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Fundamental Studies on Phosphorus-31 Relaxation Mechanisms: The Importance of Chemical Shift Anisotropy and Its Implications for ^{31}P NMR Studies of Organometallic Compounds

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Phosphorus-31 NMR spectroscopy has become a key physical technique in the arsenal of the inorganic and organometallic chemist. Recent developments in pulsed FT methods and high-field spectrometers have made accessible a range of powerful 2D experiments to probe complex coupling networks[1] and chemical exchange phenomena.[2] Critical to the optimization of 1D ^{31}P experiments and to the effective application of 2D techniques is an understanding of ^{31}P relaxation mechanisms. Although a number of studies have been reported for organophosphorus compounds,[3] few such measurements have been made for ^{31}P nuclei in transition-metal complexes[4] and fundamental information directly relevant to the implementation of 2D experiments is lacking. In this report we wish to demonstrate the dominance of the chemical shift anisotropy mechanism for ^{31}P relaxation in several organometallic complexes, via solution and solid-state ^{31}P NMR measurements. These results represent the first reported for phosphido ligands, provide additional significant data for coordinated tertiary phosphines, and have important ramifications for the quantitative interpretation of ^{31}P NMR spectra for transition-metal complexes.

Results and Discussion

Phosphorus spin–lattice relaxation may have contributions from several sources:[5] the principal mechanisms are the spin-rotation interaction, the dipolar (proton–phosphorus) interaction, and the chemical shift anisotropy (eq 1).

$$(T_1)^{-1}{}_{\mathrm{TOT}} = (T_1)^{-1}{}_{\mathrm{SR}} + (T_1)^{-1}{}_{\mathrm{DD}} + (T_1)^{-1}{}_{\mathrm{CSA}} + \text{others} \qquad (1)$$

Although the extent to which the chemical shift anisotropy (CSA) contributes to ^{31}P spin-lattice relaxation (T_1) in organometallic compounds has not been determined, this mechanism has recently been recognized as important for ^{13}C nuclei in metal carbonyls,[6] for ^{15}N in dinitrogen complexes,[7] and for ^{195}Pt in inorganic Pt(II) compounds.[8] The T_1 values for Ru$_3$(CO)$_9$(μ_3-η^2-C≡CBu^t)[μ-P(C≡CBu^t)$_2$] (**1**), Ru$_2$(CO)$_6$(μ-η^2-C≡CBu^t)(μ-PPh$_2$) (**2**), Ru$_3$(CO)$_6$(μ-CO)$_2$(μ_3-η^2-C≡CBu^t)(μ-PPh$_2$) (**3**), and Fe$_2$(CO)$_6$(μ-η^2-C≡CBu^t)(μ-PPh$_2$) (**4**) are presented in Table I. Nuclear Overhauser enhancement (NOE) factors have been obtained for complexes **1–3** to evaluate the contribution to the relaxation rate from the phosphorus–proton dipole interaction. For complex **2**, $R_{\mathrm{DD}} = (T_1)^{-1}{}_{\mathrm{DD}} = 0.0332$ s^{-1}, which represents 20% of the total relaxation rate.[9] The NOE factor for complexes

Table I. Spin–Lattice Relaxation Times for Complexes **1–4**

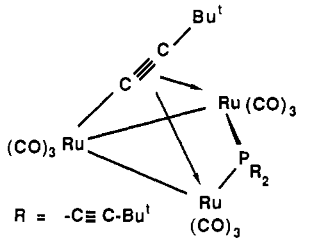
complex	relaxation time, s	NOE	conditions[a]
1	0.54		9.4 T, 300 K[b]
	1.34		5.9 T, 300 K[b]
	1.38		5.9 T, 300 K[c]
	1.68		5.9 T, 310 K[b]
	1.98		5.9 T, 320 K[b]
	2.39		5.9 T, 330 K[b]
	2.73		5.9 T, 338 K[b]
	2.12	0.03	4.7 T, 300 K[b]
	4.20		4.7 T, 338 K[b]
	9.01		1.9 T, 300 K[b]
2	2.55		9.4 T, 300 K[c]
	6.10	0.25	5.9 T, 300 K[c]
	2.79		5.9 T, 262 K[c]
	2.19		5.9 T, 250 K[c]
	1.69		5.9 T, 240 K[c]
	7.67		4.7 T, 300 K[c]
3	0.50	0.10	5.9 T, 305 K[b]
4	2.94		9.4 T, 305 K[b]
	6.76		5.9 T, 305 K[b]

[a] T_1 values for complexes **2–4** were obtained under conditions of proton noise decoupling. [b] Measurements were made in benzene-d_6. [c] Measurements were made in CDCl$_3$.

Table II. Spin–Lattice Relaxation Times for Complexes **5** and **6**

complex	relaxation time, s	NOE	conditions[a]
5	8.28	0.57	4.7 T, 310 K[c]
	6.80	0.45	5.9 T, 310 K[c]
	3.44		9.4 T, 310 K[c]
	2.29	0.15	11.8 T, 310 K[c]
6	12.3	0.55	4.7 T, 310 K[c]
	8.64	0.42	5.9 T, 310 K[c]
	8.7	0.44	5.9 T[d]
	4.20		9.4 T, 310 K[c]
	2.96	0.14	11.8 T, 310 K[c]
	2.60		11.8 T, 305 K[b]
	3.71		11.8 T, 320 K[b]
	5.95		11.8 T, 340 K[b]

[a] T_1 values for complexes **5** and **6** were obtained under conditions of proton noise decoupling. [b] Measurements were made in benzene-d_6. [c] Measurements were made in CDCl$_3$. [d] Reference 4a.



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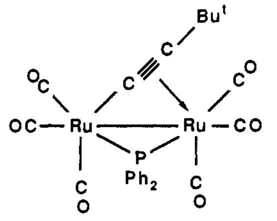

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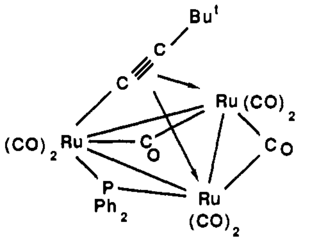

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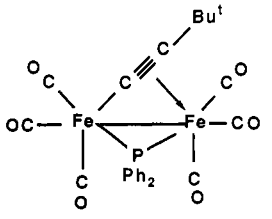

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(5) A reviewer has pointed out the possibility of a paramagnetic contribution to the relaxation rate. However, if a thermally accessible triplet state was contributing to the overall relaxation, a decrease in temperature would result in a slower relaxation rate due to the decreased triplet-state population. Furthermore, EHMO calculations on Ru$_2$(CO)$_6$(μ-η^2-C≡CH)(μ-PH$_2$) show a singlet ground state with a large HOMO–LUMO gap. The triplet state is thus too high in energy to be thermally accessible.

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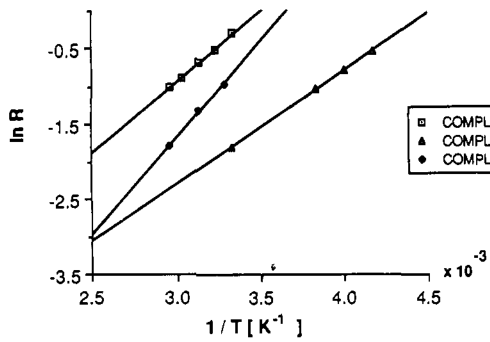
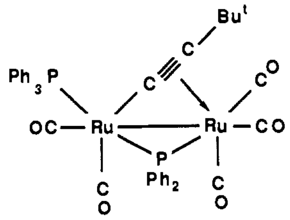


Figure 1. Dependence on ln R on $1/T$ for complexes **1**, **2**, and **6**.

1 and **3** is nonzero, but the evaluation of such a small NOE cannot be made with any certainty. For all three complexes, the dipolar mechanism clearly contributes only a small part to the total relaxation rate.

For *trans*-$Ru_2(CO)_5(PPh_3)(\mu\text{-}\eta^2\text{-}C{\equiv}CBu^t)(\mu\text{-}PPh_2)$ (**5**) and *trans*-$Ir(CO)Cl(PPh_3)_2$ (**6**) (Table II) NOE values of 0.45 and 0.42 are observed for the triphenylphosphine ligand. These values are similar to those obtained by Pregosin and co-workers in recent relaxation measurements on gold and iridium arylphosphine complexes.[4a] This is in contrast with the situation observed for coordinated alkylphosphines,[4c] in which near-optimum NOE factors were obtained. Since the efficiency of the dipolar mechanism is inversely proportional to the sixth power of the hydrogen–phosphorus separation, arylphosphine complexes can be expected to exhibit smaller NOE factors than alkylphosphine complexes. The fact that relatively short relaxation times are observed for complexes which have little NOE demonstrates that other mechanisms are contributing significantly to the overall relaxation rate.



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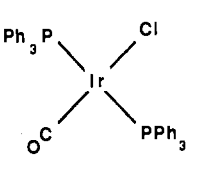

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The contribution from the spin-rotation mechanism can be evaluated by examining the temperature dependence of the relaxation rate. A plot of ln R vs $1/T$ is shown in Figure 1. For complexes **1**, **2**, and **6**, a positive slope is obtained, which indicates that the spin-rotation mechanism is not operative in the temperature ranges examined. The spin-rotation mechanism is usually found for small symmetrical molecules and has been implicated as a major contributor to relaxation in uncoordinated tertiary phosphines.[3c,d] However, variable-temperature studies of palladium complexes[4c] demonstrate that no contribution from this mechanism is observed for coordinated phosphines. The variable-temperature results obtained in this study for complex **6** confirm this. These studies highlight the fact that important differences exist between coordinated and uncoordinated phosphines in their relaxation behavior.

The reduction of T_1 with increasing field strength for all of the complexes **1**–**6** clearly demonstrates that the CSA mechanism is contributing to the relaxation rate. The anisotropy contribution is given by[10]

$$(T_1)^{-1}_{\rm CSA} = \gamma^2 B_o^2[(\sigma_{33} - \sigma_{11})^2 + (\sigma_{33} - \sigma_{22})^2 + (\sigma_{22} - \sigma_{11})^2]\tau_c/15[1 + (\gamma B_o \tau_c)^2] \quad (2)$$

assuming isotropic reorientation of the molecular frame in the coordinate system with the origin at the ^{31}P atom, in which the ^{31}P tensor is diagonal. The quantities σ_{11}, σ_{22}, and σ_{33} are the principal values of the chemical shift tensor in ppm, for which we will use the conventional assignment of $\sigma_{33} > \sigma_{22} > \sigma_{11}$. This equation shows the importance of the CSA mechanism, for which the rate is proportional to the square of the external field (B_o).

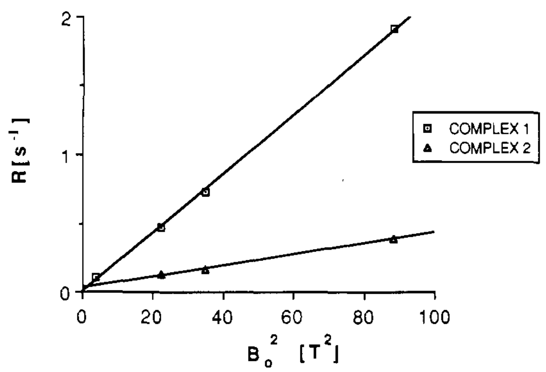

Figure 2. Influence of the external magnetic field, B_o, on the relaxation rate for complexes **1** and **2**.

Table III. Principal Components (ppm) of the ^{31}P Chemical Shift Tensor As Obtained from the Spinning Sidebands of CP/MAS Spectra

species	σ_{33}	σ_{22}	σ_{11}	$\Delta\sigma^b$	$\sigma_{\rm iso}$
1	47	−123	−438	328	−171.3
2	242	137	−10	178.5	123
3	724	185.4	−19	640.8	296.8
$Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPr^i)(\mu\text{-}PPh_2)^a$	122	0	−339	291.5	−72.3
6^a	105	−2	−30	121	24.3

[a] Values obtained from a powder spectrum. [b] $\Delta\sigma = \sigma_{33} - {}^1/_2(\sigma_{22} + \sigma_{11})$. The estimated uncertainties in the σ_{11}, σ_{22}, and σ_{33} values are ±5 ppm.

Shown in Figure 2 is the linear dependence of the relaxation rate on the square of the field strength for complexes **1** and **2**. The values of the principal elements of the shielding tensors (Table III) are calculated from the sideband intensities of the solid-state magic angle spinning spectra[11] and the method of Herzfeld and Berger.[12] These values, combined with the slope of the relaxation rate vs B_o^2 plot (Figure 2), yield a value for the molecular correlation time, τ_c, of 75 ps for complex **1** and 53 ps for complex **2**, which indicates that the extreme narrowing condition applies ($\omega\tau_c \ll 1$). In the solid-state spectrum of complex **1** (Figure 3) the isotropic peak resonates at −170.2 ppm and the measured anisotropy is 328 ppm.[13] The CSA value found for complex **1** is similar to that obtained for $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPr^i)(\mu\text{-}PPh_2)$ and is substantially larger than the 178.5 ppm value found for complex **2**.[14] These values demonstrate that a substantial contribution from the chemical shift anisotropy mechanism can be expected for these and related complexes.

We have also been interested in examining the relaxation properties of coordinated arylphosphines. The relaxation rate for triphenylphosphine in both complex **5** and Vaska's complex, *trans*-$Ir(CO)Cl(PPh_3)_2$ (**6**), is clearly field dependent as shown in Figure 4. We have also measured the powder pattern for *trans*-$Ir(CO)Cl(PPh_3)_2$.[15] We found that the CSA value for triphenylphosphine in this complex is 121 ppm, significantly larger than the anisotropy determined for uncoordinated triphenylphosphine (50 ppm).[16] There is additional solid-state evidence

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(9) The contribution from the dipolar mechanism can be evaluated by $\eta_{\rm obs} = \eta_{\rm theor}R_{\rm DD}/(R_{\rm DD} + R_{\rm others})$, where $\eta_{\rm theor} = 1.234$.

(10) (a) Petr, A.; Grossman, G.; Klose, G.; Ahlnas, T.; Gotze, T. *J. Magn. Reson.* **1986**, *67*, 231. (b) Blicharski, J. S. *Z. Naturforsch, A* **1972**, *27*, 1456.

(11) The solid-state NMR spectrum of complex **1** was obtained on a Bruker CXP-200 spectrometer, with a spin rate of 3.73 KHz, pulse interval of 60 s, and accumulation of 1348 scans.

(12) Herzfeld, J.; Berger, A. E. *J. Chem. Phys.* **1980**, *73*, 6021.

(13) The chemical shift anisotropies are calculated from $\Delta\sigma = \sigma_{33} - {}^1/_2(\sigma_{11} + \sigma_{22})$.

(14) Carty, A. J.; Fyfe, C. A.; Lettinga, M.; Johnson, S.; Randall, L. H. Submitted for publication in *Inorg. Chem.*

(15) We are grateful to a reviewer for suggesting this solid-state measurement of σ rather than an estimate of $\Delta\sigma$ based on an approximate correlation time.

(16) Bemi, L.; Clark, H. C.; Davies, J. A.; Fyfe, C. A.; Wasylishen, R. E. *J. Am. Chem. Soc.* **1982**, *104*, 438.

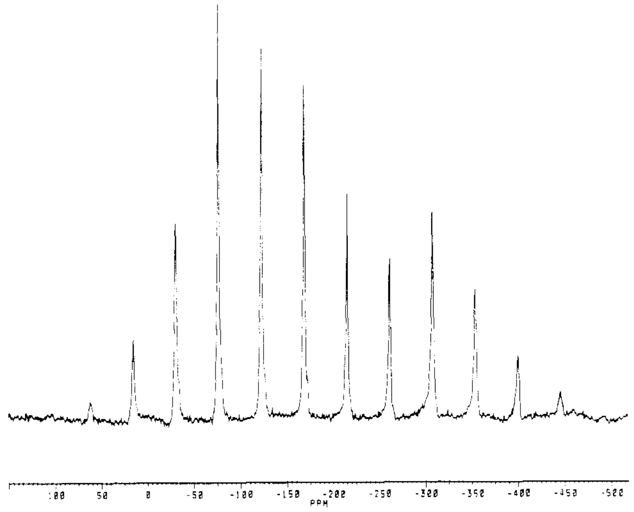

Figure 3. CP/MAS solid-state ^{31}P NMR spectrum of complex **1**.

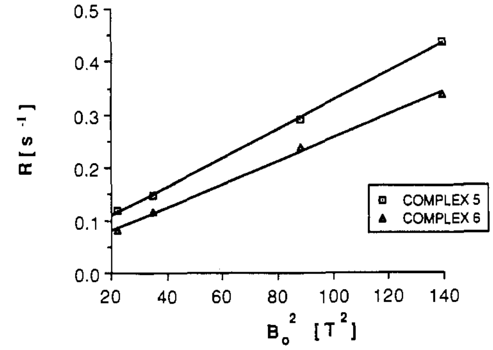

Figure 4. Influence of the external magnetic field, B_0, on the relaxation rate of triphenylphosphine for complexes **5** and **6**.

that coordinated arylphosphines have much larger shielding anisotropies than the free ligands. Thus, for $RhCl(PPh_3)_3$, which has been the subject of a single-crystal solid-state study,[17] the shielding anisotropies of the three phosphorus nuclei are 124, 125, and 222 ppm.[13] A direct result of large CSA values is shorter relaxation times in solution due to the increased efficiency of the CSA mechanism. Our data together with earlier relaxation measurements showing much shorter T_1 values for arylphosphine complexes than for the free ligands[4a] lead us to suggest that ^{31}P chemical shift anisotropy increases upon coordination.

An additional factor governing coordinated phosphine relaxation is the expected increase in τ_c upon complexation due to the reduced mobility and higher molecular weight. Since both the dipolar and the CSA mechanisms are inversely proportional to τ_c (in the extreme narrowing condition), an increase in τ_c will also decrease the observed T_1. The result of these two factors is that the relaxation times for coordinated tertiary phosphines will vary considerably from those of the free phosphines. These differences can be critical in quantitative studies of intermolecular ligand dissociation or phosphine substitution reactions.

It is clear that substantial differences in relaxation behavior exist between coordinated and uncoordinated phosphorus ligands and that the CSA mechanism can play an important role in the relaxation of phosphorus nuclei in transition-metal complexes.

Experimental Section

Table IV. ^{31}P Solution Chemical Shifts for Complexes **1-5**

complex	chem shift,[a] ppm	complex	chem shift,[a] ppm
1	-171.5	**4**	148.4
2	125.2	**5** μ-PPh_2	124.7
3	334.3	PPh_3	39.7

[a] Relative to H_3PO_4.

The ^{31}P NMR spectra were recorded on Bruker AM-500, WH-400, AM-250, AC-200, and WP-80 spectrometers equipped with a standard multinuclear probe head of 10-mm diameter. Temperatures were measured by using the proton shift of methanol or ethylene glycol and were maintained by using the Bruker VT-1000 temperature control unit. The relaxation measurements were performed by using a nonselective inversion-recovery pulse sequence, $(180-\tau-90-T_w)_n$. All solutions were degassed (freeze-thaw cycle) and were measured under dry dinitrogen. Typically 10-15 τ values were employed with a waiting time greater than $5T_1$. The data were analyzed by using a nonlinear least-squares fit to the equation $M(T) = A - Be^{-\tau/T_1}$, and estimated errors are less than 5%. NOE factors were measured by using the gated decoupling technique with a delay of 60 s. To avoid instrumental variations, these measurements were repeated five times and an average value is reported in the tables. Typical concentrations used were 0.1 M solutions. The solution ^{31}P NMR shifts of complexes **1-5** are listed in Table IV. Complexes **1-5** were prepared by literature methods[18-20] and have been characterized by elemental analysis and proton, carbon, and phosphorus NMR spectroscopies. Complex **6** was obtained from Strem Chemicals.

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Registry No. **1**, 118920-01-7; **2**, 82647-83-4; **3**, 77716-69-9; **4**, 59584-68-8; **5**, 118949-35-2; **6**, 15318-31-7.

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High-Field Magic-Angle-Spinning ^{13}C NMR Spectroscopy of $Co_4(CO)_{12}$

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The elucidation of the solution and solid-state structures of $Co_4(CO)_{12}$ has attracted the interest of metal carbonyl chemists for over 30 years.[1-12] A representation of the solid-state structure as determined by Wei and Dahl is shown in Figure 1.[10,11] The determination of this structure was complicated by a disorder of the molecule which lies on a special position requiring a 2-fold rotation axis. Redetermination of the structure confirmed the disorder model proposed by Wei and Dahl but was unable to define the separate positions for the overlapping carbonyl ligands.[12] Both orientations of the molecule are represented in Figure 1. The solution structure and has recently been shown to be same as the solid-state structure by high-field ^{13}C NMR[9] and ^{17}O NMR.[5]

Recently one of us reported the low-field (2.1 T, 22.6 MHz) variable-temperature MAS ^{13}C NMR spectra for solid Co_4(C-

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