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ASSIGNMENT OF THE ^{13}C NMR RESONANCES IN TRIALKYLPHOSPHINES FROM SPIN-LATTICE RELAXATION TIME MEASUREMENTS

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Summary

Analysis of the ^{13}C NMR chemical shift and coupling constant data for a number of straight-chain aliphatic trialkylphosphines and their transition metal carbonyl complexes suggests that complexation leads to: (1) a deshielding of C(1) and an increase in $^{1}J(^{13}C^{31}P)$, (2) a slight shielding of C(2) and a decrease in $^{2}J(^{13}C^{31}P)$, and (3) little or no change in the chemical shift for C(3) and a slight increase in $^{3}J(^{13}C^{31}P)$. Application of these rules to the assignment of the ^{13}C NMR spectrum of P(butyl)$_3$ led to conflict with prior work. A study of segmental motion in these derivatives via spin-lattice (T_1) relaxation time measurements was therefore performed, and these data are in complete agreement with the proposed assignments. These generalizations must be applied with care, however, since the presence of either unsaturation or branching near the phosphorus can interfere with this pattern.

Introduction

Assignments of the ^{13}C NMR spectra of trialkylphosphines are complicated by close similarities in the chemical shift and $J(^{13}C^{31}P)$ coupling constant data. In the course of a systematic study of the electronic effects of Group Va ligands in transition metal carbonyl complexes [1—7], we have obtained data for trialkylphosphines and their LNi(CO)$_3$ complexes which suggest that changes in the chemical shifts and coupling constants on complexation can be used to assign these spectra [8]. We wish to report herein a study of segmental motion in a series of aliphatic trialkylphosphines and their LNi(CO)$_3$ complexes via

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spin-lattice (T_1) relaxation time measurements which confirms these assignments.

Experimental

Triethyl- and tributylphosphine were purchased from Strem Chemical Company, and $Ni(CO)_4$ was purchased from Matheson Gas Products. PR_3 ligands (R = propyl, pentyl, hexyl, octyl) were synthesized by the dropwise addition of an ether solution of trichlorophosphine to a slight excess of the Grignard or alkyllithium reagent in ether solution [9], and characterized by infrared and proton magnetic resonance spectroscopy. To minimize exposure to $Ni(CO)_4$ by a reduction in vapor pressure, $Ni(CO)_4$ was dispensed directly into $CDCl_3$ to form a 4 *M* solution which was then handled by syringe. All manipulations were carried out in a well-ventilated hood that had been tested with a smoke bomb before use. $LNi(CO)_3$ complexes were prepared by the addition of a 2-ml aliquot of 4 *M* $Ni(CO)_4$ in $CDCl_3$ to an argon- or nitrogen-purged NMR tube containing 8 mmol of the phosphine in 1 ml of $CDCl_3$. The samples were allowed to stand for 10—15 min and then agitated until CO evolution had ceased. The complexes were characterized by IR spectroscopy, and were destroyed immediately after use by reaction with bromine.

^{13}C NMR spectra were obtained with a JEOL FX-60-FT spectrometer equipped with an internal ^2D lock, operating at 15.06 MHz. ^{13}C spin-lattice (T_1) relaxation times were determined from proton-decoupled partially relaxed Fourier transform (PRFT) spectra using an inversion-recovery $(—T—180°—\tau—90°—)_n$ pulse sequence [10]. The 90° and 180° pulse times were 16 and 32 μsec, T was 25 sec, and typical values of τ were 0.2, 0.4, 0.6, 0.8, 1.0 and 1.5 sec. The data were checked for linearity by plotting $\ln(A_\infty - A_\tau) = \ln(2A_\infty) - \tau/T_1$, and the T_1's were calculated with the JEOL T_1 program which uses a least squares fit to the equation:

$$\frac{(M_0 - M_z)}{2M_0} = e^{-\tau/T_1}$$

Duplicate measurements suggest a precision of ±10%.

Spin-lattice relaxation

Spin-lattice or T_1 relaxation involves a net transfer to the lattice, acting as a heat sink, of the energy absorbed by a magnetic nucleus (e.g., ^{13}C) during irradiation, and is produced by fluctuating magnetic fields localized at or near the nucleus undergoing relaxation. There are three principal mechanisms for the spin-lattice relaxation of ^{13}C nuclei: (1) chemical shift anisotropy, which increases as the square of the magnetic field strength, (2) spin-rotation, which is important for small molecules, freely rotating groups within a molecule, and some non-protonated carbons, and (3) dipole—dipole interactions with a neighboring magnetic nuclei or unpaired electron spin. In general, ^{13}C spin-lattice relaxation of protonated carbon atoms is dominated by intramolecular dipole—dipole interactions with the directly bonded protons [11,12], and T_1 for these

systems is given by [13]

$$1/T_1 = N(h/2\pi)^2 \gamma_C^2 \gamma_H^2 r_{CH}^{-6} \tau_{eff} \quad (1)$$

where N is the number of directly-bonded protons, h is Planck's constant, γ_C and γ_H are the magnetogyric ratios of ^{13}C and ^1H, and r_{CH} is the C—H bond length. For rigid molecules undergoing isotropic rotation, τ_{eff} is the correlation time for molecular motion, τ_C. When the rotation is anisotropic, or if internal rotation can occur, τ_{eff} corresponds to an average molecular correlation time for reorientation of the C—H dipole. Equation 1 is valid only under conditions of complete proton decoupling [14], and in the "extreme narrowing limit", where $1/\tau_{eff}$ is much larger than the sum of the resonance frequencies of the ^{13}C and ^1H nuclei, in radians per second [15].

Equation 1 implies that carbon atoms in a given molecule with similar values of τ_{eff} will have relaxation times that decrease as the number of directly-bonded protons increases. Under these conditions, T_1 for a methine carbon would be twice T_1 for a methylene, and three times T_1 for a methyl group. Different carbon atoms in a molecule, however, do not necessarily have the same effective correlation times due to preferred modes of internal rotation or anisotropies in rotational tumbling [16]. For compounds of moderate molecular weight in solvents of low viscosity, an increase in internal rotational motion which decreases τ_{eff} also decreases the efficiency of dipolar relaxation, and therefore increases T_1 [17]. Spin-lattice relaxation times can therefore be used to study segmental or localized motion within a molecule.

To observe segmental motion along an aliphatic chain, the overall reorientation of the molecule must be restricted. In 1-decanol this results from intermolecular hydrogen bonding [18]. In aqueous solutions of n-alkyltrimethylammonium ions, it is provided by the immobilization of the polar end of the molecule that results from micelle formation [19]. The supposition that the R_2P- substituent would provide a sufficient molecular anchor to induce segmental motion along the alkyl chains in trialkylphosphines led to this study.

Results

^{13}C spin-lattice relaxation times for a series of straight-chain aliphatic trialkylphosphines and their $LNi(CO)_3$ complexes are given in Table 1. The spectra for phosphines up to $P(pentyl)_3$ were assigned using off-resonance decoupling to identify the terminal methyl group, and the assumption that complexation leads to an increase in the magnitude of $^1J(^{13}C^{31}P)$, a decrease in $^2J(^{13}C^{31}P)$, and a slight increase in $^3J(^{13}C^{31}P)$, to assign C(1) through C(3) [8]. For phosphines with alkyl chains longer than five carbon atoms the assignments were completed by assuming segmental motion, and therefore a steadily increasing T_1 relaxation time, for C(4) through the penultimate carbon atom.

Experimental data for the nuclear Overhauser enhancement on proton decoupling in $P(butyl)_3$ [20] suggest that dipole—dipole interactions are the dominant mechanism for the relaxation of the carbon atoms in these phosphines. The general increase in T_1 as one proceeds down the alkyl chain from the phosphorus atom (see Fig. 1) is therefore consistent with the assumption that internal or segmental motion along the alkyl chain makes a significant contribution to the

TABLE 1

^{13}C NMR T_1 RELAXATION TIMES FOR TRIALKYLPHOSPHINES AND THEIR LNi(CO)$_3$ COMPLEXES

Free ligand	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)
P(ethyl)$_3$	3.0_7 [a]	3.7_6						
P(propyl)$_3$	3.7_4	4.9_1	4.3_0					
P(butyl)$_3$	1.7_4	2.3_4	2.8_5	3.2_0				
P(pentyl)$_3$	1.1_1	1.5_1	2.0_8	2.8_4	3.4_2			
P(hexyl)$_3$	0.83	1.1_9	1.4_6	2.0_4	2.8_9	3.6_2		
P(octyl)$_3$	0.84	1.0_7	1.3_7	1.4_5	1.6_2	2.2_6	2.8_3	3.5_2
LNi(CO)$_3$ complexes	C(1)	C(2)	C(3)	C(4)	C(5)			
P(ethyl)$_3$	3.7_9	5.0_0						
P(propyl)$_3$	2.2_0	2.4_9	3.0_4					
P(butyl)$_3$	1.3_2	1.8_1	2.5_6	3.6_9				
P(pentyl)$_3$	0.74	1.0_8	1.7_0	2.3_2	3.0_4			

[a] Spin-lattice (T_1) relaxation time in seconds.

overall reorientation of the C—H dipole. Since T_1 for protonated carbon atoms is proportional to the number of directly-bonded protons as well as the correlation time, it is more instructive to examine variations in either NT_1 or τ_{eff}. Effec-

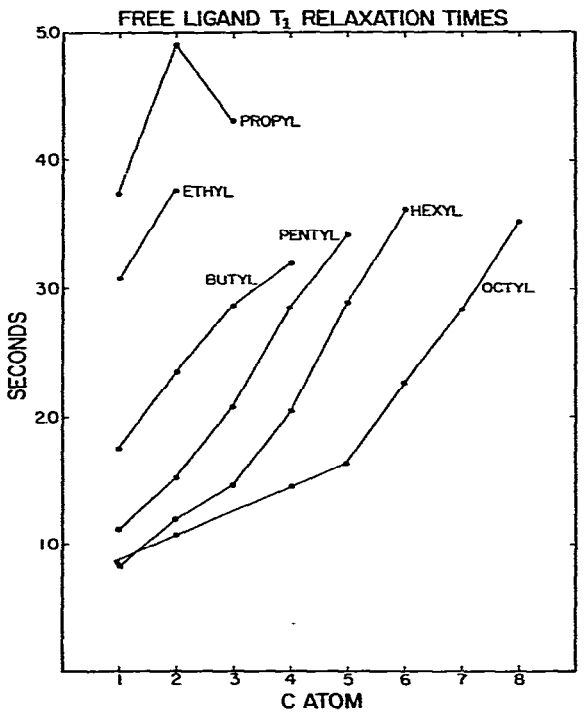

Fig. 1. A plot of the ^{13}C NMR spin-lattice (T_1) relaxation time in seconds versus the position along the alkyl chain in P((CH$_2$)$_n$CH$_3$)$_3$ ligands, (n = 1—5, 7). C(1) is assigned to the carbon attached to the phosphorus atom.

TABLE 2

τ_{eff} FOR TRIALKYLPHOSPHINES AND THEIR $LNi(CO)_3$ COMPLEXES

Free ligand	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)
$P(ethyl)_3$	7.1_8 [a]	3.9_1						
$P(propyl)_3$	5.8_9	4.4_9	3.4_2					
$P(butyl)_3$	$12._7$	9.4_2	7.7_3	4.5_9				
$P(pentyl)_3$	$19._9$	$14._6$	$10._6$	7.7_6	4.3_0			
$P(hexyl)_3$	$26._6$	$18._5$	$15._1$	$10._8$	7.6_3	4.0_6		
$P(octyl)_3$	$26._2$	$20._6$	$16._1$	$16._1$	$13._6$	9.7_5	7.7_9	4.1_7
$LNi(CO)_3$ complexes	C(1)	C(2)	C(3)	C(4)	C(5)			
$P(ethyl)_3$	5.8_1	2.9_4						
$P(propyl)_3$	$10._0$	8.8_5	4.8_3					
$P(butyl)_3$	$16._7$	$12._2$	8.6_1	3.9_8				
$P(pentyl)_3$	$29._8$	$20._4$	$13._0$	9.5_0	4.8_3			

[a] τ_{eff} in picoseconds.

tive correlation times were therefore calculated from the T_1 data [21] and are given in Table 2.

The data in Table 2 suggest a monotonic decrease in τ_{eff} as one proceeds along the alkyl chain, even for C(3) in $P(propyl)_3$. This is indicative of restricted mo-

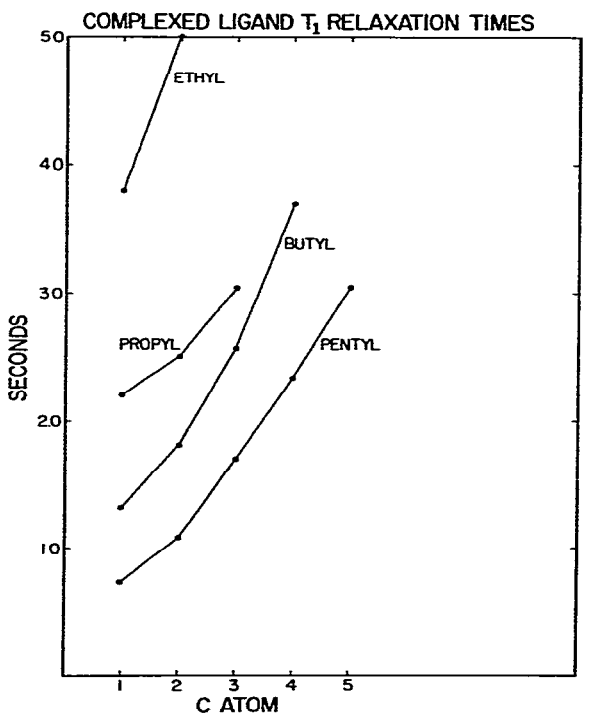

Fig. 2. A plot of the ^{13}C NMR spin-lattice (T_1) relaxation time in seconds versus the position along the alkyl chain in $LNi(CO)_3$ complexes of $P((CH_2)_nCH_3)_3$ ligands, (n = 1—4). C(1) is assigned to the carbon attached to the phosphorus atom.

tion at the end of the chain attached to the phosphorus atom. Furthermore, segmental motion appears to be the dominant contributor to τ_{eff} for P(butyl)$_3$ and larger phosphines.

The data for the free phosphines suggest a general, if not quite monotonic, increase in τ_{eff} for the C(1) carbon as the alkyl chain length increases, as one might expect. The correlation time for the terminal carbon, and perhaps the penultimate carbon as well, is remarkably constant, with major deviations only for C(2) in P(propyl)$_3$. The gradual increase in τ_{eff} for C(1), coupled with an apparently constant τ_{eff} for the terminal carbon, leads to a significant increase in the range of correlation times as the chain length increases, again as one might expect. τ_{eff} increases by a factor of 6 in P(octyl)$_3$, in good agreement with the factor of 7 observed in 1-decanol, [18] and the factor of 11 observed for micelles of n-octyltrimethylammonium bromide in aqueous solution [19].

An analogous plot of T_1 versus position along the aliphatic chain for the LNi(CO)$_3$ complexes is shown in Fig. 2. Once again, there is a monotonic decrease in the correlation time as one proceeds down the aliphatic chain from the phosphorus atom, as well as both a general increase in τ_{eff} for a given carbon atom and a drastic increase in the range of correlation times as the chain length increases. Data for (CO)$_3$NiP(propyl)$_3$, however, suggest that segmental motion becomes a dominant factor at shorter alkyl chain lengths, undoubtedly due to the increased weight of the molecular anchor that restricts overall molecular tumbling.

Discussion

Assignment of the ^{13}C NMR spectra of trialkylphosphines is often complicated by close similarities in the chemical shifts and a remarkable similarity in the magnitude of the $^{1,2,3}J(^{13}C^{31}P)$ coupling constants. Several groups have tried to assign the spectrum of P(butyl)$_3$, for example, and admit that a conclusive assignment cannot be made on the basis of chemical shift and coupling constant data alone. Mann [22] and Quin, Gordon, and Lee [23] have proposed the following assignment: C(1) > C(2) > C(3) > C(4), in order of decreasing chemical shift. Weigert and Roberts [24] have proposed an alternative assignment: C(2) > C(3) > C(1) > C(4).

Preliminary analysis of the ^{13}C NMR chemical shift and $J(^{13}C^{31}P)$ coupling constant data for trialkylphosphines and their transition metal carbonyl complexes [8] suggested several patterns that were consistent with the general rules first proposed by McFarlane [25] for the effect of quaternization of trivalent phosphorus. Complexation of straight-chain aliphatic trialkylphosphines apparently leads to: (1) a deshielding of the C(1) resonance and an increase in $^1J(^{13}C^{31}P)$ by a factor of almost two, (2) a slight shielding of C(2) and a drastic decrease in $^2J(^{13}C^{31}P)$, and (3) little or no change in the chemical shift of C(3) and an increase of about 2 Hz in $^3J(^{13}C^{31}P)$. Application of these rules leads to the following assignment for P(butyl)$_3$: C(2) > C(1) > C(3) > C(4).

The ^{13}C NMR spectra of P(ethyl)$_3$, P(propyl)$_3$, P(butyl)$_3$ and P(pentyl)$_3$ were completely assigned on the basis of these rules and off-resonance decoupling experiments, and the spectra of P(hexyl)$_3$ and P(octyl)$_3$ were partially assigned. Chemical shift and coupling constant data based on these assignments

TABLE 3

^{13}C NMR CHEMICAL SHIFTS AND $J(^{13}C^{31}P)$ COUPLING CONSTANTS FOR TRIALKYLPHOSPHINES AND THEIR $LNi(CO)_3$ COMPLEXES

Phosphine		C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)
$P(ethyl)_3$									
	ligand	18.0 [a]	9.0						
		(11.5) [b]	(12.2)						
	complex	20.1_8	7.8_9						
		(22.3)	(—) [c]						
$P(propyl)_3$									
	ligand	29.7_1	19.2_7	15.9_5					
		(11.8)	(13.2)	(11.2)					
	complex	31.1_1	18.0_5	15.9_4					
		(19.6)	(3.0)	(13.7)					
$P(butyl)_3$									
	ligand	26.8_0	27.9_4	24.3_4	13.6_0‡				
		(12.0)	(12.3)	(10.8)					
	complex	28.0_9	26.2_7	42.2_5	13.5_5				
		(19.5)	(2.0)	(12.9)					
$P(pentyl)_3$									
	ligand	26.8_0	25.2_4	33.3_8	22.0_7	13.5_7			
		(11.2)	(12.2)	(10.3)					
	complex	28.3_3	23.8_1	33.3_6	22.0_3	13.5_0			
		(19.0)	(2.5)	(12.7)					
$P(hexyl)_3$									
	ligand	27.1_1	25.6_0	30.8_5	31.3_0	22.2_4	13.6_6		
		(12.7)	(13.2)	(10.8)					
$P(octyl)_3$									
	ligand	27.1_0	25.7_1	31.3_1	29.1_6	29.0_3	31.6_7	22.4_2	13.8_0
		(12.2)	(12.7)	(10.7)					
	complex	28.4_5	24.2_0	31.3_3	29.0_6	29.0_6	31.7_7	22.5_5	13.8_3
		(18.6)	(2.4)	(13.2)					

[a] ^{13}C chemical shift in ppm downfield from TMS, ±0.06 ppm, $CDCl_3$ solution. [b] $J(^{13}C^{31}P)$ coupling constant in Hz. [c] $J(^{13}C^{31}P)$ coupling could not be resolved.

are given in Table 3. The data on segmental motion from Table 2 are in total agreement with these assignments, and can be used to complete the assignment of spectra for phosphines with alkyl chains longer than five carbon atoms.

Unfortunately, these rules must be applied with care, since the introduction of unsaturation or the presence of branching near the phosphorus atom may interfere with this pattern of behavior [26].

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