**Synthesis, Spectroscopic Properties, and X-ray Crystal Structure of [{Nb(C₅H₅)₃SiMe₃}₂H₃]⁺, a Complex Showing Large Quantum Mechanical Exchange Couplings**

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Bis(cyclopentadienyl)niobium trihydrides have been shown to exhibit quantum mechanical exchange couplings. This phenomenon, also observed with other transition metal complexes, is characterized by the presence of large temperature-dependent H-H couplings between the hydrides. Whereas the quantum mechanical nature of this phenomenon has been recognized by both Zilm and Weitekamp, the exact mechanism responsible for these couplings is still open to debate. The reactions of such trihydrides with Lewis acidic coinage cations 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, which led us to study the gold adducts. We report hereafter the preparation and crystal structure of the complexes [{Nb(C₅H₅R')₂H₃}⁺ (R = R' = H (1); R = H, R' = SiMe₃ (2); R = R' = SiMe₂ (3)), which display exchange couplings much larger than the starting trihydrides [{Nb(C₅H₅R')₂H₃}].

Complexes 1–3 were synthesized in high yield upon addition of "Au(THT)PF₆" (THT = tetrahydrothiophene), prepared in situ from AuCl(THT) and TIPF₆, to [Nb(C₅H₅R')₂H₃] in THF and recrystallization from THF/Et₂O. 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 AB₂ or an ABC pattern. In the AB₂ case, the observed coupling constant Jₐₕ 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, Jₐₕ = ½(Jₑₓ - Jₐₕ/mag - Jₐₕ/cmag). In the ABC case, if Hₕ and Hₗ show exchange couplings, then Jₐₕ = Jₑₓ - Jₐₕ/cmag.

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 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].

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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 algebraic sum of a quantum coupling strongly increasing with temperature and of a magnetic coupling \((J_{bc} = J_{benzyl})\). A good fit of the spectra could be obtained by setting \(J_{obmags} = -16\) 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 AB2 pattern results where \(J_{bc} = 156\) Hz. The process which renders signals a and c equivalent corresponds to gold jumping from \(H_3\) to \(H_2\) while remaining linked to \(H_2\); it involves an energy of activation of ca. 45 kJmol\(^{-1}\) and a frequency factor of 10\(^{14}\) s\(^{-1}\). Similar results are obtained for THF-d\(_4\) 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 AB2 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 kJmol\(^{-1}\) 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 \(J_{bc-H-H}\) as a function of temperature for 3 (in THF-d\(_4\)), \([\text{Nb}(C_5H_5(SiMe_3)_2)H_3]\) (4, in toluene-d\(_8\)), and \([\text{[Nb}(C_5H_5(SiMe_3)_2)H_3]_2\text{Ag}]^{+}\) (5, in acetone-d\(_6\)).

Figure 2. Variation of the observed \(J_{bc-H-H}\) as a function of temperature for 3 (in THF-d4), \([\text{Nb}(C_5H_5(SiMe_3)_2)H_3]\) (4, in toluene-d8), and \([\text{[Nb}(C_5H_5(SiMe_3)_2)H_3]_2\text{Ag}]^{+}\) (5, in acetone-d6).

The geometry around gold and the locations of the niobium-gold hydrido clusters 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, and the NbAuNb\(^{+}\) is angle 175.92(2)°. The coordination around the Au atom is intermedi-

\(^7\) Binsch, G. J. Am. Chem. Soc. 1969, 91, 1304.

\(^8\) Crystal data and refinement: see 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 bridges 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.