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A Novel Application of para H_2: the Reversible Addition/Elimination of H_2 at a Ru_3 Cluster Revealed by the Enhanced NMR Emission Resonance from Molecular Hydrogen

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Polarization transfer from the NMR silent p-H_2 to o-H_2 is possible through the intermediacy of a triruthenium bis-hydride cluster. In fact, a strong emission signal for the molecular H_2 resonance is observed when p-H_2 is allowed to react with $Ru_3(CO)_{11}(NCCH_3)$ in the NMR tube at RT. The break of symmetry in p-H_2 is achieved at the intermediate $H(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}$ compound where the two hydrides form an AX spin system; the build-up of the longitudinal magnetization leaves a "memory" of this intermediate in the signal of the H_2 molecule formed by reductive elimination from the bis-hydride species. The observed behavior is fully accounted for in terms of the established relaxation theory.

Introduction

The exploitation of p-H_2 effects in NMR spectra was introduced about twelve years ago by the seminal work of Weitekamp and Eisenberg;[1−3] since then a number of systems have been investigated, mainly to detect species formed in very low amounts in hydrogenation reactions.[4−7] In fact, the transfer of magnetization order to the hydrogenated products yields extraordinary enhancements of the NMR signals which, in theory, may reach values as high as 10^5 times the signal intensity of the corresponding derivatives produced with normal H_2.[3]

In this communication we report on the polarization transfer from the NMR silent p-H_2 to o-H_2, via the intermediacy of the triruthenium carbonyl cluster $H(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}$.

Experimental Section

All solvents were stored over molecular sieves and purged with nitrogen before use.

H_2 was purchased from SIAD (Bergamo, Italy) and used without further purification. Para-enriched hydrogen (about 50%) was prepared by storing H_2 over Fe_2O_3 at 77 K for 3−4 h.

$Ru_3(CO)_{11}(NCCH_3)$ was prepared according to the published method.[8]

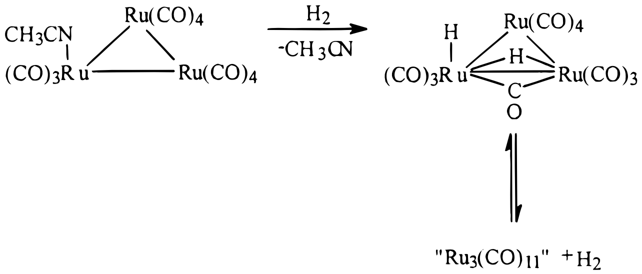
The reactions between the cluster and p-H_2 were carried out in a 5 mm resealable NMR tube. Para-H_2 was added to frozen solutions of the cluster; the sample was then warmed to RT, shaken and introduced into a JEOL EX-400 spectrometer operating at 399.65 MHz. Single scan ^1H spectra were recorded at different times after the introduction of the sample in the magnet.

The nonselective inversion recovery pulse sequence was used to obtain T_1 values.[9]

Results and Discussion

$Ru_3(CO)_{11}(NCCH_3)$ is known to react with H_2 to give $H(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}$, which, contrary to the analogous Os derivative,[10] contains a bridging carbonyl ligand.[11] This minor structural change appears responsible for the noticeable difference in reactivity with respect to the Os case. At room temperature, $H(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}$ is in equilibrium with the coordinatively unsaturated "$Ru_3(CO)_{11}$" species and H_2 (Scheme 1). In fact, $H(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}$ can be preserved only under H_2 pressure.

SCHEME 1



A typical single-scan ^1H NMR spectrum obtained by reacting p-H_2 and $Ru_3(CO)_{11}(NCCH_3)$ in the NMR tube is shown in Figure 1. The spectrum is characterized by several emission signals, in addition to the absorption peaks at 5.33 ppm (residual $CHDCl_2$ in the solvent), 1.99 ppm (free acetonitrile), and 1.50 ppm (traces of water). The most intense emission peak (at 4.61 ppm) corresponds to the free hydrogen. Two broad signals centered at −11.3 and −16.6 ppm, respectively, are assigned to the terminal and bridging hydride ligands of $H(\mu\text{-}H)Ru_3(CO)_{10}(NCCH_3)$ which is present as impurity. (Note: The presence of some $H(\mu\text{-}H)Ru_3(CO)_{10}(NCCH_3)$ is due to traces of $Ru_3(CO)_{10}(NCCH_3)_2$ in the starting material which yields $H(\mu\text{-}H)Ru_3(CO)_{10}(NCCH_3)$ when H_2 is added.) The resonances of $H(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}$ appear as very broadened humps at ca. −13.7 and −18.2 ppm, respectively. The broadening of these resonances reflects the dynamic state of the ligands, as previously established for $H(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}$.[11] (In principle, in these ALTADENA experiments the hydride resonances of $H(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}$ should appear as one adsorption and one emission, whereas they were invariably observed as broad emission signals. This behavior may be accounted for

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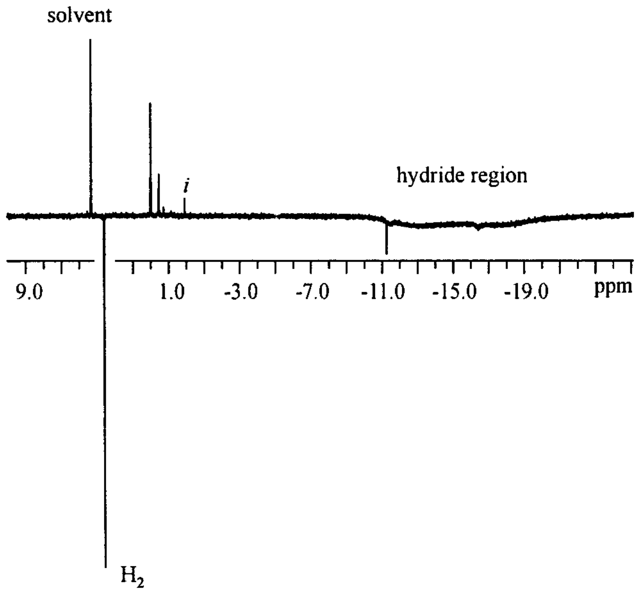


Figure 1. ^{1}H NMR spectrum obtained from the reaction of $Ru_3(CO)_{11}$-$(NCCH_3)$ (6.0 mg) and H_2 (ca. 3 atm, 50% p-H_2) in CD_2Cl_2 (ALTADENA,[14] RT, single scan).

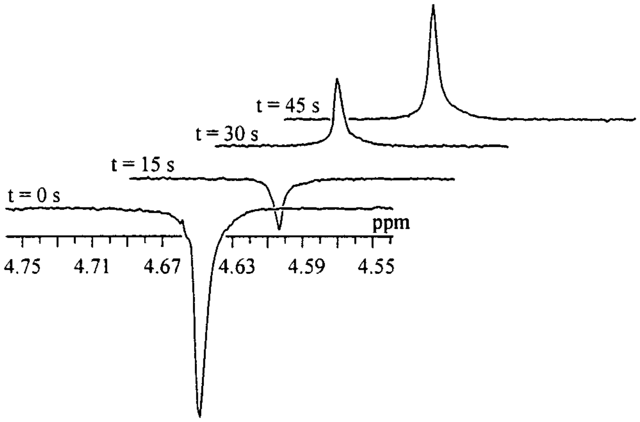


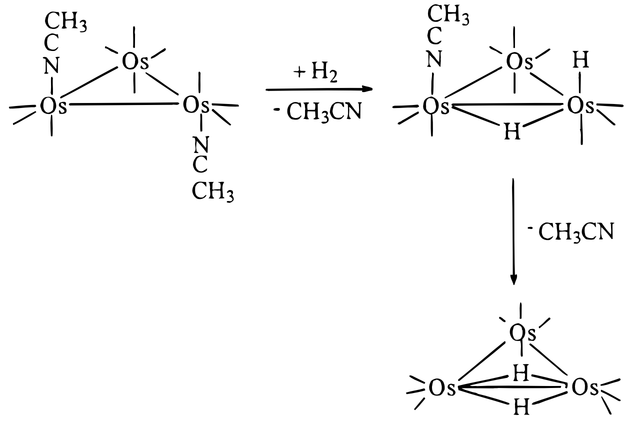
Figure 2. Recovery of the molecular hydrogen signal intensity obtained by introducing different delays (t) before the acquisition of the ^{1}H NMR spectrum.

by the exchange occurring between the terminal and the bridging hydrides, and the resulting emission signal clearly reflects the dominance of the emission part over the absorption part in the AX spin system in the absence of exchange (vide infra).) The negative, sharp signal at −11.26 ppm could be assigned to the elusive $(\mu\text{-H})_2Ru_3(CO)_{10}$ for the similarity of its chemical shift with that of the related $(\mu\text{-H})_2Os_3(CO)_{10}$.[12] However, the chemical shift value reported by Leadbeater et al. for the photochemically generated $(\mu\text{-H})_2Ru_3(CO)_{10}$[13] appears significantly different from that observed by us, causing the assignment of this resonance to be unclear.

When some delay is allowed between the time the sample reaches the probe-holding inside the magnet and the acquisition of the spectrum, the emission signal due to H_2 quickly decreases, disappears into the baseline, then an absorption peak appears whose intensity steadily grows to reach a constant value characteristic of the amount of hydrogen present (Figure 2).

Different experiments with variable cluster concentrations and p-H_2 pressures showed a direct proportionality of the H_2 emission signal intensity upon both factors. Analogous experiments performed in $CDCl_3$ and toluene-d_8 showed patterns in the hydride region analogous to that shown in Figure 1, whereas the signal assigned to free hydrogen, although drastically reduced (in some cases completely missed), never appeared as a strong emission as shown in Figure 1. This behavior is probably due to the lower solubility of the cluster in these solvents with respect to dichloromethane.

SCHEME 2



Which is the rational for the observed behavior?

From early NMR experiments,[1−7] two basic requirements were thought to be necessary to make the detection of p-H_2 effects possible: (i) both of the hydrogen atoms of p-H_2 must add to the same substrate molecule and (ii) the two added hydrogen atoms must be magnetically nonequivalent in the hydrogenated derivative. Successively, Bargon and co-workers showed that an enhanced line is also visible for systems containing two equivalent protons.[14] We confirmed this possibility by detecting a strong NMR enhanced emission signal for the equivalent hydrides of the $(\mu\text{-H})_2Os_3(CO)_{10}$ derivative obtained by the reaction of p-H_2 with $Os_3(CO)_{10}(NCCH_3)_2$.[15]

This finding was accounted for on the grounds of the occurring mechanism (Scheme 2). According to this scheme, the A_2 spin system of p-H_2 is first transformed into the AX spin system of the intermediate $H(\mu\text{-H})Os_3(CO)_{10}(NCCH_3)$ and then back again to an A_2 spin system in $(\mu\text{-H})_2Os_3(CO)_{10}$.

In an analogous way, in the experiment reported in this communication, there is a polarization transfer from p-H_2 to the AX spin system of $H(\mu\text{-H})Ru_3(\mu\text{-CO})(CO)_{10}$ and then to o-H_2 which is formed from the dihydride complex through the dissociative pathway depicted in Scheme 1: the otherwise forbidden singlet (p-H_2) to triplet (o-H_2) transition is then made possible through the intermediacy of the bis-hydride derivative.

To get more insight into the observed behavior we must rely on the full treatment of longitudinal relaxation in a homonuclear AX spin 1/2 system; it can be described by extended Solomon equations[16]

$$\frac{d}{dt}I_z^{A} = -R_1^{A}(I_z^{A} - I^{eq}) - \sigma_{AX}(I_z^{X} - I^{eq}) - \sigma_{CSA(A),d}(2I_z^{A}\,I_z^{X}) \quad (1)$$

$$\frac{d}{dt}I_z^{X} = -R_1^{X}(I_z^{X} - I^{eq}) - \sigma_{AX}(I_z^{A} - I^{eq}) - \sigma_{CSA(X),d}(2I_z^{A}\,I_z^{X}) \quad (2)$$

$$\frac{d}{dt}(2I_z^{A}\,I_z^{X}) = -R_1^{AX}(2I_z^{A}\,I_z^{X}) - \sigma_{CSA(A),d}(I_z^{A} - I^{eq}) - \sigma_{CSA(X),d}(I_z^{X} - I^{eq}) \quad (3)$$

where $I_z^{A,X}$ represents A and X longitudinal polarizations and 2 $I_z^{A}\,I_z^{X}$ the longitudinal spin order, I^{eq} being the thermal equilibrium value. R_1^{A}, R_1^{X}, and R_1^{AX} are specific longitudinal relaxation rates; σ_{AX} is the usual cross-relaxation rate; $\sigma_{\mathrm{CSA(A)},d}$ and $\sigma_{\mathrm{CSA(X)},d}$ are the so-called interference terms corresponding to cross correlation between the chemical shift anisotropy mechanism (CSA) at A and X nuclei respectively with the dipolar (d) interaction between the two A and X spins:[17]

$$\sigma_{\mathrm{CSA(A,X)},d} = -\frac{1}{5}\left(\frac{\mu_0}{4\pi}\right)\Delta\sigma_{(\mathrm{A,X})}\frac{B_0\gamma^3\hbar}{r_{\mathrm{AX}}^3}(3\cos^2\theta_{\mathrm{A,X}} - 1) \qquad (4)$$

where the various symbols have their usual meaning: $\Delta\sigma$ is the shielding anisotropy in the (assumed) case of an axial symmetry shielding tensor, whereas $\theta_{\mathrm{A,X}}$ is the angle between this symmetry axis and the r_{AX} dipolar vector. On grounds of eqs 1−3, transfer between longitudinal polarizations and longitudinal spin order can occur through chemical shift anisotropy and interference terms. This property lends itself to a possible means of polarization enhancement from p-H_2 through relaxation processes. It is, however, interesting to note that, because we are dealing with a reaction performed out of the magnet (the so-called ALTADENA experiment[18]), only one of the $\alpha\beta$ or $\beta\alpha$ spin states becomes populated (the one which has the lowest energy) after adiabatic insertion of the sample into the magnet. Assuming the $\alpha\beta$ spin state is actually populated, the density operator at time zero (i.e., when relaxation processes begin) can be written as[19]

$$\hat{\sigma}(0) = K[\hat{E}/2 - (2\hat{I}_z^{\mathrm{A}}\hat{I}_z^{\mathrm{X}}) + \hat{I}_z^{\mathrm{A}} - \hat{I}_z^{\mathrm{X}}] \qquad (5)$$

In eq 5, K is a factor arising from the initial p-H_2 polarization which should be very large (possibly of the order of 10^5 times the conventional equilibrium polarization I^{eq}), $\hat{E}$ is the identity operator, and $\hat{I}_z^{\mathrm{A}}$ and $\hat{I}_z^{\mathrm{X}}$ are the z components of the A and X spin operators, respectively. It is then a simple matter to calculate the initial value of the quantities G involved in eqs 1−3 through the relation $G(0) = Tr[\hat{\sigma}(0)\hat{G}]$

$$I_z^{\mathrm{A}}(0) = K$$

$$I_z^{\mathrm{X}}(0) = -K$$

$$2I_z^{\mathrm{A}}I_z^{\mathrm{X}}(0) = -K \qquad (6)$$

In fact, the quantity of interest is $(I_z^{\mathrm{A}} + I_z^{\mathrm{X}})$ which will become $(I_z^{\mathrm{A}} + I_z^{\mathrm{A'}})$ in the A_2 spin system and therefore be detected at the outcome. Equations 1 and 2 can be added to yield

$$\frac{d}{dt}(I_z^{\mathrm{A}} + I_z^{\mathrm{X}}) = -(R_1^{\mathrm{A}} + \sigma_{\mathrm{AX}})I_z^{\mathrm{A}} - (R_1^{\mathrm{X}} + \sigma_{\mathrm{AX}})I_z^{\mathrm{X}} + (R_1^{\mathrm{A}} + R_1^{\mathrm{X}} + 2\sigma_{\mathrm{AX}})I^{\mathrm{eq}} - (\sigma_{\mathrm{CSA(A)},d} + \sigma_{\mathrm{CSA(X)},d})(2I_z^{\mathrm{A}}I_z^{\mathrm{X}}) \qquad (7)$$

To gain some insight into the evolution of $(I_z^{\mathrm{A}} + I_z^{\mathrm{X}})$, we can expand eq 7 to first order

$$(I_z^{\mathrm{A}} + I_z^{\mathrm{X}})(t) = (I_z^{\mathrm{A}} + I_z^{\mathrm{X}})(0) + t\left[\frac{d}{dt}(I_z^{\mathrm{A}} + I_z^{\mathrm{X}})\right]_{t=0}$$

$$(I_z^{\mathrm{A}} + I_z^{\mathrm{X}})(t) = t(R_1^{\mathrm{X}} - R_1^{\mathrm{A}})K + t[\sigma_{\mathrm{CSA(A)},d} + \sigma_{\mathrm{CSA(X)},d}]K + t(R_1^{\mathrm{X}} + R_1^{\mathrm{A}} + 2\sigma_{\mathrm{AX}})I^{\mathrm{eq}} \qquad (8)$$

This demonstrates that $(I_z^{\mathrm{A}} + I_z^{\mathrm{X}})$ (which is zero at the initial time; see eq 6) can become highly polarized through CSA/dipolar interference terms or more simply through a difference in relaxation rates, the sign of this polarization depending on the actual value and sign of the two quantities $[\sigma_{\mathrm{CSA(A)},d} + \sigma_{\mathrm{CSA(X)},d}]$ and $(R_1^{\mathrm{X}} - R_1^{\mathrm{A}})$ (see eq 4).

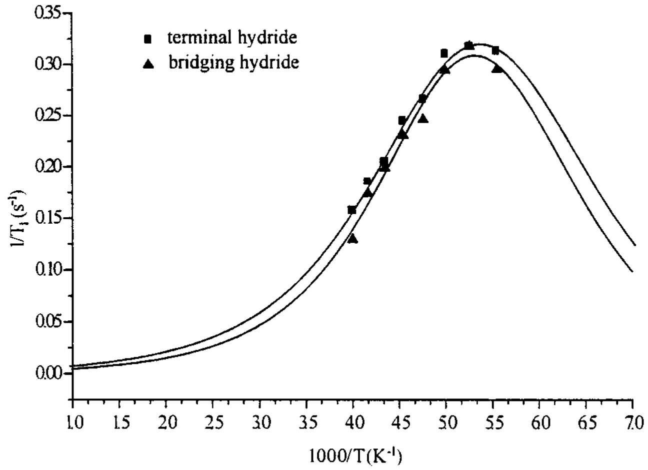


Figure 3. Experimental (■, ▲) and calculated (—) T_1 values of the bridging and terminal hydride resonances of $H(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}$ as a function of temperature.

Thus, the break of symmetry in p-H_2 is achieved at the intermediate compound, when the two hydrides form an AX spin system and, moreover, the buildup of $(I_z^{\mathrm{A}} + I_z^{\mathrm{X}})$ leaves a " memory " of this intermediate in the NMR signal of H_2 under the form of an enhanced emission.

Remarkably, the theory depicted above can also account for the occurrence of direct transfer from the A_2 longitudinal spin order to its longitudinal magnetization.[15] In this case the enhanced longitudinal magnetization can be mediated only by CSA-dipolar interference terms.

On comparing ^1H NMR spectra obtained for the reaction of p-H_2 with $Ru_3(CO)_{11}(NCCH_3)$ at different observation times, it is evident that the signal due to free hydrogen recovers to its normal intensity much faster than the hydride resonances. This is the result of the much higher relaxation rate of molecular hydrogen with respect to the bound hydride ligands. To estimate R_1 for the hydride ligands of $H(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}$ at RT, we measured their longitudinal relaxation times in the temperature range 193−243 K (where they are in the slow exchange regime), fitted the experimental data by applying the usual equation for homonuclear dipolar interaction,[20] and extrapolated this curve at higher temperature (Figure 3). The estimated values of the relaxation times for the terminal and the bridging hydrides at 298 K are of 11.9 and 14.5 s respectively. This difference in relaxation rates could be sufficient to explain the H_2 emission line. However, it is difficult to rule out any contribution from the interference terms (see eq 8). In fact, both effects can contribute depending on their respective magnitudes and signs. Concerning the evolution of this line (Figure 2), it can be seen that it starts with an enhanced negative value (due to the initial transfer from para-H_2), and then reaches its thermal equilibrium value by a complex mechanism basically determined by the relaxation rates of the protons in the ruthenium complex. Clearly the exchange rate of H_2 over the triruthenium cluster should be faster than the relaxation rate of the hydride ligands, otherwise no memory of the intermediate state could have been revealed in the molecular hydrogen resonance.

Conclusions

We demonstrated that an enhanced NMR emission signal can be observed for molecular hydrogen as a consequence of the reversible interaction of p-H_2 on a Ru_3 cluster. Thereby nuclear spin polarization is observed even if the hydrogen atoms derived from *p*-H_2 result in chemically and magnetically equivalent positions. Furthermore, the results reported herein introduce a time scale which allows the estimation of the rate of hydrogen exchange in transition metal complexes with respect to the longitudinal relaxation times of the hydride ligands.

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