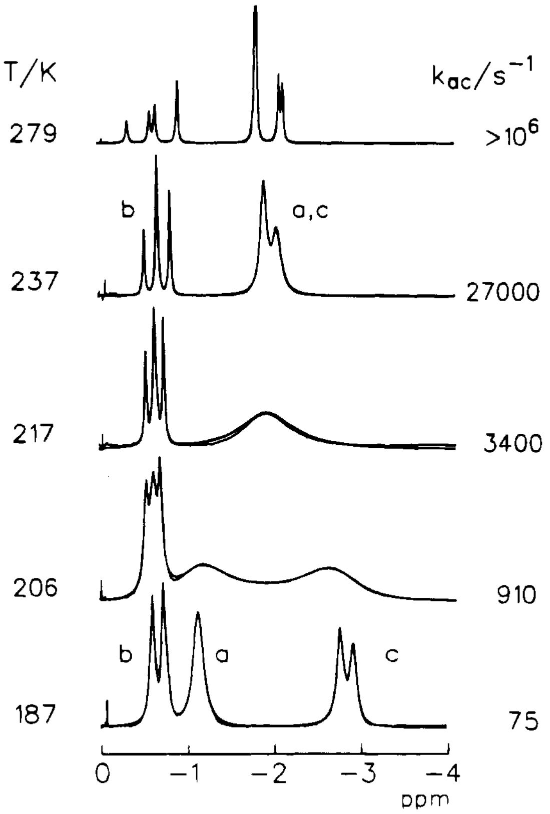

Figure 1. 500-MHz high-field ^1H NMR spectra of **3** in Freons at various temperatures and line-shape analysis. Signals a−c represent respectively H[1H], H[2H], and H[3H].

The superposed experimental and calculated 500-MHz hydride signals of **3** dissolved in a Freon mixture are shown on Figure 1 as a function of temperature. For the calculations,

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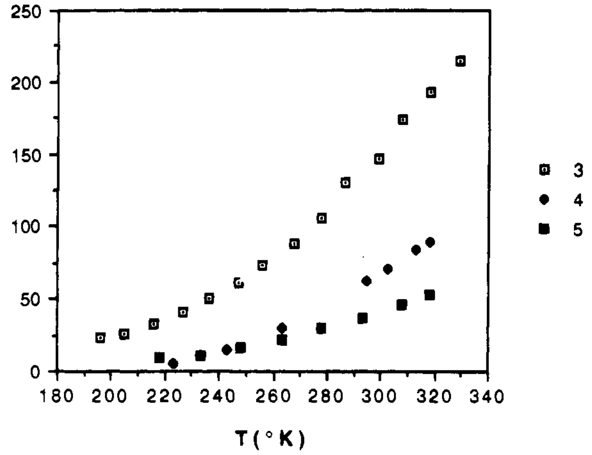

Figure 2. Variation of the observed J_{H-H} as a function of temperature for **3** (in THF-d_8), $[Nb(C_5H_3[SiMe_3]_2)_2H_3]$ (**4**, in toluene-d_8), and $\{[Nb(C_5H_3[SiMe_3]_2)_2H_3]_2Ag\}^+$ (**5**, in acetone-d_6).

the usual density matrix formalism for intramolecular exchange was used.[7] At 187 K, an ABC pattern is observed where J_{bc} = 70.8 Hz represents the algebric sum of a quantum coupling strongly increasing with temperature and of a magnetic coupling ($J_{bc} = J_{ex} - J_{bc/mag}$). A good fit of the spectra could be obtained by setting $J_{ab/mag} = -16$ Hz in the whole temperature range covered. As temperature increases, signals a and c broaden and coalesce. At the same time a doublet–triplet transition is observed for signal b. At 237 K a typical AB_2 pattern results where J_{bc} = 156 Hz. The process which renders signals a and c equivalent corresponds to gold jumping from H_a to H_c while remaining linked to H_b; it involves an energy of activation of ca. 45 kJ·mol^{-1} and a frequency factor of 10^{14} s^{-1}. Similar results are obtained for THF-d_8 as solvent, where, however, the J_{bc} couplings are smaller, e.g. 138 Hz at 237 K, but reach a value of 363 Hz at 308 K. In THF-d_8, broadening and coalescence of the AB_2 pattern are observed at high temperature, arising from a fluxional process rendering all hydrides equivalent. This process is likely to involve the rotation of a dihydrogen molecule and exhibits an energy of activation of ca. 60 kJ·mol^{-1} and a frequency factor of about 10^{13} s^{-1}.

It is clear that complexes **1**–**3** show H–H coupling constants larger than the starting niobium trihydrides, which was totally unexpected. For example, Figure 2 shows the variation of observed J_{H-H} as a function of temperature for **3**, the niobium trihydride precursor $[Nb(C_5H_3[SiMe_3]_2)_2H_3]$ (**4**),[2d] and the silver adduct $\{[Nb(C_5H_3[SiMe_3]_2)_2H_3]_2Ag\}^+$ (**5**; for the purpose of comparison, we have plotted J_{obs} of **4** and **5**, which both show AB_2 spectra, whereas for **3** we give J_{obs} in the AB_2 temperature range and a calculated value corresponding to $^1/_2(J_{bc} - J_{ab/mag})$ in the ABC temperature range).[3b] The structure of the cation of **3**,[8] which shows an imposed C_2 symmetry, is depicted in Figure 3. The most important results are the following. The metal core consists of an almost linear arrangement of Nb, Au, and Nb atoms in which the Nb–Au separation is 2.965(1) Å, comparable to those of other niobium–gold hydrido clusters which lie between 2.99 and 2.91 Å,[9] and the NbAuNb′ is angle 175.92(2)°. The coordination around the Au atom is intermediate between tetrahedral and square planar (the dihedral angle between the planes H[1H]AuH[2H] and H[1H]′AuH[2H]′ is 23(5)°). In addition, the structure shows the presence of two hydrides close to one another (H[2H]–H[3H] = 1.45(14) Å) while H[2H] occupies a bridging position between Nb and Au (Nb–H[2H] = 1.94(10) Å, Au–H[2H] = 1.84(10) Å, Nb–H[3H] = 1.77(10) Å); the third hydride occupies a normal bridging position between Nb and Au (Nb–H[1H] = 1.77(10) Å, Au–H[1H] = 1.76(10) Å). These results must be considered with great care because of the uncertainty in the locations of the hydrides by X-ray crystallography, e.g. the large esd's associated with their locations; however, the geometry around gold suggests a significant contribution of direct metal–metal bonding, which in turn implies the reduction of the niobium(V) trihydride to a niobium(III) dihydrogen complex.

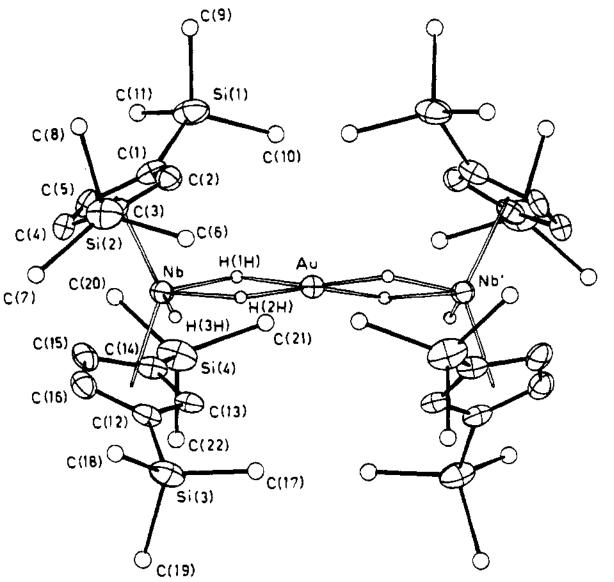

Figure 3. ORTEP view of **3**. Important bond distances: Nb–Au = 2.965(1) Å; H[2H]–H[3H] = 1.45(14) Å; Nb–H[1H] = 1.77(10) Å, Au–H[1H] = 1.76(10) Å; Nb–H[2H] = 1.94(10) Å; Au–H[2H] = 1.84(10) Å; Nb–H[3H] = 1.77(10) Å. A complete list of bond distances and angles is given in the supplementary material.

In conclusion, we report in this paper an unusual niobium–gold complex. The geometry around gold and the locations of the hydrides suggest a significant narrowing of the distance between one of the bridging hydrides and the terminal hydride whereas the observation by NMR of large quantum mechanical exchange couplings is in agreement with this narrowing and compatible with our proposal that rotational tunneling of dihydrogen could be the origin of this phenomenon.

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Supplementary Material Available: Full textual details of the synthesis and characterization of **1**–**3**, 500-MHz high-field ^{1}H NMR spectra of **3** in THF at various temperatures and line-shape analysis (Figure 4), 500-MHz high-field ^{1}H NMR spectra of **3** in Freons at very low temperatures (Figure 5), and Tables S1–S6, giving atom coordinates and isotropic thermal parameters, anisotropic thermal parameters for the non-hydrogen atoms, complete bond distances and angles, weighted least-squares planes, and crystallographic data for **3** (18 pages). Ordering information is given on any current masthead page.

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