Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting information

Towards measuring reactivity on micro-to-millisecond timescales with laser pump, NMR probe spectroscopy

Meghan E. Halse, Barbara Procacci, Robin N. Perutz, and Simon B. Duckett

Magnetic and chemical evolution: AA'XX' spin system

Consider the case where the *p*-H_2-derived protons in the product molecule are chemically equivalent but magnetically inequivalent by virtue of different scalar couplings to a second pair of chemically equivalent heteronuclei (AA'XX' system).[1] This situation is typically encountered when there are two chemically equivalent heteronuclei coordinated to the metal centre in the same plane as the hydrides, for example complex **3** in scheme 1 of the main text. The difference in scalar coupling that makes the hydrides magnetically inequivalent comes from the difference in the *trans* and *cis* coupling between the hydrides and the heteronuclei ($\Delta J = J_{trans} - J_{cis}$, where $J_{cis} = J_{AX} = J_{A'X'}, J_{cis} = J_{AX'} = J_{A'X}$) and can be quite large (10's of Hz for ^{1}H -^{31}P couplings).
As derived in Ref. 2, if we assume that the homonuclear coupling between the *X* spins is very small, $J_{XX'} \ll J_{AA'}$ and $J_{XX'} \ll \Delta J$, the density matrix as a function of time contains four components as shown in Eq. S1, where I_z, S_z, T_z, and R_z are the longitudinal angular momentum operators for the A, A', X and X' spins, respectively, and ZQ_x and ZQ_y are the zero-quantum coherences of the *p*-H_2-derived protons.

$$\rho^{\mathrm{AA'XX'}}(\tau) = -c_1(\tau)\tfrac{1}{2}(2I_{1z}I_{2z}) - c_2(\tau)ZQ_x - c_3(\tau)2ZQ_y(T_z - R_z) - c_4(\tau)2\tfrac{1}{2}(I_z - S_z)(T_z - R_z) \quad \text{(S1)}$$

The time-dependent amplitudes of the four terms in the density matrix were derived for the pure magnetic evolution case in Ref. 2. Following the same methodology as was used for the AX case in the main text, we can derive the combined effects of the chemical evolution and the coherent magnetic evolution during the pump-probe delay for an AA'XX' system by assuming that the oxidative addition of *p*-H_2 to the metal centre follows a pseudo-first order rate process with rate constant, *k*. In the high-field regime, the amplitude of the longitudinal two-spin-order term will evolve in the same manner as for the AX spin system (see Eq. 14 in the main text). The evolution of the remaining terms in the density matrix (Eq. S1) must be solved simultaneously. In order to make the problem amenable to an analytical solution, we define a single effective zero-quantum relaxation rate, R_{ZQ}, to describe the relaxation behaviour of all three terms: ZQ_x, $2ZQ_y(T_z - R_z)$, and $\tfrac{1}{2}2(I_{1z} - I_{2z})S_z$.

$$dc_2(\tau)/d\tau = k\exp(-k\tau) - R_{ZQ}c_2(\tau) - \pi\Delta J\, c_3(\tau) \quad \text{(S2a)}$$

$$dc_3(\tau)/d\tau = \pi\Delta J c_2(\tau) - R_{ZQ}c_3(\tau) - 2\pi J_{\mathrm{AA'}}c_4(\tau) \quad \text{(S2b)}$$

$$dc_4(\tau)/d\tau = 2\pi J_{\mathrm{AA'}}c_3(\tau) - R_{ZQ}c_4(\tau) \quad \text{(S2c)}$$

The solution to this system of equations for the boundary conditions: $c_2(0) = c_3(0) = c_4(0) = 0$, is given in Eq. S3, where $k' = k - R_{ZQ}$, $\omega = 2\pi\sqrt{J_{AA'}^2 + \Delta J^2}$, $\xi = \Delta J/J_{AA'}$, and $\varepsilon = \omega/k'$.

$$c_2(\tau) = \frac{k}{k'}\exp(-R\tau)\frac{1}{1+\xi^2}\left(1 - \exp(-k'\tau) + \frac{\xi^2}{1+\varepsilon^2}\big(\cos\omega\tau + \varepsilon\sin\omega\tau - \exp(-k'\tau)\big)\right) \quad \text{(S3a)}$$

$$c_3(\tau) = \frac{k}{k'}\exp(-R\tau)\frac{\xi}{\sqrt{1+\xi^2}}\frac{1}{1+\varepsilon^2}\big(\sin\omega\tau - \varepsilon\cos\omega\tau + \varepsilon\exp(-k'\tau)\big) \quad \text{(S3b)}$$

$$c_4(\tau) = \frac{k}{k'}\exp(-R\tau)\frac{\xi}{1+\xi^2}\left(1 - \frac{1}{1+\varepsilon^2}\big(\cos\omega\tau + \varepsilon\sin\omega\tau + \varepsilon^2\exp(-k'\tau)\big)\right) \quad \text{(S3c)}$$

If the rate constant is much larger than the difference in *J* coupling between the hydrides and the heteronucleus, i.e. 0 > *ε* << 90°, we can make the same approximations as in the AX case (Eq. 17) to obtain the following:

$$c_2(\tau) = \frac{k}{k_2'}\exp(-R\tau)\frac{1}{1+\xi^2}\big(1 + \xi^2\cos(\omega\tau - \varepsilon) - \exp(-k_2'\tau)\big), \quad \text{(S4a)}$$

$$c_3(\tau) = \frac{k}{k'}\exp(-R\tau)\frac{\xi}{\sqrt{1+\xi^2}}\big(\sin(\omega\tau - \varepsilon) + \varepsilon\exp(-k'\tau)\big), \quad \text{(S4b)}$$

$$c_4(\tau) = \frac{k}{k'}\exp(-R\tau)\frac{\xi}{1+\xi^2}\big(1 - \cos(\omega\tau - \varepsilon) - \exp(-k'\tau)\big). \quad \text{(S4c)}$$

As in the AX spin system, in the limit where 0 < ε << 90° and for times longer than the inverse of the rate constant ($\tau \gg 1/k'$), the effect of the chemical evolution manifests in the oscillation of the signal amplitudes as a phase shift equal to the NMR dephasing parameter, ε. In this case, the magnetic oscillation frequency that defines the dephasing parameter is dependent on the J coupling constants of the system, $\omega = 2\pi\sqrt{J_{AA'}^2 + \Delta J^2}$, where the dominant coupling is the difference between the *trans* and *cis* couplings.

References

1 J. A. Pople, W. G. Schneider and H. J. Bernstein, *Canadian Journal of Chemistry-Revue Canadienne De Chimie*, 1957, **35**, 1060-1072.
2 M. E. Halse, B. Procacci, S. L. Henshaw, R. N. Perutz and S. B. Duckett, *J. Magn. Reson.*, 2017, **278**, 25-38.