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Scalar and Dipolar Contributions of Rhenium to the Relaxation Properties of Coordinated Ligands

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The longitudinal relaxation times (T_1) of the hydridic ligands and of ^{31}P in $[HRe(CO)_4PPh_3]$ (**1**), $[HRe(CO)_5]$ (**2**), and $[Re_2(\mu\text{-}H)_2(CO)_8]$ (**3**) have been measured as a function of the temperature and of the applied magnetic field. In **1** the relaxation of ^{31}P is dominated by the scalar interactions with the quadrupolar isotopes of rhenium up to 7 T. The field dependence of the relaxation rate of phosphorus has allowed the calculation of the coupling constant $^1J(Re\text{-}P)$ (1260 ± 20 Hz) and of the Re relaxation time (22 ± 1 ns). For the hydridic ligand, dipolar interactions with rhenium account for more than 60% of the observed relaxation rate. $^1J(H\text{-}Re)$ for **1** has been estimated as 440 Hz. The relaxation of the classical hydrides in **2** and **3** is completely determined by dipolar interactions with rhenium. $^1J(H\text{-}Re)$ for **2** has been determined to be 385 Hz. The length of the Re–H bond (189 ± 1 pm) in **3** has been calculated from the fitting of the temperature dependence of ^1H relaxation. Anisotropic reorientation was observed for compound **1**. The relevance of the H–Re dipolar interaction in classical rhenium polyhydrides is discussed.

In recent years, the study of the relaxation mechanisms of ligands coordinated to metal centers has received increasing interest. As far as organometallic compounds are concerned, a number of works have been reported on hydrides and molecular hydrogen,[1] carbonyls,[2] and phosphines.[3] The importance of the dipolar interaction in the relaxation of hydrogen has been used to propose the value of T_1 at the minimum $[T_1(\min)]$ as a tool in the assignment of the classic or nonclassic structures in metal polyhydrides.[1a] This elegantly simple and effective proposal has been subjected to criticisms,[1b,e] modifications,[1a] and tests,[1c] rhenium polyhydrides being the main subject of debate.[1b] Concerning the phosphine ligands, it has been shown that dipole–dipole (dd) and spin rotation (sr) are the main mechanisms in the relaxation of ^{31}P in free phosphines,[3b,4] but the coordination to transition metals increases the chemical shift anisotropy (csa),[3a] leading to an increase of the longitudinal relaxation rate (R_1), which becomes proportional to the square of the applied field (B_0) according to[5]

$$R_1(\text{csa}) = (2/15)\gamma_P^2(\Delta\sigma)^2B_0^2[\tau_c/(1 + \omega_P^2\tau_c^2)] \quad (1)$$

where γ_P is the magnetogyric ratio of ^{31}P, $\Delta\sigma$ is the chemical shift anisotropy, ω_P is the Larmor frequency of ^{31}P, and τ_c is the molecular correlation time, assuming an isotropic reorientation of the molecule.

We report here on the studies of the relaxation behavior at variable temperature and variable field of ^{31}P and ^1H in $[HRe(CO)_4PPh_3]$ (**1**). The experimental results show that the contribution of the two quadrupolar isotopes of rhenium[6] is relevant in the longitudinal relaxation rates of both ^1H and ^{31}P. Indeed, while it is common to observe line broadening due to an increase of the transverse relaxation rate for a nucleus with spin $^1/_2$ bound to a quadrupolar nucleus, rarely are dipolar[7] or scalar coupling contributions due to the quadrupolar isotopes[8a] dominant in the longitudinal relaxation rate of nuclei with high γ. These observations prompted us to study also the field and temperature dependence of the longitudinal relaxation times of the classical hydridic ligands in $[HRe(CO)_5]$ (**2**) and $[Re_2(\mu\text{-}H)_2(CO)_8]$ (**3**) and the effectiveness of the rhenium isotopes as a source of dipolar interactions in these compounds.

Results and Discussion

Field Dependence of T_1 of ^{31}P in $[HRe(CO)_4PPh_3]$. $^{31}P\{^1H\}$ T_1 values of toluene-d_8 solutions of **1** have been measured at 298 K (^{31}P δ = 15.2) with the nonselective inversion recovery technique at variable field strength. The experimental results (shown in Figure 1 as T_1 vs B_0^2) rule out the dominance of the dd or sr mechanisms, which are not field dependent in the extreme narrowing conditions,[5] as shown by eqs 2 and 3, where r is the distance

$$R_1(\text{dd}) = (2/15)(\mu_0/4\pi)^2\gamma_I^2\gamma_S^2(h/2\pi)^2r^{-6}S \times (S + 1)\tau_c\left[\frac{1}{1 + \omega_-^2\tau_c^2} + \frac{3}{1 + \omega^2\tau_c^2} + \frac{6}{1 + \omega_+^2\tau_c^2}\right] \quad (2)$$

$$R_1(\text{sr}) = 8\pi^2IC^2kT\tau_{sr}/3h^2 \quad (3)$$

between the interacting nuclei, $\omega_- = \omega(I) - \omega(S)$, $\omega_+ = \omega(I) + \omega(S)$, and $\omega = \omega(I)$, I being the observed nucleus, $\omega(I)$ and $\omega(S)$ are the Larmor frequencies of the interacting nuclei, I is the molecular moment of inertia, C^2 is the average of the square of the spin-rotation tensor diagonal elements, and τ_{sr} is the spin-rotation correlation time ($\tau_{sr} = I/6kT\tau_c$), the other symbols having their usual meaning.

The *increase* of T_1 with the field is opposite to what is expected when csa dominates the relaxation. The only mechanism that accounts for the observed field dependence is the scalar coupling (sc) of the second kind,[5a] due to the fluctuating magnetic fields provided by the rapidly relaxing quadrupolar isotopes of rhenium. The scalar relaxation rate follows eq 4, assuming that $T_1 = T_2$

$$R_1(\text{sc}) = [(70/3)\pi^2J^2T_1(\text{Re})]/[1 + (\Delta\gamma)^2B_0^2(T_1(\text{Re}))^2] \quad (4)$$

for a quadrupolar isotope,[5,8a] where J is the scalar coupling constant between ^{31}P and Re, $\Delta\gamma$ is the difference between the magnetogyric ratios of the two nuclei, B_0 is the applied magnetic field, and $T_1(\text{Re})$ is the longitudinal relaxation time of rhenium.[9]

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(1) See for instance: (a) Crabtree, R. H. *Acc. Chem. Res.* **1990,** *23,* 95 and references therein. (b) Cotton, F. A.; Luck, R. L.; Root, D. R.; Walton, A. R. *Inorg. Chem.* **1990,** *29,* 43 and references therein. (c) Luo, X.; Crabtree, R. H. *Inorg. Chem.* **1990,** *29,* 2788. (d) Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1988,** *110,* 7031. (e) Amman, C.; Isaia, F.; Pregosin, P. S. *Magn. Reson. Chem.* **1988,** *26,* 236.

(2) See for instance: (a) Beringhelli, T.; Molinari, H.; D'Alfonso, G. *J. Chem. Soc., Dalton Trans.* **1987,** 2083. (b) Beringhelli, T.; Molinari, H.; D'Alfonso, G. *J. Organomet. Chem.* **1985,** *285,* C35. (c) Beringhelli, T.; Molinari, H.; Pastore, A. *J. Chem. Soc., Dalton Trans.* **1985,** 1899. (d) Aime, S.; Gobetto, R.; Osella, D.; Hawkes, G. E.; Randall, E. W. *J. Chem. Soc., Dalton Trans.* **1984,** 1863. (e) Hawkes, G. E.; Randall, E. W.; Aime, S.; Osella, D.; Elliot, J. E. *J. Chem. Soc., Dalton Trans.* **1984,** 279.

(3) (a) Randall, L. H.; Carty, A. J. *Inorg. Chem.* **1989,** *28,* 1194. (b) Jans-Burli, S.; Pregosin, P. S. *Magn. Reson. Chem.* **1985,** *23,* 198. (c) Appel, D. M.; Boyd, A. S.; Robertson, I. W.; Roundhill, D. M.; Stephenson, T. A. *Inorg. Chem.* **1982,** *21,* 449. (d) Bosch, W.; Pregosin, P. S. *Helv. Chim. Acta* **1979,** *62,* 838. (e) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: Berlin, 1979; see also references therein.

(4) (a) Ramarajan, K.; Herd, M. D.; Berlin, D. K. *Phosphorus Sulfur* **1981,** *11,* 199. (b) Robert, J. B.; Taieb, M. C.; Tabony, J. *J. Magn. Reson.* **1980,** *38,* 99. (c) Wilkie, C. A. *J. Magn. Reson.* **1979,** *33,* 127. (d) Koole, N. J.; De Koning, A. J.; De Bie, M. J. A. *J. Magn. Reson.* **1977,** *25,* 375.

(5) (a) Abragam, A. *The Principles of Nuclear Magnetism*; Oxford University Press: London, 1961. (b) Howarth, O. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; Chapter 5.

(6) $^{185}Re(I = {}^5/_2)$ natural abundance (na) 37.07%, $\gamma = 6.1057 \times 10^7$ rad T^{-1} s^{-1}, $Q = 3.0 \times 10^{-28}$ m^2; $^{187}Re(I = {}^5/_2)$ na 62.93%, $\gamma = 6.1682 \times 10^7$ rad T^{-1} s^{-1}, $Q = 2.8 \times 10^{-28}$ m^2.

(7) Noggle, J. H.; Shirmer, R. E. *The Nuclear Overhauser Effect*; Academic Press: New York, 1971; Chapter 2.

(8) (a) Mlynarik, V. *Prog. NMR Spectrosc.* **1986,** *18,* 277 and references therein. (b) Rhodes, M.; Aksnes, D. W.; Strange, J. H. *Mol. Phys.* **1968,** *15,* 541.

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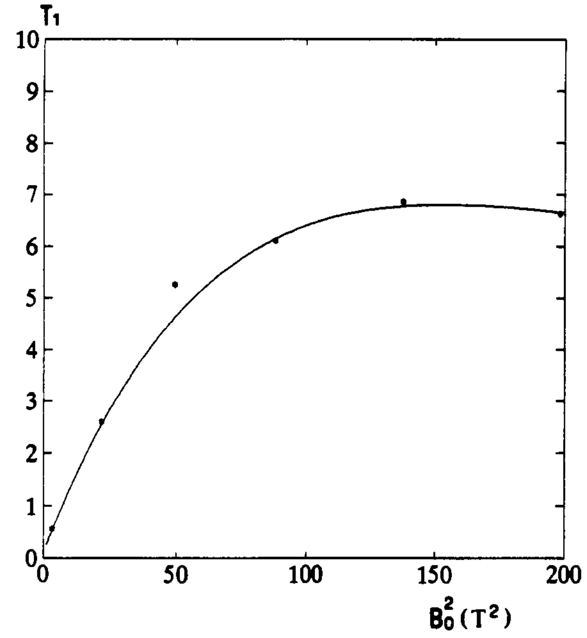

Figure 1. Field dependence of the longitudinal relaxation times of ^{31}P in $[HRe(CO)_4PPh_3]$ (298 K, toluene-d_8).

Figure 1 shows that, according to eq 4, which requires T_1(sc) to be proportional to B_0^2, the scalar coupling mechanism is the dominant one up to 7.0 T; it becomes less important at very high fields, where csa contributions can play a major role. The nonselective proton–phosphorus NOE, at 298 K and 7.0 T, is η = 0.16, indicating that R_1(dd) for ^{31}P is only ca. 0.02 s^{-1}. The overall field dependence of the relaxation rate can therefore be expressed as

$$R_1 = R_1(\mathrm{sc}) + R_1(\mathrm{csa}) + R_1(\mathrm{others}) = [a/(1 + bB_0^2)] + cB_0^2 + d \quad (5)$$

where the field dependence is accounted for by the first two terms, and R_1(others) means all the non-field-dependent contributions (dd, sr, and others). The fitting of the experimental results according to eq 5 allows an estimate of the four parameters *a*, *b*, *c*, and *d*. The T_1 measured at 7 T has not been included in the fitting procedure because the temperature of the experiment was not accurate, but it is shown in Figure 1 to emphasize the general behavior.

From the values of *a* and *b*, ^1J(P–Re) (1260 ± 20 Hz) and T_1(Re) (22 ± 1 ns) have been calculated. This is, to the best of our knowledge, the first estimate of a coupling between P and Re. The reduced coupling constant ($^1K = 1114 \times 10^{19}$ N A^{-2} m^{-3}) is comparable to those reported for similar tungsten compounds (cf., for instance, $[W(CO)_5PPh_3]$, where ^1J = 280 Hz and $^1K = 1364 \times 10^{19}$ N A^{-2} m^{-3}).[3c] The rhenium relaxation time is of the same order of magnitude as those obtained for $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ (44 ns at 298 K)[2c] and $[Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^-$ (13 and 26 ns at 238 K).[2a]

The *c* constant is function of two unknowns: $\Delta\sigma$ and τ_c. The estimates of the correlation time through the modified Stokes–Debye equation[10] can be different by a factor 3, according to the different assumptions made in the calculations: 18 ps, if the "usual" *f* factor of 0.16 is used and the volume is calculated for an oblate spheroid, or 49 ps, if the more realistic *f* factor of 0.27 is used and the volume is calculated as the smallest sphere that encloses the molecule. On the other hand, from T_1 and $^{13}C\{^1H\}$ NOE measurements on the ortho and para carbons[11] of the phenyl rings, τ_c = 26 and 45 ps, respectively, can be calculated (T_1 = 1.7 and 1.05 s, η = 2 for both). These latter results suggest the presence of an independent motion of the phenyls, and we cannot also rule out an anisotropic tumbling that requires different correlation times for the carbon–hydrogen and the rhenium–phosphorus interactions (vide infra). The value of $\Delta\sigma$ has therefore a very high uncertainty, and it ranges from 107 to 65 ppm. The upper value appears more reasonable, since it is only slightly smaller than others reported for PPh_3 terminally bound ($\Delta\sigma$ = 121 ppm in *trans*-$Ir(CO)Cl(PPh_3)_2$,[3a] and $\Delta\sigma$ = 124, 125, 222 ppm in $[RhCl(PPh_3)_3]$[12a]). On the contrary, the lower one is probably too small, since it is similar to that reported for free PPh_3 ($\Delta\sigma$ = 50 ppm).[12b] However, it should be observed that the values of R_1(csa) calculated at high fields (R_1(obs) − R_1(sc) − R_1(dd)) in the present case are ca. 1 order of magnitude smaller than those reported in ref 3a for terminally bound triphenylphosphines, in a solvent of comparable viscosity.

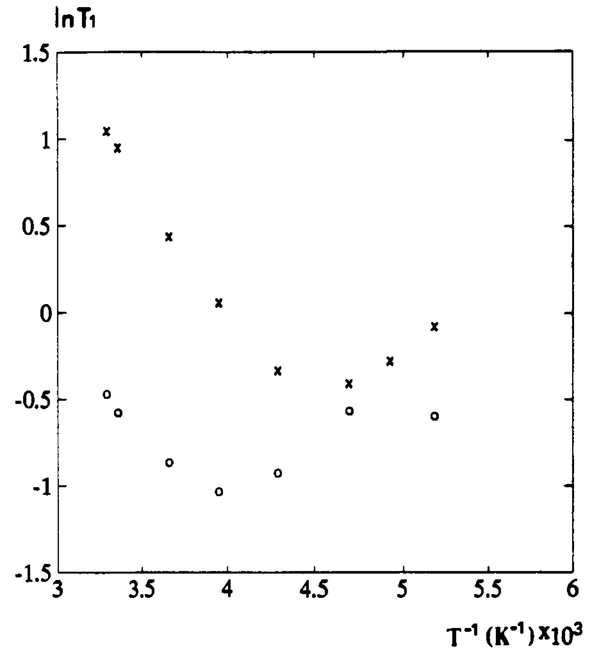

Figure 2. Temperature dependence of the longitudinal relaxation times of ^{31}P in $[HRe(CO)_4PPh_3]$ (toluene-d_8): O, 1.87 T; ×, 4.7 T.

The small value of the constant *d* (0.048 ± 0.008 s^{-1}) confirms the small relevance of relaxation mechanisms different from sc and csa.

Temperature Dependence of T_1 of ^{31}P in $[HRe(CO)_4PPh_3]$. ^{31}P T_1 values have also been measured at variable temperature at 1.87 and 4.7 T, and the experimental results are shown in Figure 2. At high temperatures the T_1 values decrease on decreasing the temperature: this confirms that the sr mechanism is not the dominant one, since eq 3 predicts an increase of T_1 on lowering the temperature.[5]

The linear dependence of ln T_1 vs T^{-1}, at high temperatures, is expected according to eq 4 when $(\Delta\gamma)^2B_0^2(T_1(\mathrm{Re}))^2 > 1$, and the temperature dependence is through the quadrupolar T_1 of Re. In fact, it is generally accepted that, in the extreme narrowing conditions, the relaxation of a quadrupolar nucleus like rhenium is related to the rotational correlation time τ_c according to eq 6,[5,8]

$$R_1(\mathrm{q}) = (12\pi^2/125)(e^2qQ/h)^2(1 + \eta^2/3)\tau_c \quad (6)$$

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(9) We do not make a distinction between the two isotopes of rhenium, since differences in their T_1 and *J* values are expected to change the ^{31}P relaxation rate less than 5%.

(10) Boeré, R. T.; Kidd, R. G. *Annu. Rep. NMR Spectrosc.* **1982**, *13*, 319. The poor accuracy of the Stokes–Debye formula ($\tau_c = V\eta/kT$, where *V* is the molecular volume and η the viscosity of the solution) for nonspherical molecules in solution is well-known. The microviscosity factor, *f*, introduced by Gierer-Wirtz in order to account for the difference in size between solute and solvent molecules, is useful when both the species are almost spherical and a single correlation time is expected.

(11) The ^{13}C resonances of the phenyls are partly overlapped with those of toluene, but they are clearly detectable in some spectra of the T_1 measurements owing to the difference in the relaxation times [δ = 134.41 (ipso, *J*(C–P) = 48 Hz), 133.68 (ortho, *J*(C–P) = 12 Hz), 130.58 (para, *J*(C–P) = 2 Hz), 128.59 ppm (meta, *J*(C–P) = 9 Hz)].

(12) (a) Naito, A.; Sastry, D. L.; McDowell, C. A. *Chem. Phys. Lett.* **1985**, *115*, 19. (b) Bemi, L.; Clark, H. C.; Davies, J. A.; Fyfe, C. A.; Wasylishen, R. E. *J. Am. Chem. Soc.* **1982**, *104*, 438.

where e^2qQ/h is the quadrupolar coupling constant (QCC) and η is the asymmetry parameter. The rotational correlation time has an Arrhenius-type temperature dependence ($\tau_c = \tau_0 \exp(E_a/RT)$, where E_a is the activation energy for the reorientation). $T_1(^{31}P)$ is therefore proportional to τ_c^{-1}.

The minima observed in the temperature dependence of T_1 are shifted at higher temperatures on decreasing the field (Figure 2). This field dependence is opposite to what is expected for dipole–dipole relaxation (at higher temperatures on increasing the field), and it is further evidence that the relaxation is due to scalar coupling of the second kind. Equation 4 predicts a minimum in T_1 when $(\Delta\omega)^2(T_1(\mathrm{Re}))^2 = 1$ ($\Delta\omega = \Delta\gamma B_0$), and the smaller the difference between the Larmor frequencies of the nuclei ($\Delta\omega$), the larger T_1(Re) is required to be to fulfill this condition. Previous relaxation studies of ^{13}C, performed on carbonyl ligands bound to rhenium in other hydrido carbonyl clusters,[2c] showed that their relaxation is due to scalar coupling of the second kind, but their T_1's increase on lowering the temperature, at 1.87 T. This different behavior is due to the smaller $(\Delta\omega)^2$ for ^{13}C compared to ^{31}P at 1.87 T ($(\Delta\omega)^2 = 76.3 \times 10^{14}$ rad^2 s^{-2} for ^{31}P and 1.10×10^{14} rad^2 s^{-2} for ^{13}C), which leads to the occurrence of the minimum T_1 for ^{13}C at high temperature (above 300 K) at low field. Indeed, the study of the chemical exchange of ^{13}CO in $[Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^-$ at 9.39 T suggested the presence of a minimum in T_1 at 278 K.[13]

A minimum T_1 due to scalar relaxation of the second kind was observed at 0.5 T for ^{31}P in neat PBr_3,[8b] where the coupling between ^{31}P and bromine quadrupolar isotopes dominates the relaxation.

Rhenium Relaxation Properties of [HRe(CO)$_4$PPh$_3$]. T_1 of Re can be easily calculated at the temperatures of the minima observed in Figure 2 (T_1 = 11 and 4.6 ns at 253 K (1.87 T) and 213 K (4.7 T), respectively). T_1(Re) at 298 K has been previously estimated as 22 ns: the plot of ln T_1(Re) vs $1/T$ (298, 253, and 213 K) gives therefore the activation energy of the motional reorientation which dominates its relaxation ($E_a = 9.71 \pm 0.03$ kJ/mol). The values of E_a estimated for the temperature dependence of ^{31}P relaxation at 1.87 and 4.7 T are 8.5 ± 0.8 and 11.6 ± 0.5 kJ/mol, respectively, supporting the idea that the same reorientation process rules the relaxation of both phosphorus and rhenium.

From the value of T_1(Re) at 298 K, assuming a vanishing value of η, a very rough estimate of the electric quadrupolar coupling constant of rhenium in compound **1** can be obtained through eq 6 ($e^2qQ/h = (1.6\text{–}1.0) \times 10^3$ MHz). The major source of uncertainty is the τ_c value, but the order of magnitude of the QCC is not unreasonable since (i) a value of 77 MHz was estimated for the highly symmetrical ReO_4^- ion in solution[14] and (ii) a value of 753 MHz can be calculated for [HRe(CO)$_5$] with C_{4v} symmetry (vide infra), from the data concerning the related compound [HMn(CO)$_5$],[15] using the ratio of quadrupolar moments ($Q(\mathrm{Re})/Q(\mathrm{Mn}) = 25.5$).[14a]

Temperature and Field Dependences of T_1 of ^1H in [HRe(CO)$_4$PPh$_3$]. The relaxation times of the hydridic ligand in **1** (^1H $\delta = -4.36$, $^2J(\mathrm{H\text{-}P}) = 22.7$ Hz) have been measured under the same experimental conditions at 1.87 and 4.7 T. The results are reported in Table I and plotted in Figure 3. The field and temperature dependences indicate that the dipole–dipole mechanism dominates the relaxation of the hydrogen atom. Experiments on diluted solutions (1:5) did not show any significant change in the values of T_1, indicating the prevalence of intramolecular dipolar interactions.

The possible sources of intramolecular dipolar relaxations are the hydrogens of phenyls, the phosphorus, and the rhenium atom to which the hydride is bound. The phosphorus atom can be ruled out for the small dipolar contribution of all the hydrogens to the

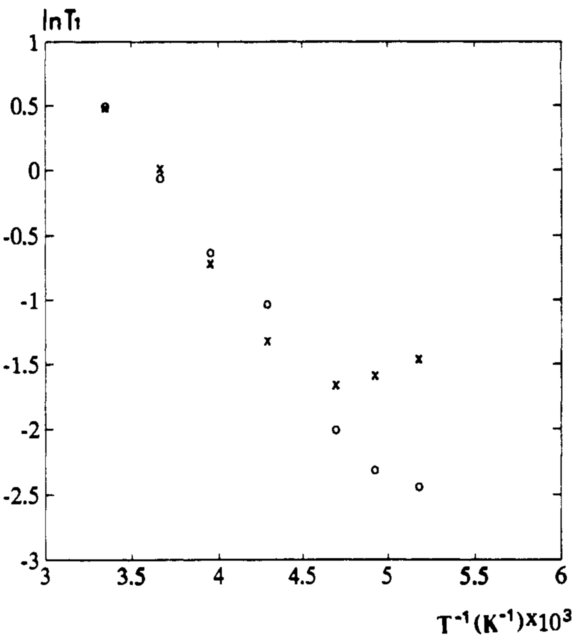

Figure 3. Field and temperature dependence of the longitudinal relaxation times of ^1H in [HRe(CO)$_4$PPh$_3$] (toluene-d_8): ○, 1.87 T; ×, 4.7 T.

Table I. Field and Temperature Dependences of the Longitudinal Relaxation Times (T_1)

[HRe(CO)$_4$PPh$_3$] (**1**) (Toluene-d_8), ^{31}P

field dependence (298 K)		temp dependence		
field, T	T_1, s	temp, K	T_1, s[a]	T_1, s[b]
1.87	0.562	304	0.626	2.84
4.7	2.59	298	0.562	2.59
7.04	5.27	273	0.421	1.55
9.39	6.12	253	0.356	1.06
11.7	6.86	233	0.397	0.716
14.1	6.63	213	0.567	0.664
		203		0.756
		193	0.550	0.922

[HRe(CO)$_4$PPh$_3$] (**1**) (Toluene-d_8), ^1H

temp, K	T_1, s[a]	T_1, s[b]	temp, K	T_1, s[a]	T_1, s[b]
298	1.64	1.62	213	0.134	0.189
273	0.976	1.01	203	0.099	0.203
253	0.531	0.488	193	0.087	0.231
233	0.356	0.267			

[HRe(CO)$_5$] (**2**) (Toluene-d_8), ^1H

temp, K	T_1, s[a]	temp, K	T_1, s[b]
297	8.61	294	8.15
270	4.27	290	7.85
255	2.78	271	5.13
		253	2.94
		227	1.27
		206	0.578
		197	0.319
		187	0.261

[Re$_2$(μ-H)$_2$(CO)$_8$] (**3**) (Toluene-d_8), ^1H

temp, K	T_1, s[a]	temp, K	T_1, s[b]
297	1.84	296	2.03
272	1.13	271	1.08
248	0.646	248	0.690
227	0.352	227	0.396
208	0.178	206	0.226
198	0.122	197	0.184
190	0.099	187	0.175
183	0.092	178	0.170

[a] 1.87 T. [b] 4.7 T.

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(13) Beringhelli, T.; D'Alfonso, G.; Molinari, H.; Hawkes, G. E.; Sales, K. *J. Magn. Reson.* **1988**, *80*, 45.

(14) (a) Kidd, R. G. *J. Magn. Reson.* **1981**, *45*, 88. In the solid state, the QCC of the anion ReO_4^- is very sensitive to the small distortion induced by the counterion. (b) See: Klobasa, D. G.; Burkert, P. K. *Magn. Reson. Chem.* **1987**, *25*, 154. These authors report QCC = 109 MHz for NH_4ReO_4 and 24.4 MHz for $(CH_3)_4PReO_4$ at 273 K.

(15) Farrar, T. C.; Quinting, G. R. *J. Phys. Chem.* **1986**, *90*, 2834.

^{31}P relaxation, as above discussed.

The selective and nonselective longitudinal relaxation times of the hydride have been therefore measured at 4.7 T and 294 K. The results, 1.75 and 1.50 s, respectively, indicate that only 33% of the relaxation is due to interactions with other hydrogens.[16] Molecular modeling shows indeed that, in the limit of an idealized octahedral geometry, only one of the phenyl hydrogens is near the hydride. The remaining contribution to the relaxation rate is therefore due to the dipolar interaction with rhenium.

We should note that the temperature dependence of ^1H relaxation times gives an activation energy of ca. 16 kJ/mol. This indicates that the reorientation, which changes the motional regime of the hydride at 213 K at 4.7 T, is different from the one of rhenium and phosphorus. The assumption of a single correlation time is therefore not strictly correct even for such small molecules.

The transverse relaxation time (T_2 = 0.90 s) for ^1H has also been measured at 294 K at 4.7 T using the Carr–Purcell–Meiboom–Gill sequence. Since for the hydride R_1 is dominated by dipolar interactions but R_2 should have a contribution from the scalar coupling interaction of the second kind,[8a,15] the difference between the two rates gives R_2(sc):[8a]

$$R_2 - R_1 = (4\pi^2/3)[J(\text{H-Re})]^2S(S+1)T_1(\text{Re}) \quad (7)$$

and accordingly ^1J(H–Re) = 440 Hz can be calculated. The reduced coupling constant, ^1K(Re–H) = 159 × 10^{19} N A^{-2} m^{-3}, is comparable to that for W–H interactions in the related tungsten complexes $[HW(CO)_4PR_3]^-$ (R = OMe, Me) (^1J = 54 Hz, ^1K = 106 × 10^{19} N A^{-2} m^{-3})[17a] and $[HW(CO)_5]^-$ (^1J = 53.4 Hz, ^1K = 105 × 10^{19} N A^{-2} m^{-3}).[17b]

The value of the H–Re coupling constant is too small to make effective the scalar coupling relaxation with rhenium (R_1(sc) = 0.002 s^{-1} at 4.7 T and 298 K). Indeed, the short relaxation time of rhenium and the significant difference in the Larmor frequencies, even at low fields ($(\Delta\omega)^2(T_1(\text{Re}))^2$ = 72 at 1.87 T and 298 K), would require a coupling constant at least greater than 1 order of magnitude to make this relaxation comparable to the dipolar one. The ^{31}P isotope, on the contrary, has a greater J and a smaller γ and meets the requirements for the scalar coupling relaxation. On the other hand, the longer bond distance and the smaller γ make less effective its dipolar interactions with rhenium.

Relaxation Times of [HRe(CO)$_5$]. Proton relaxation times of toluene-d_8 solutions of $[HRe(CO)_5]$ (**2**) (^1H δ = −5.45, 298 K) have been measured with the nonselective inversion recovery technique at variable temperature at 1.87 and 4.7 T. The experimental results are reported in Table I and plotted in Figure 4a. The measured relaxation times are longer than those of $[HRe(CO)_4PPh_3]$ because of the expected shorter correlation time and the absence of any other hydrogen atom in the molecule. The contribution of the interaction with solvent deuterons[15] has been estimated from measurements at 298 K and 1.87 T using nondeuterated toluene as solvent: the measured T_1 (6.9 s) indicates that only 3% of the relaxation is due to solute–solvent interaction. The relaxation is therefore intramolecular and dipolar, being field independent and increasing on lowering the temperature. The main relaxation contribution is the dipole–dipole interaction of ^1H with the bound rhenium atom. The overall shape of this molecule can be described as a sphere, and the value of the correlation time obtained through the Stokes–Debye equation (f = 0.16) is 8.4 ps. At 298 K in the extreme narrowing regime, the distance Re–H calculated through eq 2 (170 pm) is comparable to the distances determined by neutron diffraction in other rhenium hydrides (e.g. mean value in $[H_7Re(dppe)]$ 167.2 (7) pm,[18a] mean value in $[H_5Re(PMePh_2)_3]$ 168.8 (5) pm,[18b] mean value for the terminal hydrides in $[Re_2H_4(\mu\text{-}H)_4(PEt_2Ph)_4]$ 166.9 (7)pm[18c]).

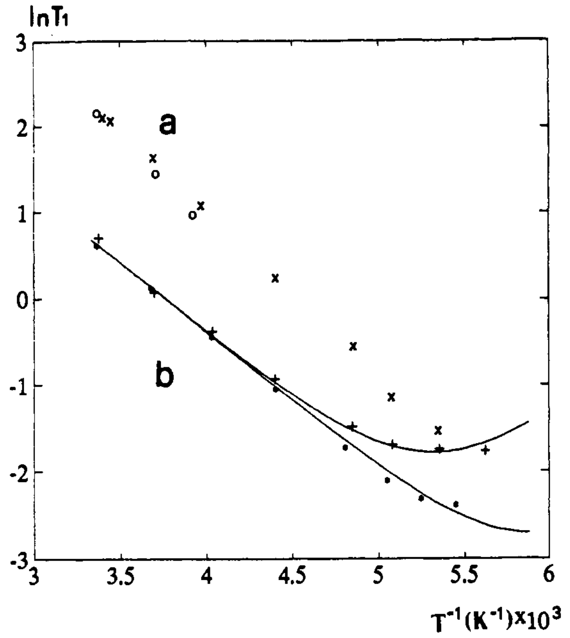

Figure 4. Field and temperature dependence of the longitudinal relaxation times of ^1H. (a) $[HRe(CO)_5]$ (toluene-d_8): ○, 1.87 T; ×, 4.7 T. (b) $[Re_2(\mu\text{-}H)_2(CO)_8]$ (toluene-d_8): ✱, 1.87 T; +, 4.7 T.

No minimum is observed in the temperature dependence of T_1. It can be easily shown that the dipolar relaxation rate between ^1H and rhenium is highest when $(\omega(\text{H}))\tau_c = 0.926$. Using the value of τ_c at 4.7 T so calculated and the distance of 170 pm, a minimum T_1 of 0.190 s is predicted, and this could be reached at temperatures lower than the lowest experimental temperature (0.261 s at 187 K).

In order to estimate the Re–H coupling constant in this compound, the measurements of the longitudinal and of the transverse relaxation times have been performed at 4.7 T and 290 K (T_1 = 7.85 s, T_2 = 0.687 s). Through eq 7, ^1J(Re–H) = 385 Hz has been calculated. The value of T_1(Re) needed in eq 7 has been estimated (T_1(Re) = 78 ns) from the data of ref 15 concerning $[HMn(CO)_5]$ (T_1(Mn) = 86.4 μs, 288.3 K) assuming that

$$T_1(\text{Re})/T_1(\text{Mn}) = (Q_{\text{Mn}}/Q_{\text{Re}})^2[\tau_c(\text{Mn})/\tau_c(\text{Re})] = (Q_{\text{Mn}}/Q_{\text{Re}})^2[\eta(\text{Mn})/\eta(\text{Re})](r_{\text{Mn}}/r_{\text{Re}})^3$$

the main difference being due to the ratio of the electric nuclear quadrupolar moments Q.

Relaxation Times of [Re$_2$(μ-H)$_2$(CO)$_8$]. Proton relaxation times of toluene-d_8 solutions of $[Re_2(\mu\text{-}H)_2(CO)_8]$ (**3**) (^1H δ = −9.38 ppm, 298 K) have been measured with the nonselective inversion recovery technique at variable temperature at 1.87 and 4.7 T. The experimental results are reported in Table I and plotted in Figure 4b. The field and temperature behavior is in line with that expected for a dipolar relaxation.

The importance of the mutual relaxation of the hydrides was checked by measuring T_1 for a partly deuterated sample, the dipolar relaxation rate due to a deuterium atom being 0.063 times the one due to a hydrogen atom at the same distance.[7] The difference in the experimental relaxation rates of the two resonances (T_1(HH, −9.38 ppm) = 2.03 s, T_1(HD, −9.35 ppm) = 2.23 s) allowed the estimate of the dipolar H–H relaxation, which was found to be 9.5% of the total relaxation rate.

The fitting of the temperature dependence of the relaxation times, according to eq 2 and allowing for the double interaction with rhenium, gave τ_0 = 0.14 ± 0.02 ps, E_a = 13.3 ● 0.3 kJ/mol, and r = 189 ± 1 pm.

The latter value is in fair agreement with the Re–H bridging distances determined by neutron diffraction in the equatorial isomer of $[Re_3(\mu\text{-}H)_3(CO)_{11}(PPh_3)]$ (182.2 (8) pm)[19] or in

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(16) Hall, L. D.; Hill, H. D. W. *J. Am. Chem. Soc.* **1976**, *98*, 1269.

(17) (a) Slater, S. G.; Lusk, R.; Schumann, B. F.; Darensbourg, M. *Organometallics* **1982**, *1*, 1662. (b) Darensbourg, M. Y.; Slater, S. *J. Am. Chem. Soc.* **1981**, *103*, 5914.

(18) (a) Howard, J. A. K.; Mason, S. A.; Johnson, O.; Diamond, I. C.; Crennell, S.; Keller, P. A.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1988**, 1502. (b) Emge, T. J.; Koetzle, T. F.; Bruno, J. W.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 4012. (c) Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872.

$[Re_2H_4(\mu\text{-}H)_4(PEt_2Ph)_4]$ (mean 187.8 (7) pm).[17c]

Conclusions

The contributions of scalar coupling of the second kind has been shown to be the main relaxation mechanism for phosphorus atoms bound to rhenium. Therefore, within this class of compounds, greater efficiency can be achieved by recording ^{31}P spectra at low temperature and at fields as low as allowed by sensitivity problems.

The importance of the dipolar contribution from rhenium should be taken into account when one considers the ^1H relaxation of rhenium hydrides, especially the classical ones. According to eq 2, the small γ of rhenium isotopes[6] is partly counterbalanced by the factor $S(S + 1) = 8.75$, which makes the "effective γ" ca. 18×10^7 rad T^{-1} s^{-1} (compare with 10.8394×10^7 rad T^{-1} s^{-1} for ^{31}P and 26.7522×10^7 rad T^{-1} s^{-1} for ^1H). In the extreme narrowing condition, for a hydride bound to it ($r = 168$ pm), a rhenium atom is effective as a hydrogen atom at 195 pm, as far as dipolar interactions are concerned (provided that the correlation times of the two interactions are the same). At the temperature of the highest dipolar H–H relaxation rate, the rhenium dipolar contribution is equal to that of a hydride at 182 pm, a distance only 8% greater than the Re–H distance.

The relevance of the dipolar relaxation with rhenium is confirmed also by evaluating the relaxation times of the hydrides in $[H_7Re(dppe)]$. For this compound, the solution NMR spectrum shows a single resonance for which the experimental T_1(min) is 67 ms,[20] at 250 MHz. We have calculated T_1(min) for the four different types of hydrides, using the distances provided by the neutron diffraction structure.[17a] The analysis of the contributions shows that, for three types of hydrides (T_1 = 72, 69, and 71 ms, respectively) rhenium accounts for ca. 30% of their overall relaxation rate, since each of them has only two hydrogens that are sufficiently near to be comparable to or slightly more efficient than rhenium in the dipolar interactions. Only the singular hydride (T_1 = 40 ms) has four short-range (177–178 pm) interactions with other hydrogens, which make its relaxation with rhenium "only" 18% of its overall R_1. In rhenium polyhydrides, therefore, the metal–hydrogen interaction should not be neglected when the distances between hydrogens or the number of possible H_2 moieties in fluxional systems are estimated through NMR measurements.

These observations are supported also by reports,[21] appearing in the literature after the preparation of this paper, that generalize the relevance, in the relaxation of the hydrides, of the dipolar interactions with the metal itself and with the hydrogens of the ligands.

Experimental Section

Compound **1** was prepared according to literature methods.[22] Different solutions were used for T_1 measurements. An amount of 200 mg was dissolved in 3 mL of toluene-d_8 (ca. 0.1 M) for the preliminary measurements at 1.87 and 4.7 T. The concentration dependence of the relaxation times was verified against that of a dilute solution (8 mg in 0.5 mL, ca. 0.028 M). All the solutions were carefully degassed with repeated freeze-thaw cycles before the measurements. Most of the experiments were made on a solution prepared by dissolving 124 mg in 2.5 mL of toluene-d_8 (ca. 0.08 M). An appropriate amount of this solution, after the ^{31}P measurements at 32.44 and 121 MHz, was then transferred into a 5-mm NMR tube, and after repeated freeze–thaw cycles, the tube was sealed under vacuum and used for the other measurements on ^1H and ^{31}P.

Compound **2** was prepared by following literature method,[23] distilled under vacuum, and trapped directly into a 5-mm NMR tube, while, for the sparingly soluble compound **3**, prepared according to literature methods,[24] a saturated (<30 mg in 1 mL, <0.05 M) solution was used. The partially deuterated derivative of **3** was obtained by exchange with D_2O in the presence of Florisil.[24] The solutions were degassed thoroughly, and the tubes were sealed under vacuum after several freeze–thaw cycles.

The relaxation time measurements were performed using the standard inversion recovery and Carr–Purcell–Meiboom–Gill pulse sequences. In each measurement the waiting period was 8–10 times the expected relaxation time and a total of 13–20 variable delays were employed. The spectrometers used were Bruker WP80, Bruker AC200, Bruker AM300, Bruker AM400, Bruker AM500, and Bruker AMX600. The temperatures were controlled by a variable-temperature unit which ensured a precision of ±1 K for all the spectrometers except the AMX600, where the precision was ±0.1 K. The temperature was calibrated using methanol solutions.[25]

The calculation of the relaxation times was made using the nonlinear three-parameter fitting routine of the spectrometers or a commercial program of data handling (ASYSTANT PLUS). The results are the mean of at least two measurements, and the standard deviations of the reported values range from 2 to 8%.

The fitting of the field dependence of T_1 was made both with ASYSTANT PLUS and with the program MINUIT (from the CERN Computer Center). The two programs gave fitting parameters with differences on the order of 5–10%. Mean values have been used for the subsequent calculations. MINUIT was used also for the fitting of the temperature dependence of T_1 in $[Re_2(\mu\text{-}H)_2(CO)_8]$. No attempts were made to fit the temperature dependence of ^1H in $[HRe(CO)_4PPh_3]$ because of the presence of different types of dipolar interactions; in the case of $[HRe(CO)_5]$, due to the absence of a defined minimum in the temperature dependence, the values of r and τ_0 are highly correlated and several couples of possible values can be found.

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(19) Wei, C.; Garlaschelli, L.; Bau, R.; Koetzle, T. F. *J. Organomet. Chem.* **1981**, *213*, 63.

(20) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126.

(21) (a) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173. (b) Luo, X.-L.; Howard, J. A. K.; Crabtree, R. H. *Magn. Reson. Chem.*, in press. (c) Luo, X.-L.; Liu, H.; Crabtree, R. H. *Inorg. Chem.*, submitted for publication.

(22) Flitcroft, N.; Leach, J. M.; Hopton, F. J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 137.

(23) Beck, W.; Heber, W.; Braun, G. *Z. Anorg. Allg. Chem.* **1961**, *308*, 23.

(24) Andrews, M. A.; Kirtley, S. W.; Kaesz, H. D. *Inorg. Chem.* **1977**, *16*, 1556.

(25) Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679.