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Phosphorus Longitudinal Relaxation Times as a Probe of the Coordination Site of the Phosphine Ligands in Rhenium Complexes

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The metal−phosphorus coupling constant, ${}^1J(M-P)$, is a fundamental tool for the characterization of coordination compounds in solution, being sensitive to the oxidation state, to the coordination number of the metal, and to the geometrical arrangement of the atoms around the coupled nuclei.[1] However, when one of the two spins is quadrupolar, its fast relaxation often hampers the direct observation of the coupling in the NMR spectrum of the spin $^1/_2$ nucleus[2] and this is the case for rhenium (^{185}Re, $I = {}^5/_2$, natural abundance (na) 37.07%; ^{187}Re, $I = {}^5/_2$, na 62.93%).

Recently we have studied the relaxation behavior of ^{31}P in $[ReH(CO)_4PPh_3]$[3] and have shown that the longitudinal relaxation, at least up to 7 T, is due to the fast fluctuating magnetic fields provided by the quadrupolar isotopes of rhenium to which ^{31}P is scalarly coupled. This mechanism is the so called scalar coupling of the second kind[2] (sc) and the relative relaxation rate is defined according to eq 1, where S is the nuclear spin

$$R_1(\mathrm{sc}) = (8/3)[S(S+1)]\pi^2 J^2\{T_2(\mathrm{Re})/[1 + (\Delta\gamma)^2 B_0^{\,2}(T_2(\mathrm{Re}))^2]\} \quad (1)$$

quantum number of rhenium, J is the scalar coupling constant between phosphorus and rhenium, T_2(Re) is the transverse relaxation time of the quadrupolar metal, $\Delta\gamma$ is the difference of the magnetogyric ratios of the involved nuclei, and B_0 is the applied magnetic field. The longitudinal relaxation time $[T_1 = (R_1)^{-1}]$ of ^{31}P is observed, therefore, to be sensitive to the value of the ${}^1J(P-Re)$, a parameter that, to the best of our knowledge, has never been observed or measured directly.

We report here on the relaxation properties of ^{31}P in other mono and polynuclear rhenium compounds. The results show that sc is the mechanism ruling the relaxation at low fields and that, in some cases, comparison of the ^{31}P longitudinal relaxation times, which are sensitive to ${}^1J(P-Re)$, can be used to assign the relative ^{31}P coordination geometry in rhenium compounds.

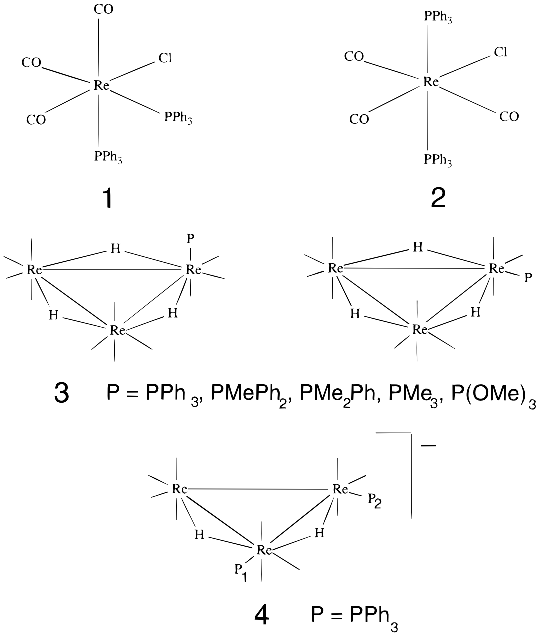
Results and Discussion

Field and Temperature Dependence of ^{31}P T_1 in the Two Isomers of $[Re(CO)_3Cl(PPh_3)_2]$. The longitudinal relaxation times, T_1, of ${}^{31}P\{{}^1H\}$ in $CDCl_3$ solutions of the two isomers *fac*-$[Re(CO)_3Cl(PPh_3)_2]$ (**1**) (δ 3.64 ppm) and *trans-mer*-$[Re(CO)_3Cl(PPh_3)_2]$ (**2**) (δ 9.34 ppm) (Chart 1) have been measured at 1.87, 4.7, and 7.04 T at 302 K (Table 1). ${}^{31}P\{{}^1H\}$ nuclear Overhauser enhancements (NOE) have also been measured at 4.7 T and 302 K: $\eta = 0.04$ and 0 for **1** and **2**, respectively.

Table 1. Longitudinal Relaxation Times of ^{31}P in the Two Isomers of $[Re(CO)_3Cl(PPh_3)_2]$ in $CDCl_3$

	T_1 (s)		
T (K)	**1**	**2**	B_0 (T)
310	1.84(3)	0.28(3)	1.87
302	1.55(9)	0.26(2)	
302	4.79(5)	1.18(3)	4.7
291	4.06(2)	1.04(3)	
266	2.40(2)	0.77(3)	
250	1.69(1)	0.69(1)	
237	1.22(5)	0.60(1)	
221	0.87(4)	0.55(2)	
302	4.87(3)	2.23(3)	7.04

Chart 1



The increase of T_1 with the applied field[4] at 302 K and the absence of NOE indicate that the scalar coupling mechanism is operative and dominant at low fields for both the isomers. The contribution of the chemical shift anisotropy (csa) mechanism, dominant in the relaxation of ^{31}P in other PPh_3 complexes,[5] is relevant here only over 7 T and is more effective in the *fac* isomer.

The relaxation times of both the species have also been measured at variable temperature at 4.7 T (Table 1). The observed decrease with the temperature indicates that T_1 is proportional to the reciprocal of the molecular correlation time τ_c, that has an Arrhenius type temperature dependence $[\tau_c = \tau_0 \exp(E_a/RT)$, E_a being the activation energy for the molecular reorientation]. The sc mechanism is a function of τ_c through

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(1) (a) Appleton, T. G.; Clark, H. C.; Manzer, L. E., *Coord. Chem. Rev.* **1973**, *10*, 335 and references therein. (b) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: Berlin, 1979. (c) Jameson, C. J. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds; VCH Publishers: New York, 1987; Chapter 6. (d) Verkade, J. G.; Mosbo, J. A. Reference 1c, Chapter 13.

(2) (a) Abragam, A. *The Principles of Nuclear Magnetism*; Oxford University Press: London, 1961. (b) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Pitman Ed.: London, 1983.

(3) Beringhelli, T.; D'Alfonso, G.; Minoja, A. P., Freni, M. *Inorg. Chem.* **1992**, *31*, 848.

(4) Under the extreme narrowing conditions, two relaxation mechanisms are field dependent: the one due to the scalar coupling of the second kind (eq 1) and the one due to the chemical shift anisotropy (csa).[2] However, while for the former, the relaxation times increase with the applied magnetic field, the opposite is true for the csa mechanism since for this $R_1(\mathrm{csa}) = [T_1(\mathrm{csa})]^{-1} = (2/15)\gamma_I^{\,2}B_0^{\,2}\Delta\sigma^2\tau_c$, where τ_c is the molecular correlation time and $\Delta\sigma$ is the chemical shielding anisotropy, the other symbols having the usual meanings.[2]

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Table 2. Longitudinal Relaxation Times[a] (T_1/s) of ^{31}P in $[Re_3(\mu\text{-}H)_3(CO)_{11}PR_3]$

	$PR_3 =$ PPh_3	$PR_3 =$ $PMePh_2$[b]	$PR_3 =$ PMe_2Ph	$PR_3 =$ PMe_3	$PR_3 =$ $P(OMe)_3$
axial	6.7(2)	6.5(1)	6.9(2)	7.9(7)	3.3(5)
equatorial	0.86(2)	1.15(6)	1.39(3)	2.07(3)	0.79(5)

[a] 81.015 MHz, 298 K, CD_2Cl_2. [b] ax 4.7(2) s, eq 0.91(2) s in $CDCl_3$.

T_2(Re), which is, in turn, proportional to $(\tau_c)^{-1}$.[6] Until T_2(Re) is great enough to make $(\Delta\gamma)^2B_0{}^2(T_2(Re))^2 \gg 1$ in eq 1, T_1(^{31}P) is proportional to T_2(Re) and therefore to $\tau_c{}^{-1}$. In the present case, this holds for both the isomers and the reorientation energy is lower for the C_{2v} *mer* isomer: 7.9(1) kJ/mol *vs* 12.8(3) kJ/mol.

Assuming that at low fields the relaxation is due only to the sc mechanism, ^1J(P−Re) and T_2(Re) for both compounds have been calculated: ^1J(P−Re) = 710 Hz and T_2(Re) = 9.5 ns for the *fac* isomer and ^1J(P−Re) = 1760 Hz and T_2(Re) = 17 ns for the *mer* isomer.

The difference in the coupling constants is significant: the ^1J with rhenium is observed to be smaller in the *fac* isomer where both the P−Re bonds are *trans* to a carbonyl, than in the *mer* isomer where they are mutually *trans*. Similar effects in ^1J(P−M) have been previously observed also in pentacoordinated Rh(I) complexes[7] and in the *cis* and *trans* isomers of the octahedral $[W(CO)_4(PR_2R')_2]$ (*e.g* $^1J(P-W)_{cis} = 225-230$ Hz and $^1J(P-W)_{trans} = 265-275$ Hz).[8]

^{31}P Longitudinal Relaxation in the Axial and Equatorial Isomers of the Triangular Clusters $[Re_3(\mu\text{-}H)_3(CO)_{11}PR_3]$. Recently we have studied[9] the interconversion of the axial and equatorial isomers of $[Re_3(\mu\text{-}H)_3(CO)_{11}L]$ (**3**) (L = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, $P(OMe)_3$) (Chart 1). The ^{31}P longitudinal relaxation times have now been measured on equilibrium mixtures of these isomers. As reported in Table 2, the T_1 values for of the axial ligands are always remarkably longer than those for the equatorial ligands, whatever the electronic or steric properties of the phosphines.

Measurements performed on the $PMePh_2$ derivatives have shown that the relaxation of ^{31}P is dominated also in these cases by the scalar coupling mechanism. In fact, dipolar relaxation is irrelevant ($\eta = 0$ and 0.05 for the equatorial and the axial isomer), and for both the isomers T_1 increases with the field: at 298 K $T_1(P_{ax})$ = 1.9(1), 6.5(1), and 6.4(1) s and $T_1(P_{eq})$ = 0.22(1), 1.15(6), and 2.04(6) s at 1.87, 4.7, and 7.04 T, respectively.

The increase of the values of the T_1's of both the axial and equatorial resonances on passing from the PPh_3 to the PMe_3 derivatives is due to the change of the rotational correlation time of the whole molecule. The short T_1 of the small $P(OMe)_3$ ligand is due to the increased ^1J(P−Re) for the greater electron-withdrawing power of the OMe group with respect to Ph.[1b−d]

The ^1J(P−Re) for the $PMePh_2$ derivatives, calculated from the results at 1.87 and 4.7 T, are 634 Hz for the axial isomer and 1605 Hz for the equatorial one, while T_2(Re) is 10 ns for both species.

Therefore also in these cluster complexes the difference in the T_1 values of the axial and the equatorial sites stems from the different Re−P coupling constants, which reflect the difference in the *trans* ligand (a carbonyl and a bridging hydride, respectively).

It is worth noting that, for rhenium compounds, this marked difference of the ^{31}P T_1's must be taken into account to get NMR signals with reliable relative intensities.

^{31}P Longitudinal Relaxation in the Triangular Cluster Anion *eq,eq*-$[Re_3(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]^-$. Two ^{31}P resonances (δ 21.7 and 6.3 ppm) are observed for *eq,eq*-$[Re_3(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]^-$,[10] (**4**, see Chart 1, based on the solid state structure). They have been unambiguously assigned, through $^1H\{^{31}P\}$ selective decoupling experiments, to P_2 and to P_1, respectively. The coupling pattern of the ^{1}H spectrum[11] and the ^{31}P chemical shifts do not allow to establish unambiguously if P_2 is axial or equatorial. The measurements of the relaxation times have shown that both have T_1's that increase with the field indicating that sc is the relaxation mechanism: T_1 = 0.24(2), 0.79(2), and 1.15(7) s for P_1 and T_1 = 0.19(1), 0.53(1), and 0.87(5) s for P_2 at 1.87, 4.7 and 7.01 T, respectively, at 298 K in acetone-d_6. The ^1J(P−Re) and the T_2(Re) values calculated according to eq 1 are 1790 Hz and 10 ns for P_1 and 2070 Hz and 8.5 ns for P_2. The high values of the coupling constants (or the short values of the relaxation times) are in agreement with both the phosphines being *trans* to ligands other than CO. However, no inference can be made about which is which *only* on the basis of the differences in T_1 because the two phosphines belong to metal fragments bearing different ligands. Indeed from the expected order of *trans*-influence[12] the ^1J(P−M) of a phosphine *trans* to a metal−metal interaction would be predicted smaller (the T_1 longer) than the one of a phosphine *trans* to a bridging hydride, *if the two phosphines were bound to the same metal or to metals with the same coordination sphere*.

Conclusion

We have shown that the longitudinal relaxation time of ^{31}P bound to rhenium is dominated by the scalar coupling mechanism, and that, therefore, it depends on the value of ^1J(Re−P), which is sensitive to the nature of the ligands *trans* to ^{31}P. The absolute value of T_1 is affected by several factors such as the bulkness of the ligands, the charge of the compound, the viscosity of the solvent, the temperature, and so on. However, when other evidences are lacking or ambiguous, e.g. the coupling constants with the hydrides, the *comparison* of the ^{31}P relaxation times can be a useful tool to establish the relative coordination geometry of the P ligands, in the presence of isomers or when the ligands are bound differently to the same metal or, in cluster compounds, to different rhenium sites, *provided that they have the same coordination sphere*. For instance, we are currently successfully using this criterion for the identification of the coordination geometry of the phosphines in the cluster complexes $[Re_3(\mu\text{-}H)_3(CO)_9(PR_3)_3]$,[13] and $[Re_4(\mu\text{-}H)_5(CO)_{12}(PR_3)_2]^-$,[14] where the comparison is among $ReH_2(CO)_3PR_3$ moieties. Indeed, when we compare the T_1 of phosphines bound to metal moieties that do not bear the same

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(6) The quadrupolar longitudinal and transverse relaxation rates are given by[2] $R_1(q) = R_2(q) = (T_1)^{-1} = (T_2)^{-1} = \{(3/10)\pi^2(2I + 3)/[I^2(2I - 1)]\}(1 + \eta^2/3)(e^2qQ/h)^2\tau_c$, where I is the spin quantum number of the quadrupolar isotope, η is the asymmetry parameter, and $(e^2qQ/h)^2$ is the quadrupolar coupling constant.

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(11) ^{1}H NMR δ −16.15 ppm (d, 1H, $J(H-P_1)$ = 24 Hz), −16.83 ppm (dd, 1H, $J(H-P_2)$ = 14.5 and $J(H-P_1)$ = 4.5 Hz) (acetone-d_6, 200 MHz, 298 K). In hydrido carbonyl cluster compounds of rhenium the values of the coupling constants of the hydrides with the *trans* ligands are generally smaller than or comparable with those with the *cis* ligands, at variance with what is observed for related compounds containing other metals.

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ligands, electronic and/or steric factors can overcome or smooth the differences expected on the basis of the change of the *trans* ligand.

Experimental Section

The ^{31}P spectra have been recorded on a Bruker WP 80 SY, a Bruker AC 200, and a Varian XL 300. The temperatures were measured using the standard calibration solutions (CH_3OH/CD_3OD or ethylene glycol/DMSO-d_6) and controlled by the appropriate spectrometer unities. All the solutions were carefully degassed before the measurements and kept under nitrogen. The relaxation times (uncertainties in parentheses) have been calculated through the nonlinear three-parameters fit of the data collected by nonselective inversion recovery experiments. The relaxation delay was set 5−10 times the longer T_1 and from 8 to 14 variable delays were employed. If the case, the experiments were run twice optimized for the long or the short T_1. For the NOE measurements two spectra were recorded with the decoupler on during the waiting and the acquisition times, but the offset was properly shifted during the waiting time, set equal to $10T_1$. The 4K data were zero filled twice and the NOE was calculated comparing both the heights and the integrated intensities of the resonances. The reported results are the average of these measurements. All the experiments were repeated at least twice and were reproducible. The calculations of ^1J(Re−P) and T_1(Re) through eq 1 have been made for the most abundant ^{187}Re, being the nuclear properties (γ and Q) of the two isotopes very similar. Compounds **1**−**4** have been prepared and characterized following literature methods.[15,16,9,10] The concentration of the solutions was typically 0.05−0.02 M or less for the sparingly soluble monomeric compounds.

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