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# Observation of a Complex Formed between RhH$_2$ and CH$_4$ Molecules

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Electron-spin-resonance (ESR) spectroscopy has revealed that the RhH$_2$ (X$^2$A$_1$) molecule is strongly complexed with CH$_4$ in argon matrices at low temperatures. The spectrum of RhH$_2$, previously observed and analyzed[1] is found to be replaced by the distinctive spectrum of RhH$_2$–CH$_4$ during the addition of relatively small amounts of CH$_4$. The complex is unique and interesting in its own right but also perhaps for its relevance to Rh catalyst interactions. Rhodium is well-known as a catalytically versatile transition metal, and although the conditions here are far from that application, the hydride–methane interaction may be instructive.

It is necessary to first discuss the ESR[1] and theoretical[2] results for RhH$_2$; its X-band spectrum is shown in Figure 1A. Both experiment and theory agree that it has a bent ($C_{2v}$) structure with a $^2$A$_1$ ground state. Two low-lying excited states $^2$A$_2$ and $^2$B$_1$ are coupled to the X$^2$A$_1$ state to produce large shifts (from $g_e$) in $g_z$ and $g_y$, respectively, resulting in the two sets of strong doublets in Figure 1A. $g_x$ is at higher field, near $g_e$. (Here $z$ lies along the $C_2$ axis and $y$ is in the plane of the molecule). The doublets are the result of hyperfine splitting (hfs) due to the interaction of the unpaired spin with the $^{103}$Rh ($I = {}^1/_2$) nucleus. Also, each of the four lines is seen to be split into a triplet by much smaller hf interactions with the two equivalent $^1$H ($I = {}^1/_2$) nuclei. The magnetic parameters for the RhH$_2$ molecule in an argon matrix at 4 K[1] are given in Table I.

Figures 1B and C indicate how the spectrum of RhH$_2$ changes when increasing amounts of methane are introduced into the argon. (The experimental procedure was the same as in the previous study[1] but with methane (Matheson, ≥99.97% purity) added to the argon). Even in Figure 1A, where the argon contains an added ~0.001% of CH$_4$, there are indications of new signals at low and high fields. The CH$_4$ is increased to only 0.01% in Figure 1B, and the spectrum clearly shows the doublet centered at ~2210 G and the strengthening of the features near 2750 G. When the concentration of methane is increased by a factor of about 10 (see Figure 1C), the signals due to the unperturbed RhH$_2$ molecule in argon almost disappear and are replaced by two strong doublets with a spacing of 77(1) G. It is seen that $g_z$ (the low-field doublet) is more affected by the complex formation than $g_y$, but the $^{103}$Rh hfs has increased only slightly, from 70[1] to 77 G. The other noticeable hf effect is the narrowing and increase in intensity of the two lines associated with $g_z$, whereas the high-field doublet still shows about the same $^1$H hfs as in uncomplexed RhH$_2$. Attempts to resolve any splittings in the two lines centered at 2210 G were not successful, indicating that $|A_z(^1\text{H})|$ is less than about 5 G. Thus, anisotropy has developed in the hf interaction at the two hydrogen nuclei in complexed RhH$_2$. Column three of Table I lists the new magnetic parameters of the RhH$_2$–CH$_4$ complex.

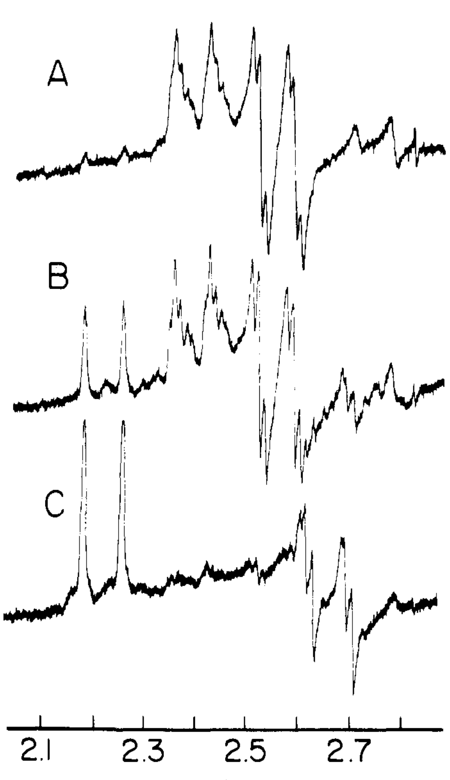

**Figure 1.** ESR spectra of the RhH$_2$ molecule and the RhH$_2$–CH$_4$ complex in an argon matrix at 4 K ($\nu$ = 9.5586 GHz). (A) Spectrum of the $^{103}$Rh$^1$H$_2$ molecule in argon containing a trace of CH$_4$ (this spectrum is essentially the same as that in Figure 2, ref 1), (B) in argon containing approximately 0.01% CH$_4$, and (C) in argon containing about 0.1% CH$_4$.

**Table I.** Magnetic Parameters of the RhH$_2$ Molecules and the RhH$_2$–CH$_4$ Complex in Argon Matrices at 4 K

| parameter | RhH$_2$ | RhH$_2$/CH$_4$ |
|---|---|---|
| $g_x$ | (2.002) | (2.002) |
| $g_y$ | 2.6814(9) | 2.5793(9) |
| $g_z$ | 2.8632(9) | 3.0915(9) |
| $\lvert A_x(^{103}\text{Rh})\rvert$ (MHz) | 280(60) | 322(60) |
| $\lvert A_y(^{103}\text{Rh})\rvert$ (MHz) | 248(1) | 281(1) |
| $\lvert A_z(^{103}\text{Rh})\rvert$ (MHz) | 276(1) | 324(1) |
| $\lvert A_y(^1\text{H})\rvert$ (MHz) | 44(3) | 54(3) |
| $\lvert A_z(^1\text{H})\rvert$ (MHz) | 44(3) | <22 |

The dipole moment of the dihydride has been calculated as 2.67 D in the Rh$^+$H$_2^-$ direction,[2] and the complexing is expected to result from dipole-induced dipole interaction with the CH$_4$. (We assume, in these dilute conditions, that only one CH$_4$ is interacting with each RhH$_2$ molecule.) A possible model could assume that optimum approach places a CH$_2$ group of methane in the $zx$ plane perpendicular to the plane of RhH$_2$, such that the conformation is H$_2^-$–Rh$^+$···H$_2^{(-)}$–CH$_2^{(+)}$. Then the principal perturbation of the orbital containing the unpaired spin, which is largely on the Rh atom, is through interaction with the two hydrogens of methane. Complexation appears to leave the ground-state orbital of RhH$_2$ largely unaffected if judged by the small changes in hyperfine splittings; however, the $g_z$ and $g_y$ values are significantly shifted. These shifts are determined by the interaction with orbitals occupied in the excited states relative to that in the ground state. If this is ascribed to shifts in the energy level spacings, then the $^2$A$_2$ state, calculated to lie at 0.53 eV in RhH$_2$,[2] must decrease in energy relative to the X$^2$A$_1$ state to account for the increase in $\Delta g_z$, while the $^2$B$_1$ (at 0.68 eV[2]) would rise in energy to account for the decrease in $\Delta g_y$. Crudely, the spin in these two states occupies d$_{xy}$ (a$_2''$) and d$_{xz}$ (b$_1''$) orbitals, respectively, so that one can rationalize differences in their interactions with the negatively-polarized hydrogens on the CH$_4$.

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(1) Van Zee, R. J.; Li, S.; Hamrick, Y. M.; Weltner, W., Jr. *J. Chem. Phys.* **1992**, *97*, 8123–8129.

(2) Balasubramanian, K.; Liao, D.-W. *J. Phys. Chem.* **1988**, *92*, 6259–6264.

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Other models would show orientation of the $CH_2$ group in the plane of the $RhH_2$, interaction through a single H–C of $CH_4$, or possibly an alteration of the H–Rh–H angle in the complex. Theoretical calculations would be of value in understanding the interactions.

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