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A FOURIER TRANSFORM CARBON-13 NMR STUDY OF TRIVALENT COMPOUNDS OF PHOSPHORUS, ARSENIC, ANTIMONY AND BISMUTH AND THEIR $LNi(CO)_3$ COMPLEXES

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Summary

^{13}C NMR chemical shift data are reported for a number of trivalent derivatives of P, As, Sb and Bi and their $LNi(CO)_3$ complexes. Data for EMe_3 and EPh_3 (E = P, As, Sb and Bi), EEt_3 and EBu_3 (E = P, As and Sb) and $PhEX_2$ and Ph_2EX (E = P, As; X = Cl, Me, Et, Bu) are presented, as well as data for many of the corresponding metal carbonyl complexes. The spectra of $AsBu_3$ and $SbBu_3$ are assigned using T_1 (spin-lattice) relaxation time measurements. The effect of variations in the Group VA atom and the effect of complexation on the chemical shifts of alkyl- and aryl-carbon resonances are discussed. Resonance substituent constants of the aryl derivatives are analyzed.

Introduction

Despite an abundance of publications on the ^{13}C NMR spectra of organonitrogen and organophosphorus compounds, there have been relatively few data reported for the corresponding arsenic, antimony and bismuth derivatives. In the course of a systematic study of the electronic effects of Group VA ligands in transition metal carbonyl complexes [1–6] we have obtained data on the ^{13}C NMR chemical shifts of a number of trivalent compounds of the Group VA elements as well as their $LNi(CO)_3$ complexes.

Experimental

R_3E derivatives (E = As, R = Et, Bu; E = Sb, R = Et) were synthesized by the dropwise addition of an ether solution of the trihalide to a slight excess of the Grignard or alkyllithium reagent in ether solution [7]. R_2EPh and $REPh_2$ derivatives

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(E = P, As; R = Me, Et, Bu) were synthesized by the reaction of the corresponding $PhECl_2$ or Ph_2ECl intermediate with a Grignard or alkyllithium reagent in ether solution [8]. All other materials were purchased from commercial sources. Compounds were purified when possible by vacuum distillation or fractional crystallization and characterized by a combination of infrared and proton magnetic resonance spectroscopy.

^{13}C NMR chemical shifts were measured in $CDCl_3$ solution on a JEOL FX-60-FT spectrometer equipped with an internal ^2D lock and operating at a ^{13}C resonance frequency of 15 MHz. Pulse widths corresponding to flip angles of 30–40° and a repetition rate of 2.2 seconds were used. Chemical shifts were measured relative to the internal $CDCl_3$ solvent resonance and are reported in ppm downfield from TMS using the conversion $\delta(TMS) = \delta(CDCl_3) + 76.98$ ppm such that positive chemical shifts correspond to resonances that are deshielded relative to TMS. Chemical shifts were reproducible to within ± 0.06 ppm for all compounds, and in many cases to within ± 0.03 ppm. Spectra were obtained by dissolving approximately 8 mmol of the ligand in 1 ml of $CDCl_3$. $LNi(CO)_3$ complexes were synthesized in situ by the addition of a 2-ml aliquot of 4 *M* $Ni(CO)_4$ in $CDCl_3$. Care must be taken in the handling of nickel carbonyl complexes! Procedures for minimizing exposure to these complexes have been discussed elsewhere [4,6].

^{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 [9]. All T_1 measurements were obtained with a Varian XL-200 spectrometer operating at 50 MHz with a probe temperature of 22°C. The 90° and 180° pulse times were 15.5 and 31 μsec, respectively. 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 T_1's were calculated with the Varian 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 at least $\pm 10\%$.

Assignment of ^{13}C NMR Spectra

Assignment of the ^{13}C NMR spectra of most compounds in this study was either a trivial task, e.g., EEt_3 (E = P, As, Sb), or was based upon well-established arguments, for example, EPh_3 (E = P, As, Sb, Bi). There has been some controversy, however, over the assignment of the spectrum of PBu_3 [10–13], since the magnitude of the J(CP) coupling constant is not a clear indication of the position along the alkyl chain, and there was therefore some question in our minds about the correct assignment of the spectra of the corresponding tributyl-arsine and -stibine derivatives.

We have previously reported the use of T_1 relaxation time measurements to assign the ^{13}C NMR spectra of trialkylphosphines and their $LNi(CO)_3$ complexes [13]. This was predicated on the assumption that the spin-lattice relaxation of protonated carbon atoms is dominated by intramolecular dipole–dipole interactions with the directly bonded protons [14,15]: $1/T_1 = N(h/2\pi)^2\gamma_C{}^2\gamma_H{}^2r_{CH}{}^{-6}\tau_{eff}$, and that internal or segmental motion along the alkyl chain makes a significant contribution to the average molecular correlation time for the reorientation of the C–H dipole (τ_{eff}).

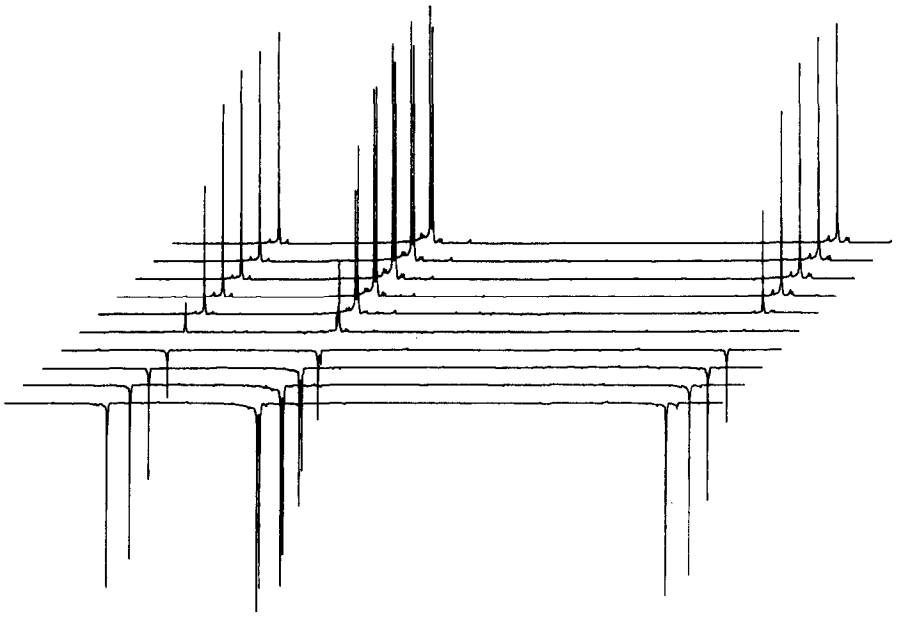

Fig. 1. Partially-relaxed Fourier transform ^{13}C NMR spectra for $AsBu_3$ in $CDCl_3$ solution at 50 MHz. The T_1 relaxation times suggest an assignment (from left to right) of C(2), C(3), C(1) and C(4).

Since data from our previous study seemed to validate both assumptions, we have used measurements of T_1 relaxation times to assign the ^{13}C NMR spectra of both $AsBu_3$ and $SbBu_3$.

Since the C(1) and C(3) resonances in $AsBu_3$ could not be resolved at the field strength used in our previous studies of PBu_3 [13], T_1 measurements for $AsBu_3$ (Fig. 1) and $SbBu_3$ were obtained at a resonance frequency of 50 MHz. For

TABLE 1

^{13}C NMR SPIN-LATTICE (T_1) RELAXATION TIMES AND τ_{eff} CORRELATION TIMES FOR TRIBUTYL-PHOSPHINE, -ARSINE AND -STIBINE

	T_1 (sec) [a]			τ_{eff} (psec)		
	P [b]	As	Sb	P	As	Sb
C(1)	2.0_9	2.8_7	3.0_5	$10._6$	7.6_8	7.2_3
C(2)	2.9_3	3.7_9	4.0_7	7.5_3	5.8_2	5.4_2
C(3)	3.6_1	4.4_3	4.7_6	6.1_1	4.9_8	4.6_3
C(4)	4.2_3	4.8_0	5.1_3	3.4_8	3.0_6	2.8_7

[a] All measurements in $CDCl_3$ solution at 22°C at a resonance frequency of 50 MHz. [b] T_1 measurements for PBu_3 at 15 MHz were reported by Bodner and Bauer, J. Organometal. Chem., 226 (1982) 85.

Fig. 2. T_1 RELAXATION TIMES FOR EBu_3

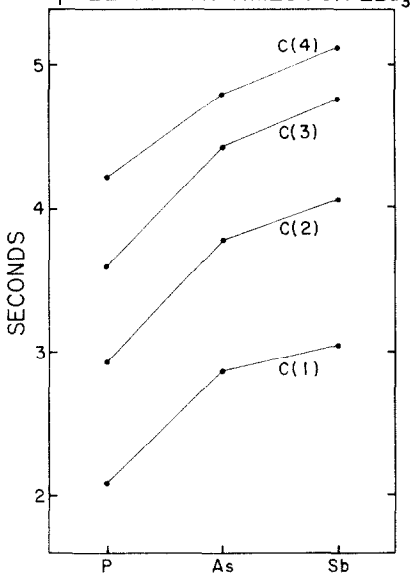

Fig. 3. EBu_3 and $Bu_3ENi(CO)_3$ $\delta^{13}C$

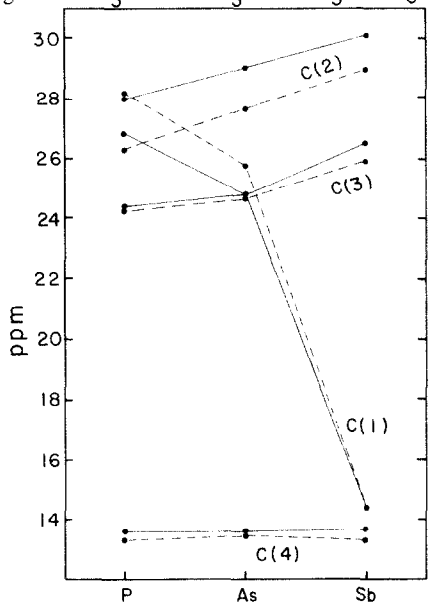

Fig. 2. ^{13}C NMR spin-lattice (T_1) relaxation times (in seconds) at 50 MHz for tributyl derivatives of phosphorus, arsenic and antimony.

Fig. 3. ^{13}C NMR chemical shifts for EBu_3 (solid lines) and $Bu_3ENi(CO)_3$ (dashed lines) derivatives as the Group VA atom is changed from P to As and Sb.

purposes of comparison, the relaxation times for PBu_3 were remeasured at this frequency, and data for all three compounds are given in Table 1. There are significant differences between the T_1 data for PBu_3 at 15 vs. 50 MHz which may result in part from differences in the ambient temperatures of the spectrometer probes [16].

As can be seen in Fig. 2, there is a gradual increase in T_1 or decrease in τ_{eff} as one proceeds down the alkyl chain from the Group VA substituent for all three EBu_3 derivatives. As shown in Fig. 3 there is also a gradual increase in T_1 for all four carbon atoms with increasing atomic weight of the Group VA atom. Correlations between T_1 and atomic weight increase steadily from 0.934 for C(1) to 0.998 for C(4).

^{13}C NMR chemical shifts for a number of trivalent Group VA derivatives and their $LNi(CO)_3$ complexes are given in Table 2.

Substituent effects on alkyl carbon chemical shifts

There is a regular increase in the shielding of the methyl carbon resonance in trimethyl derivatives of N, P, As, Sb and Bi as one proceeds down Group VA, reminiscent of a similar effect that has long been known for the haloalkanes [17–19]. Although this shielding correlates ($r = 0.801$) with Pauling electronegativities [20], it correlates even better with atomic number ($r = -0.920$) and a fraction of this effect is reasonably ascribed to a neighboring diamagnetic screening [21] that has been

(Continued on p. 311)

TABLE 2

^{13}C NMR CHEMICAL SHIFTS FOR ER_3, $PhER_2$ AND Ph_2ER LIGANDS OF P, As, Sb AND Bi AND THEIR $LNi(CO)_3$ COMPLEXES

Ligand	Substituent		P	As	Sb	Bi
EMe_3	CH_3	ligand	15.9_3 [a]	10.9_7	-3.6_2	$-5._6$
		complex	19.2_7 [b]	14.0_9	-2.2_5	
EEt_3	CH_2	ligand	18.0_0	16.3_3	11.3_9	
		complex	20.1_8	18.1_5	10.4_5	
	CH_3	ligand	9.0_8	10.5_1	5.4_1	
		complex	7.8_9	9.1_5	6.1_9	
EBu_3	$^1CH_2$	ligand	26.8_0	24.7_9	14.4_1	
		complex	28.0_9	25.7_5	14.4_4	
	$^2CH_2$	ligand	27.9_4	29.0_3	30.1_0	
		complex	26.2_7	27.6_0	28.9_0	
	$^3CH_2$	ligand	24.3_4	24.8_4	26.4_8	
		complex	24.2_5	24.6_8	25.9_1	
	$^4CH_3$	ligand	13.6_0	13.6_0	13.7_0	
		complex	13.3_5	13.5_0	15.5_0	13.3_1
EPh_3	C(1)	ligand	137.1_3	139.5_8	138.3_3	155.4
		complex	135.6_5	133.9_6	133.9_6	
	C(2,6)	ligand	133.6_1 [c]	133.6_5	136.1_6	137.5_0
		complex	133.1_2	132.7_1	135.3_6	
	C(3,5)	ligand	128.4_0 [c]	128.5_9	128.7_9	130.4_8
		complex	128.5_6	128.9_4	129.2_8	
	C(4)	ligand	128.5_4	128.3_7	128.5_1	127.7_1
		complex	129.8_2	129.6_5	129.8_2	
$PhECl_2$	C(1)	ligand	140.1_5	145.0_0		
	C(2,6)	ligand	131.7_7	129.7_1		
	C(3,5)	ligand	128.7_6	129.0_2		
	C(4)	ligand	128.8_9	131.9_8		
$PhEMe_2$	C(1)	ligand	142.0_8	142.9_3		
		complex	138.3_2	138.7_4		
	C(2,6)	ligand	130.0_5	131.2_3		
		complex	129.5_5	130.5_0		
	C(3,5)	ligand	127.8_5	128.1_9		
		complex	128.4_5	128.8_0		
	C(4)	ligand	127.5_1	127.6_6		
		complex	130.1_9	129.4_1		
	CH_3	ligand	14.0_0	10.7_5		
		complex	18.6_5	14.2_8		
$PhEEt_2$	C(1)	ligand	138.1_0	140.0_0		
		complex	134.5_8	135.6_7		
	C(2,6)	ligand	131.7_6	132.2_9		
		complex	131.9_0	131.7_1		
	C(3,5)	ligand	127.7_6	128.0_3		
		complex	128.4_9	128.6_6		
	C(4)	ligand	127.9_8	127.7_8		
		complex	129.8_7	129.4_5		
	CH_2	ligand	19.6_6	18.5_0		
		complex	23.3_2	21.0_6		
	CH_3	ligand	9.3_5	10.4_2		
		complex	8.3_5	9.2_1		

TABLE 2 (continued)

Ligand	Substituent		P	As	Sb	Bi
$PhEBu_2$	C(1)	ligand	138.6_9	140.7_4		
		complex	135.4_4	136.3_4		
	C(2,6)	ligand	132.1_2	132.4_4		
		complex	131.8_8	131.5_0		
	C(3,5)	ligand	128.0_2	128.1_3		
		complex	128.4_9	128.4_9		
	C(4)	ligand	128.3_5	127.8_4		
		complex	129.8_2	129.2_2		
	$^1CH_2$	ligand	27.9_3	26.4_8		
		complex	30.5_7	27.8_3		
	$^2CH_2$	ligand	27.7_0	28.6_8		
		complex	26.8_2	27.2_2		
	$^3CH_2$	ligand	24.1_1	24.5_3		
		complex	24.3_0	24.0_8		
	$^4CH_3$	ligand	13.5_5	13.4_2		
		complex	13.4_7	13.0_2		
Ph_2ECl	C(1)	ligand	138.5_6	142.0_7		
	C(2,6)	ligand	131.5_3	131.5_2		
	C(3,5)	ligand	128.4_1	128.6_7		
	C(4)	ligand	130.1_3	129.8_9		
Ph_2EMe	C(1)	ligand	139.9_0	141.5_9		
		complex	137.6_2	138.3_5		
	C(2,6)	ligand	131.6_9	132.3_7		
		complex	131.4_1	131.3_9		
	C(3,5)	ligand	128.0_1	128.3_9		
		complex	128.5_7	128.8_6		
	C(4)	ligand	127.9_1	128.0_3		
		complex	129.6_3	129.4_5		
	CH_3	ligand	12.0_9	10.0_6		
		complex	17.6_8	13.7_0		
Ph_2EEt	C(1)	ligand	138.4_8	140.4_9		
		complex	136.3_9	136.9_2		
	C(2,6)	ligand	132.4_9	132.7_8		
		complex	132.0_2	131.6_0		
	C(3,5)	ligand	128.1_5	128.3_1		
		complex	128.5_3	128.5_1		
	C(4)	ligand	128.2_3	127.9_8		
		complex	129.6_3	129.1_2		
	CH_2	ligand	20.4_1	20.2_9		
		complex	23.7_8	22.0_4		
	CH_3	ligand	9.8_8	10.5_4		
		complex	8.6_2	8.8_4		
Ph_2EBu	C(1)	ligand	138.8_1	140.9_0		
		complex	136.7_9	137.6_6		
	C(2,6)	ligand	132.4_9	132.8_9		
		complex	132.0_4	131.9_6		
	C(3,5)	ligand	128.1_3	128.3_7		
		complex	128.4_9	128.8_8		
	C(4)	ligand	128.2_3	128.0_5		
		complex	129.5_5	129.4_8		
	$^1CH_2$	ligand	27.9_7	27.4_6		
		complex	30.5_0	28.7_1		

TABLE 2 (continued)

Ligand	Substituent		P	As	Sb	Bi
	$^{2}CH_2$	ligand	27.6_0	28.4_4		
		complex	26.8_9	27.2_8		
	$^{3}CH_2$	ligand	24.0_9	24.4_9		
		complex	24.2_7	24.3_1		
	$^{4}CH_3$	ligand	13.5_9	13.5_0		
		complex	13.4_7	13.3_1		

[a] ^{13}C NMR chemical shift in ppm downfield from TMS, ±0.08 ppm, $CDCl_3$ solution, for the free ligand. [b] ^{13}C NMR chemical shift in ppm downfield from TMS, ±0.08 ppm, $CDCl_3$ solution, for the corresponding $LNi(CO)_3$ complex. [c] The C(2,6) and C(3,5) resonances were assigned on the basis of the magnitude of the $J(^{13}C^{31}P)$ coupling in the phosphine and then assumed valid for the arsine, stibine and bismuthine analogs.

observed in isovalent but not isoelectronic compounds such as $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ [5].

A similar decrease in the chemical shift has been observed for the methyl carbon resonance in O, S, Se and Te analogs with increasing atomic number of the Group VIA element [22], and there is an excellent correlation ($r = 0.996$) between the chemical shifts of the methyl carbon resonance in these PhXMe derivatives and the EMe_3 chemical shift data in Table 2, when X and E are members of the same row of the Periodic table. This effect is also observed for the C(1) resonance in EEt_3 and EBu_3, and there is an excellent correlation between the chemical shifts of the trimethyl compounds and the C(1) chemical shifts for the corresponding triethyl (0.999) and tributyl (0.996) derivatives. This behavior is also observed in the metal carbonyl complexes of these ligands, although the range of chemical shifts is considerably larger.

If substituent effects are calculated by comparing the chemical shifts in the trialkyl derivatives with the corresponding carbon in the unsubstituted alkane, the α substituent effects decrease in the order P > As ≫ Sb. The α substituent effect for Sb is so small that the C(1) and C(4) chemical shifts in $SbBu_3$ differ by only 0.7 ppm (Fig. 3). The β substituent effects for the EBu_3 derivatives increase in the order P < As < Sb.

The effects of complexation on the chemical shifts and $J(^{13}C^{31}P)$ coupling constants in trialkylphosphines have been reported previously [13]. These data are in accord with the effects observed by McFarlane for quaternization of the trivalent phosphorus [23]. The data in Table 2 suggest similar effects on the ^{13}C NMR chemical shifts for complexation of either phosphine or arsine derivatives. As shown in Fig. 3 there is a significant deshielding of C(1) and shielding of C(2), and little or no effect on the C(3) or C(4) chemical shifts. The behavior of the stibines is less predictable. Complexation leads to a shielding of C(1) in $SbMe_3$ and $SbEt_3$, but no effect is observed for $SbBu_3$. C(2) is deshielded on complexation in $SbEt_3$ and shielded in $SbBu_3$.

Substituent effects on aromatic carbon chemical shifts

^{13}C NMR data for PPh_3, $AsPh_3$, $SbPh_3$ and $BiPh_3$ were first reported by Gansow and Kimura [24]. Data obtained by Fourier transform spectroscopy for the P, As

and Sb derivatives were then reported by Bodner and Gaul, [25] and continuous wave data for the Sb and Bi derivatives were reported by Ouchi, Uehiro and Yoshino [26]. Data for the As and Sb compounds at higher field strength have recently been reported by Kuykendall and Mills, [27] and for P, As, Sb and Bi by Wuyts, Van de Vondel and Van der Kelen [28]. The assignments of the various groups for all four EPh_3 derivatives agree with the exception of the C(1) resonance in $BiPh_3$. Gansow and Kimura reported a chemical shift of 131.1 ppm, while neither Ouchi et al., nor Van der Kelen et al., observed this resonance. We have observed a broad resonance, as might be expected for a carbon coupled to a ^{209}Bi spin 9/2 nucleus, with a chemical shift of 155.4 ppm. Our data are in accord with the Sadtler index of ^{13}C spectra where the C(1) chemical shift of $BiPh_3$ is given as 155.3 ppm [29].

The controversy over the assignment of the C(1) resonance in $BiPh_3$ is significant since a correlation was originally suggested by Gansow and Kimura between the C(1) chemical shift in these triaryl derivatives and the electronegativity of the Group VA atom [24]. Kuykendall and Mills [27] have also reported a correlation, this time between the C(1) chemical shift and the Sanderson's equalized electronegativity [30], such that an increase in the electronegativity of the Group VA atom is supposedly mirrored by an increase in the chemical shift of the C(1) carbon. When the C(1) chemical shift for $BiPh_3$ in Table 2 is used instead of the value of Gansow and Kimura, an excellent correlation is still observed between the C(1) chemical shift and electronegativity ($r = -0.973$), but the sign of the correlation has changed, the chemical shift now increases as the electronegativity decreases. Any correlation with electronegativity would therefore seem to be fortuitous, and the preliminary conclusion that the inductive effect of the ligand dominates the paramagnetic term of the chemical shift equation [24] is questionable.

There is no obvious correlation between the ^{13}C NMR chemical shifts of the C(1) resonance in trialkyl derivatives of P, As, Sb and Bi and the C(1) resonance in the analogous triphenyl derivatives. With the exception of $BiPh_3$, the C(1) chemical shift in the aryl derivatives is not as sensitive to changes in the Group VA atom as the C(1) resonance in the corresponding alkyl compounds. The effect of complexation is also different. There is a shielding of both C(1) and C(2,6) on complexation of triaryl derivatives of P, As and Sb.

Maciel and Natterstad [31] have argued that contributions to the ^{13}C NMR chemical shift from both inductive and ring current effects should be approximately the same at both the C(3,5) and C(4) positions in mono-substituted benzenes, and that substituent effects on the π-electron density can be obtained by studying the corrected C(4) chemical shift, δ':

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

We have analyzed the corrected chemical shift data for a series of mono-substituted benzene derivatives [1] using a two-parameter equation and the Swain–Lupton substituent constants [32]. In this equation:

$$\delta' = fF_X + rR_x$$

F_X is the inductive or field parameter and R_X is the resonance parameter for substituent X, and f and r are the relative contributions to the ^{13}C NMR chemical shift from inductive and resonance effects. A least squares analysis of these data

suggested normalized values of f and r of 3 and 97%, respectively [1], in accord with the postulates of Maciel and Natterstad.

Analysis of the corrected chemical shifts of the mono-, di- and tri-aryl ligands in Table 2 and their $LNi(CO)_3$ complexes provides several generalizations. As we have noted previously [25], the resonance effect of the PPh_2 substituent is marginal at best, there is no significant delocalization of electron density on the phosphorus onto the phenyl ring. The corrected chemical shift for the PPh_2 substituent is only 0.14 ppm, whereas the corrected chemical shifts for the Cl, OCH_3, and NH_2 substituents are -3.36, -8.73 and -10.95 ppm, respectively [1]. Van der Kelen et al., [28] have also concluded that the p_π–p_π interaction between the P and the phenyl ring in PPh_3 is minimal.

There is a negligible delocalization of electron density into the π framework of the phenyl ring in the $AsPh_2$ and $SbPh_2$ substituents, where the corrected chemical shift is -0.28 ppm or less. The corrected chemical shift for $BiPh_3$, however, is -2.77 ppm, suggesting a significant delocalization of electron density from the Group VA atom onto the phenyl ring, as noted by Van der Kelen et al. [28]. Upon complexation, these substituents become moderately electron-withdrawing from π framework, with corrected chemical shifts as large as 1.7 ppm, but they are still weaker than substituents such as CO_2CH_3, for which the corrected chemical shift is 4.40 ppm. $PhAsCl_2$ is the only ligand studied here in which the Group VA atom becomes significantly electron-withdrawing, the corrected chemical shift for the $AsCl_2$ substituent is 2.96 ppm.

For both phosphine and arsine derivatives, substitution of an alkyl group for one or more of the phenyl groups leads to no significant increase in the p_π–p_π conjugation between the Group VA atom and the phenyl ring, although there is a tendency for the alkyl groups to make the Group VA atom an electron-releasing substituent. Finally, in most cases, the arsines are slightly more electron-releasing to the π framework than the corresponding phosphines.

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