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A CARBON-13 NMR STUDY OF PHOSPHINE, PHOSPHITE, ARSINE AND STIBINE LIGANDS AND THEIR $LNi(CO)_3$, $LCr(CO)_5$ AND η-$(C_5H_5)Mn(CO)_2L$ COMPLEXES

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Summary

^{13}C NMR chemical shift and $J(^{13}C^{31}P)$ coupling constant data are presented for $PPh_{3-n}Me_n$ (n = 0, 1 and 2), $P(OPh)_3$, PEt_3, $AsPh_3$ and $SbPh_3$ ligands, and some corresponding $LNi(CO)_3$, $LCr(CO)_5$ and η-$(C_5H_5)Mn(CO)_2L$ complexes. Analysis of the ^{13}C NMR chemical shift data for the C(4) resonance in these C_6H_5X derivatives suggests: *(1)* a resonance substituent parameter $R = 0.005$ for X = PPh_2 and $R = 0.09$ for X = $(CO)_5CrPPh_2$, *(2)* a decrease in the resonance interaction of the Group VA atom with the phenyl ring in EPh_3 derivatives in the order $E = P > As > Sb$, and *(3)* an increase in the electron density at the phosphorus atom in $PPh_{3-n}Me_n$ derivatives in the order: $PPh_3 < PPh_2Me < PPhMe_2$. There appears to be an anomalous shielding of the C(1) resonance in these derivatives upon complexation, and with increasing electronegativity of the Group Va atom. The electron-withdrawing character of the metal carbonyl moiety appears to increase in the order: η-$(C_5H_5)Mn(CO)_2L < LNi(CO)_3 < LCr(CO)_5$. The magnitude of the $^1J(^{13}C^{31}P)$ and $^3J(^{13}C^{31}P)$ coupling in trialkyl and triaryl phosphines increases upon complexation, while the magnitude of the $^2J(^{13}C^{31}P)$ coupling decreases. As a result, in $(Me_2PhP)Ni(CO)_3$, the $^3J(^{13}C^{31}P)$ coupling to the C(3,5) resonance of the phenyl group is larger than the $^2J(^{13}C^{31}P)$ coupling to the C(2,6) resonance. In contrast, complexation of triphenyl phosphite leads to an apparent increase in the magnitude of the $^2J(^{13}C^{31}P)$ coupling and a decrease in the magnitude of the $^3J(^{13}C^{31}P)$ coupling. The signs of the one-, two- and three-bond $J(^{13}C^{31}P)$ coupling constants in $Ph_3PMo(CO)_5$ have been determined to be positive.

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Introduction

While there has been considerable interest in the ^{13}C NMR spectra of free Group VA ligands [1-5], and the ^{13}C NMR carbonyl chemical shifts and $^2J(^{13}C^{31}P)$ through-metal nuclear spin—spin coupling constants in $L_nM(CO)_m$ complexes [6], only limited data have been reported concerning the effect of complexation upon the ligand chemical shifts and coupling constants [3]. As part of a systematic study of the ^{13}C NMR spectra of transition metal carbonyl complexes, we wish to report herein the ^{13}C NMR chemical shift and $J(^{13}C^{31}P)$ coupling constant data for $PPh_{3-n}Me_n$ ($n = 0$, 1 and 2), $P(OPh)_3$, PEt_3, $AsPh_3$ and $SbPh_3$ ligands, and some corresponding $LNi(CO)_3$, $LCr(CO)_5$ and η-$(C_5H_5)Mn(CO)_2L$ complexes.

Experimental

Triphenylphosphine, triphenylarsine, triphenylstibine, triethylphosphine and triphenyl phosphite were purchased from the Aldrich Chemical Co. Dimethylphenylphosphine and methyldiphenylphosphine were purchased from the Pressure Chemical Co. All ligands were used without further purification. The synthesis and characterization of $LCr(CO)_5$ [6], $LNi(CO)_3$ [7], and η-$(C_5H_5)Mn(CO)_2L$ [8] complexes employed classical literature techniques, and have been detailed elsewhere.

^{13}C NMR spectra were obtained in deuterochloroform solution on a Varian Associates XL-100-FT spectrometer operating at 25.16 MHz equipped with an internal ^{2}D lock. Chemical shifts were measured relative to the internal $CDCl_3$ solvent resonances and are reported in ppm *downfield* from TMS using the conversion:

$$\delta_{TMS} = \delta_{CDCl_3} + 76.98 \text{ ppm}$$

such that increasingly *positive* chemical shifts correspond to resonances which are increasingly deshielded relative to TMS. All chemical shifts are the result of at least two independent measurements with a precision of at least ±0.03 ppm.

Results

The ^{1}H-decoupled ^{13}C NMR spectrum of the phenyl resonances in $Ph_3PCr(CO)_5$, shown in Fig. 1, is characteristic of the typically well-resolved spectra obtained for Group VA ligands and their transition metal carbonyl complexes. The assignment of the C(1) and C(4) resonances for the phenyl group in $PPh_{3-n}Me_n$ and $P(OPh)_3$ derivatives was based upon the relative intensities and the magnitude of the $J(^{13}C^{31}P)$ coupling, $[^1J(^{13}C^{31}P) \gg {}^4J(^{13}C^{31}P)]$. The assignment of the C(2,6) and C(3,5) resonances was based upon the relative magnitude of the $J(^{13}C^{31}P)$ coupling, $[^2J(^{13}C^{31}P) > {}^3J(^{13}C^{31}P)]$, with the exception of $(PhMe_2P)Ni(CO)_3$, where the assignment was based upon the observation that little or no variation in the chemical shift of the C(3,5) resonance occurs upon complexation. In $(PhMe_2P)Ni(CO)_3$ it would appear that the coupling to the *meta* position [$^3J(^{13}C^{31}P)$ 8.6 Hz] is slightly larger than the coupling to the *ortho* position [$^2J(^{13}C^{31}P)$ 5.0 Hz]. The assignment of the spectra of $AsPh_3$ and $SbPh_3$ derivatives was chosen to mirror the assignment of PPh_3. The ^{13}C NMR chemical shift and coupling constant data are presented in Table 1.

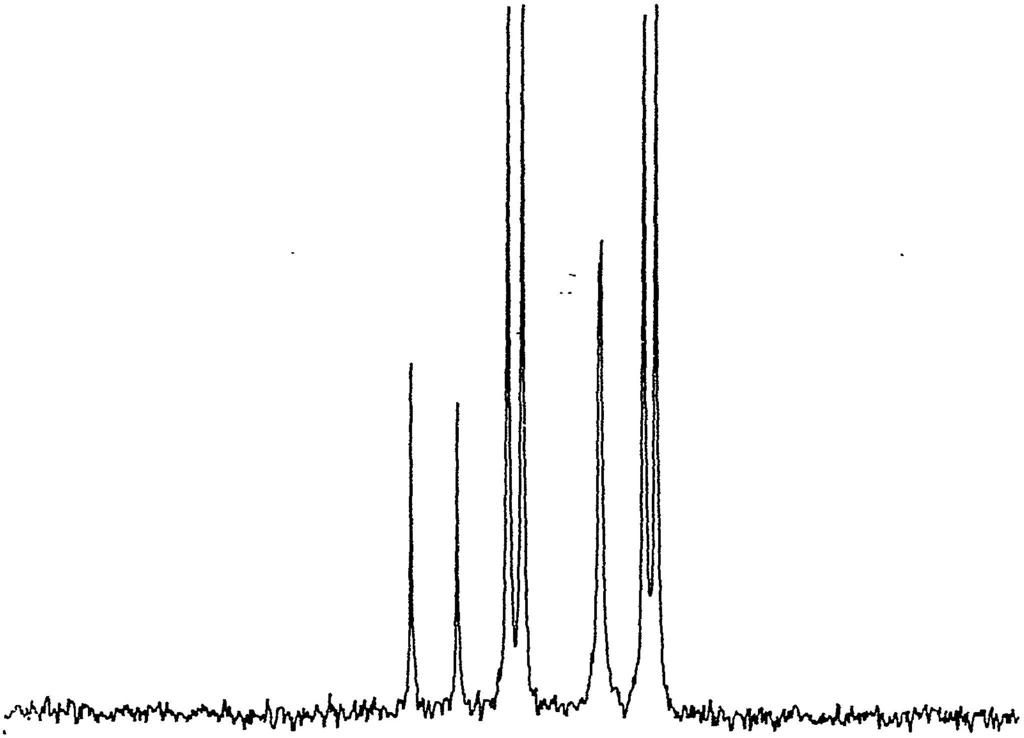

Fig. 1. The ^{1}H decoupled Fourier transform ^{13}C NMR spectrum of the PPh_3 resonances in $Ph_3PCr(CO)_5$, 1024 scans, 10 second pulse delay, 90° flip angle. In order of increasing magnetic field [chemical shift, $J(^{13}C^{31}P)$ coupling constant]: C(1), 135.24(35.9); C(2,6), 132.73(11.5); C(4), 130.08; and C(3,5), 128.54(9.5).

The chemical shift data reported for PPh_3 [1-3,9] suggest the existence of a solvent dependence but not a concentration dependence. The chemical shifts of the C(1), C(2,6) and C(3,5) resonances in PPh_3 relative to the C(4) resonance are 8.74, 5.06 and —0.14 ppm in acetone/carbon disulfide solution [9], and 8.59, 5.07 and —0.14 ppm in deuterochloroform solution. The slight shielding of the C(1) resonance relative to C(4) in deuterochloroform solution may be indicative of a hydrogen bonding interaction.

Discussion

^{13}*C NMR chemical shifts*

We have suggested [10] that the corrected chemical shifts, δ', for monosubstituted benzene derivatives, C_6H_5X, defined by Maciel [11] as,

$$\delta' = \delta_{C(4)} - \delta_{C(3,5)}$$

are a linear measure of the resonance substituent effects of the X substituents. It is therefore of interest to note that whereas δ' is —12.09 and 4.40 ppm* for

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[*] Positive values of δ' correspond to C_6H_5X derivatives wherein the C(4) resonance is *downfield*, i.e., at a more positive chemical shift than the C(3,5) resonance.

TABLE 1

^{13}C NMR CHEMICAL SHIFTS[a] AND $J(^{13}C^{31}P)$ COUPLING CONSTANTS[b]

Ligand	Complex	C(1)	C(2,6)	C(3,5)	C(4)	CH_2	CH_3
PPh_3		137.1_3 $(11._5)$	133.6_1 $(19._4)$	128.4_0 $(7._2)$	128.5_4		
	$CpMn(CO)_2L$	137.9_5 $(40._7)$	132.6_9 $(10._9)$	127.9_7 $(10._0)$	129.3_2		
	$LCr(CO)_5$	135.2_4 $(35._9)$	132.7_3 $(11._5)$	128.5_4 $(9._5)$	130.0_8		
	$LNi(CO)_3$	135.6_5 $(34._5)$	133.1_2 $(13._6)$	128.5_6 $(9._3)$	129.8_2		
PPh_2Me		139.9_0 $(13._0)$	131.6_9 $(18._0)$	128.0_1 $(5._0)$	127.9_1		12.0_9 $(14._4)$
	$LNi(CO)_3$	137.6_2 (33.0)	131.4_1 $(13._6)$	128.5_7 $(9._3)$	129.6_3		17.6_8 $(22._3)$
$PPhMe_2$		142.0_8 $(13._6)$	130.0_5 $(17._2)$	127.8_5 $(5._7)$	127.5_1		14.0_0 $(13._6)$
	$LNi(CO)_3$	138.3_2 $(32._3)$	129.5_5 $(5._0)$	128.4_5 $(8._6)$	130.1_9		18.6_5 $(22._3)$
$AsPh_3$		139.5_8	133.6_5	128.5_9	128.3_7		
	$LCr(CO)_5$	136.1_4	132.4_0	129.0_6	130.0_3		
	$LNi(CO)_3$	136.9_6	132.7_1	128.9_4	129.6_5		
$SbPh_3$		138.3_3	136.1_6	128.7_9	128.5_1		
	$LCr(CO)_5$	132.0_5	134.9_9	129.4_8	130.2_8		
	$LNi(CO)_3$	133.9_6	135.3_6	129.2_8	129.8_2		
$P(OPh)_3$		151.4_9 $(3._4)$	120.5_6 $(6._9)$	129.5_6	124.1_5		
	$CpMn(CO)_2L$	151.7_8 $(6._8)$	121.7_1 $(4._7)$	129.5_2	124.6_1		
	$LCr(CO)_5$	150.9_7 $(8._1)$	121.1_9 $(5._0)$	129.8_9	125.3_1		
	$LNi(CO)_3$	151.2_1 $(2._9)$	121.7_6 $(5._0)$	129.7_7	125.2_0		
PEt_3						18.0_0 $(11._5)$	9.0_8 $(12._2)$
	$LCr(CO)_5$					20.1_5 $(22._3)$	6.7_9 $(2._2)$
	$LNi(CO)_3$					20.1_6 $(22._3)$	7.8_9 (0)

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[a] In ppm downfield from TMS, ±0.03 ppm, deuterochloroform solution. [b] In Hz, ±0.5 Hz.

X = NMe_2 and X = CO_2CH_3, δ' for the free PPh_3 ligand is only 0.14 ppm. These data would suggest the absence of any significant donation or withdrawal of electron density from the π framework in C_6H_5X by the X = PPh_2 substituent [3,5]. Based upon the correlation [10] observed between δ' and the resonance substituent parameter of Swain and Lupton [12], one obtains R = 0.005 for X = PPh_2. In contrast, we note that δ' for the complexed PPh_3 ligand is 1.26, 1.35 and 1.54 ppm for $LNi(CO)_3$, η-$(C_5H_5)Mn(CO)_2L$ and $LCr(CO)_5$ complexes respectively. There thus appears to be a net withdrawal of electron density from the π framework by the $(CO)_5CrPPh_2$ substituent which may be characterized by a resonance substituent parameter $R = 0.09$. This may be compared with values of $R = 0.140$ and 0.186 for $X = CO_2H$ and CF_3 [12]. A similar analysis yields values of δ' for the free $AsPh_3$ and $SbPh_3$ ligands of -0.22 and -0.28 ppm, which increase upon complexation to 0.71 and 0.54 ppm for $LNi(CO)_3$ complexes, and 0.97 and 0.80 ppm for $LCr(CO)_5$ complexes. Previous work [6,7] has suggested that the σ-donor/π-acceptor ratio for $AsPh_3$ and $SbPh_3$ ligands is equal to or greater than this ratio for PPh_3, thus the decrease in δ': $E = P > As > Sb$, for both $Ph_3ENi(CO)_3$ and $Ph_3ECr(CO)_5$ complexes would suggest a decrease in the resonance interaction of the Group VA atom with the phenyl ring in this order.

If we define $\Delta C(4)$ to be the difference between the C(4) chemical shifts of the free ligand and its corresponding $LNi(CO)_3$ complex,

$$\Delta C(4) = \delta_{C(4)}\ \mathrm{LNi(CO)_3\ complex} - \delta_{C(4)}\ \mathrm{free\ ligand}$$

then $\Delta C(4)$ times the number of equivalent phenyl groups decreases from 3.84 ppm for PPh_3 to 3.44 ppm for PPh_2Me and 2.68 ppm for $PPhMe_2$. Thus the withdrawal of electron density from the π framework of the phenyl ring in the $LNi(CO)_3$ complex decreases in the order: $L = PPh_3 > PPh_2Me > PPhMe_2$. This observation is in accord with studies of phosphine basicity [13] which suggest that the methyl group is a significantly better electron-donor towards phosphorus than the phenyl group, and with the slight decrease in δ' for the free ligand from 0.14 to -0.10 and -0.34 ppm in this order.

It is of interest to note that the C(1) resonance for the phenyl group in $PPh_{3-n}Me_n$ ligands is shielded with decreasing phosphine basicity [13]. In EPh_3 derivatives the C(1) resonance for the phenyl group is shielded with increasing electronegativity of the Group Va atom, $E = As < Sb < P$ [14]. Upon complexation with $Ni(CO)_3$, the C(1) resonance in PPh_3, $AsPh_3$ and $SbPh_3$ is shielded by 1.51, 2.62 and 4.37 ppm respectively, while complexation with $Cr(CO)_5$ shields the C(1) resonance by 1.89, 3.44 and 6.25 ppm respectively.

For all ligands studied to date, the effect of complexation on the ^{13}C NMR spectral parameters appears to increase in the order: η-$(C_5H_5)Mn(CO)_2L < LNi(CO)_3 < LCr(CO)_5$, in accord with what one may argue would be the order increasing electron-withdrawing character of the metal carbonyl substituent.

$J(^{13}C^{31}P)$ nuclear spin—spin coupling

The analysis of $J(^{13}C^{31}P)$ coupling constant data for phosphine and phosphite ligands, and their transition metal carbonyl complexes, is complicated by the observation of an inversion in the sign of the reduced coupling constant.

$$K_{CP} = (2\pi/\hbar\gamma_C\gamma_P)\, J(^{13}C^{31}P)$$

$^1J(^{13}C^{31}P)$ coupling is negative in trialkyl phosphines [2] and triaryl phosphines [9,15,16] and positive in diethyl phosphonates $(EtO)_2P(O)CH_2X$ [17] and tetra-alkyl phosphonium ions [2], while $^2J(^{13}C^{31}P)$ coupling is positive in phosphines and negatives in phosphonates and phosphonium ions. This is in agreement with the observation of McFarlane [2] that $^1J(^{13}C^{31}P)$ and $^3J(^{13}C^{31}P)$ coupling increases and $^{2}J(^{13}C^{31}P)$ coupling decreases upon quaternization of the phosphorus atom. Gansow and Kimura [3] have suggested that the $^{1}J(^{13}C^{31}P)$ coupling constant in PPh_3 increases from 21 to 36 Hz upon complexation with $Mo(CO)_5$. Bundgaard and Jakobsen [9] have shown that the $^{1}J(^{13}C^{31}P)$ coupling constant in PPh_3 is −12 Hz. We have employed the selective proton decoupling techniques of Jakobsen [9,15,16] to show that the $^{1}J(^{13}C^{31}P)$, $^{2}J(^{13}C^{31}P)$ and $^{3}J(^{13}C^{31}P)$ coupling constants in $Ph_3PMo(CO)_5$ have the same sign as the $^{3}J(^{1}H^{31}P)$ and $^{4}J(^{1}H^{31}P)$ coupling constants, i.e., *positive*. It thus appears that the $^{1}J(^{13}C^{31}P)$ coupling constant in PPh_3 increases from −12 to +36 Hz upon complexation with $Mo(CO)_5$. These data may be compared favorably with the increase in the $^{1}J(^{13}C^{31}P)$ coupling in PMe_3 from −14 to +56 Hz upon quaternization of the phosphorus [2]. The correlation suggested by Mann [5] between $^{1}J(^{13}C^{31}P)/s_C$ and s_P*, which was based upon an assumed positive $^{1}J(^{13}C^{31}P)$ coupling constant for PPh_3, appears questionable at best, as is the value of the C—P—C bond angle in $P(t\text{-}Bu)_3$ calculated from these data.

It is evident that complexation of PPh_3 and PEt_3 leads to an increase in the $^{1,3}J(^{13}C^{31}P)$ couplings and a decrease in the $^{2}J(^{13}C^{31}P)$ coupling, in accord with predictions [2]. McFarlane has suggested that the increase in the one- and three-bond couplings, and the decrease in the two-bond coupling upon quaternization of the phosphorus are independent of whether the intervening atoms are carbon or oxygen. Thus, the apparent increase in the $^{2}J(^{13}C^{31}P)$ coupling and decrease in the $^{3}J(^{13}C^{31}P)$ coupling upon complexation of $P(OPh)_3$, which has also been observed upon quaternization [4], is suggestive of an inversion in the sign of these coupling constants. This would be in accord with data reported by McFarlane which indicates a decrease in the $^{2}J(^{13}C^{31}P)$ coupling constant from 10 to −8 Hz upon quaternization of $P(OMe)_3$. Selective proton decoupling experiments were attempted for $P(OPh)_3$ and $(PhO)_3PMo(CO)_5$ without success. Work is presently underway to determine the signs of these coupling constants from the $\{^{31}P\}$—^{13}C spectra.

It has been argued [18] that the introduction of an electronegative substituent induces a rehybridization which concentrates *s* character in the bonds towards the least electronegative element. Thus, it would be tempting to assume that the $^{1}J(^{13}C^{31}P)$ coupling constant is Fermi contact dominated and analyze the increase in the coupling constant upon quaternization or complexation in terms of an increase in the *s* character of the phosphorus [19]. Unfortunately, McFarlane has noted that this coupling constant increases from −13.6 Hz for PMe_3 to 55.5 Hz for $Me_4P^+I^-$ and 56.1 Hz for Me_3PS. Unless we assign approximately equal electronegativities to the Me and S substituents, it would appear that we must attribute the increase in this coupling constant to an increase in the effective nuclear charge of the phosphorus and/or carbon [20].

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* s_C and s_P represent the *s* character in the hybrid carbon and phosphorus orbitals respectively.

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