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^1H, ^{13}C and ^{31}P NMR studies of some $(C_6H_5)_{3-n}PR_n$ and $(C_6H_5)_{3-n}PR_nCr(CO)_5$ ($n = 0$–3; R = H, CH_3, C_2H_5, i-C_3H_7, t-C_4H_9) derivatives

E. VINCENT,* L. VERDONCK and G. P. VAN DER KELEN
Laboratory for General and Inorganic Chemistry-B, University of Gent, Krijgslaan 271, B-9000 Gent, Belgium

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Abstract—The ^{31}P chemical shift of the $(C_6H_5)_{3-n}PR_n$ and $(C_6H_5)_{3-n}PR_nCr(CO)_5$ ($n = 0$–3; R = H, CH_3, C_2H_5, i-C_3H_7, t-C_4H_9) derivatives is dominated by the steric effect. A small inductive effect is also operative but there are no indications of notable $(d_{Cr} \rightarrow d_P)\pi$ back-bonding. The ^{13}C chemical shift of the phenyl carbon atoms indicates that $(p_{ring}-d_P)\pi$ electron delocalization is unimportant.

The ^{13}C chemical shift of the carbonyl carbon atoms, which is mainly governed by the mean excitation energy, confirms the conclusion that there are no notable changes in $(d_{Cr} \rightarrow d_P)\pi$ back-bonding in this series of compounds.

INTRODUCTION

In a previous report [1] on the $(C_6H_5)_{3-n}PX_n$ (n = 0–3, X = Cl, Br, I) ligands (L) and the corresponding $LCr(CO)_5$ complexes, we discussed the NMR parameters in terms of the electronegativity effect and the size of the X substituent and also of the π bonding. However, insufficient experimental information was available for a proper evaluation of the relative importance of these effects.

Therefore, we intend to study the $(C_6H_5)_{3-n}PH_n$ ($n = 0$–3) and $(C_6H_5)_2PR$ (R = CH_3, C_2H_5, i-C_3H_7, t-C_4H_9) ligands (L_n) and the corresponding $L_nCr(CO)_5$ complexes.

In these series the electronegativity effect is minimized, but there is a wide variety in the size of the substituent R. The low electronegativity of the substituents on phosphorus also prevents a marked π bonding.

Thus, the importance of the steric factor on the NMR parameters and information on the electron distribution around the nucleus under study should be determinable.

EXPERIMENTAL

Synthesis. (a) Ligands: $L_n = (C_6H_5)_{3-n}PH_n$ ($n = 0$–3) and $(C_6H_5)_2PR$ (R = CH_3, C_2H_5, i-C_3H_7, t-C_4H_9).

PH_3 is commercially available. The phenylphosphines $C_6H_5PH_2$ and $(C_6H_5)_2PH$ were prepared by the reduction of $C_6H_5PCl_2$ and $(C_6H_5)_2PCl$, respectively, with $LiAlH_4$ in dry ether [2]: $C_6H_5PH_2$ (coloured liquid, b.p. 37°C, 6 torr), $(C_6H_5)_2PH$ (coloured liquid, b.p. 117°C, 2.5 torr).

$(C_6H_5)_2PCH_3$ [colourless liquid, b.p. 95°C (1 mmHg)] and $(C_6H_5)_2PC(CH_3)_3$ [colourless solid, b.p. 119.5°C (2 mmHg)] are synthesized by the reaction of $(C_6H_5)_2PCl$ with, respectively, CH_3Li and $(CH_3)_3CLi$ in dry ether [3].

The other tertiary phosphines, $(C_6H_5)_2PCH_2CH_3$ [colourless liquid, b.p. 120–121°C (1.5 mmHg)] and $(C_6H_5)_2PCH(CH_3)_2$ [colourless solid, b.p. 114°C (1 mmHg)], are prepared using standard Grignard reactions.

(b) Complexes: $LCr(CO)_5$.

The synthesis of the chromium carbonyl complexes is based on the method developed by STROHMEIER [4–6]:

$$Cr(CO)_6 \xrightarrow{h\nu} \{Cr(CO)_6\}^* \xrightarrow{THF} CO$$

$$+ THFCr(CO)_5 \xrightarrow{L} LCr(CO)_5 + THF.$$

Instrumentation. The ^{31}P and ^{13}C NMR spectra are obtained on a Bruker HFX_5 spectrometer in the Fourier Transform mode. The ^{13}C spectra are obtained at 22.63 MHz.

The chemical shift is calculated with respect to TMS using the convention

$$\delta = \frac{\nu_s - \nu_{ref}}{\nu_{ref}} \cdot 10^6 \text{ (ppm)}.$$

The ^{31}P spectra are measured at 36.43 MHz and the reference is $P(OCH_3)_3$.

The ^1H chemical shifts and coupling constants are measured on a Varian SM 360 NMR spectrometer at 60 MHz with reference to the internal standard TMS.

All the recordings were made on saturated solutions in $CDCl_3$.

RESULTS AND DISCUSSION

^{31}P *chemical shift of* $(C_6H_5)_2PCH_{3-n}(CH_3)_n$ ($n = 0$–3) *ligands (group* L_1)

The electronegativities of the alkyl groups are practically invariant. Calculated values according to HUHEEY [7] range from 2.34 to 2.39. The effect of the electronegativity difference on $\langle 1/r^3 \rangle$ in the paramagnetic term [1] is expected to be negligible. The $\delta^{31}P$ data, (Table 1) accordingly show no additive substituent effect with the Taft $\sum \sigma^*$ induction constants [8].

The $\delta^{13}C$ data of the phenyl carbon atoms and the derived δ' data (see further ^{13}C) suggest that $(p_{ring} \rightarrow d_P)\pi$ contributions are negligible. Hyperconjugation of the type $(C_6H_5)_2P^- = CRH^+$ is also excluded by the observation that the δ' data indicate no electron delocalization towards the phenyl ring system.

Electronic effects are, therefore, certainly not the major factor in determining the $\delta^{31}P$ chemical shift.

* Scholar of the Institute for Chemical Research in Industry and Agriculture (I.W.O.N.L.).

Table 1. ^{31}P NMR data of $(C_6H_5)_2PR$ and $(C_6H_5)_2PRCr(CO)$ derivatives

R	$(C_6H_5)_2PR$ $\delta 31_P$ (ppm)	θ[a]	$\Sigma\sigma^*$	$(C_6H_5)_2PRCr(CO)_5$ $\delta 31_P$ (ppm)
H	-180.7	128	0.430	-107.9
CH_3	-167.5	136	0.330	-104.9
C_2H_5	-152.0	140	0.315	- 92.0
C_6H_5	-146.1	145	0.645	- 85.6
$i\text{-}C_3H_7$	-139.3	150	0.305	- 80.8
$t\text{-}C_4H_9$	-122.8	157	0.275	- 68.0

[a] θ: ligand cone angle of Tolman [9].

For the different alkyl groups the ligand cone angle (θ), according to TOLMAN [9, 10], is a very useful steric parameter. A plot of $\delta^{31}P$ vs θ shows a quasi linear correlation (Fig. 1). As a test, $(C_6H_5)_2PH$ and $(C_6H_5)_3P$, with quite different electronic properties and symmetry $\{(C_6H_5)_3P\}$, are included and they also fit the curve.

This clearly emphasizes the dominant role of the steric factor in determining the molecular properties of derivatives with bulky substituents.

^{31}P chemical shift of $(C_6H_5)_2PCH_2CH_{3-n}(CH_3)_n$ ($n = 0$–3) ligands (group L_2)

The steric factor in the group L_2 compounds should obviously be less important than in the L_1 derivatives. The experimental $\delta^{31}P$ data [7] (Table 2) indeed show a small chemical-shift range. However, the trend of $\delta^{31}P$ vs θ is inversed with respect to the L_1 series and shows no simple additive substituent effects. On the other hand, a satisfactory correlation exists between $\delta^{31}P$ and $\sum \sigma^*$. Obviously the long-range inductive effect seems to be the dominant factor here which indirectly suggests

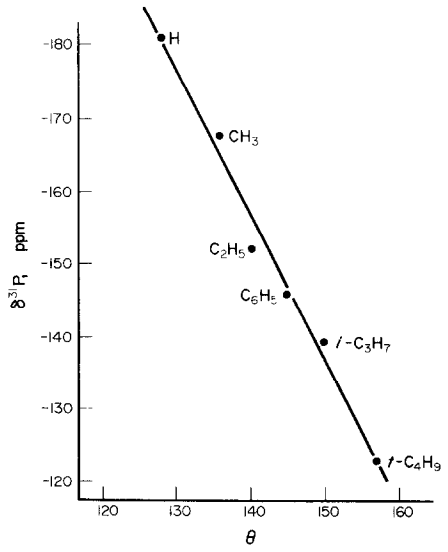

Fig. 1. Plot of $\delta^{31}P$ vs θ for the ligands $(C_6H_5)_2PR$.

Table 2. ^{31}P NMR data of $(C_6H_5)_2PCH_2R$

R	$\delta 31_P$ (ppm)	$\Sigma\sigma^*$
CH_3	-152.0	0.315
C_2H_5	-157.6	0.300
$i\text{-}C_3H_7$	-161.0	0.300
$t\text{-}C_4H_9$	-163.9	0.300

that for the group L_1 derivatives the inductive effect is overcompensated by the steric effect.

^{31}P chemical shift of $(C_6H_5)_{3-n}PH_n$ ($n = 0$–3) ligands (group L_3)

Substitution of a hydrogen atom in $(C_6H_5)_{3-n}PH_n$ by a phenyl group causes an electron withdrawal (increasing parameter $\sum \sigma^*$) at the phosphorus and a simultaneous increase of the steric factor (parameter θ), both acting as deshielding factors. This is clearly reflected in the large chemical shifts (Table 3). The small chemical shift range for the group L_1 compounds, thus, can obviously be explained by the fact that the inductive and the steric effects operate in opposite direction.

^{31}P chemical shift of the $L_1Cr(CO)_5$ and $L_3Cr(CO)_5$ complexes

Complexation of L_1 and L_3 with $Cr(CO)_6$ results in deshielding (Tables 1 and 3) due to the decrease of electron density at the phosphorus. The general trend upon substitution, however, is analogous to that for the free ligands.

A plot (Fig. 2) of $\delta^{31}P$ of the free ligands vs $\delta^{31}P$ of the complexes displays a good correlation indicating that essentially the same effects are operative in the free ligands and in the complexes. Therefore, notable changes in the $(d_{Cr} \rightarrow d_P)\pi$ back-bonding are excluded.

^{13}C NMR of the phenyl carbon atoms in $(C_6H_5)_{3-n}PH_n$ and $(C_6H_5)_{3-n}PH_nCr(CO)_5$ ($n = 0$–2)

Substitution of a phenyl group by a hydrogen atom in the ligands results in an inversion of the sign of the δ' parameter (Table 4). This parameter indicates a $(p_{ring} \leftarrow d_P)\pi$ delocalization. The negative values thus imply that on substitution negative charge is accumulated on the phosphorus which in turn can only be drained towards the phenyl ring.

On complexation a charge deficit occurs on the phoshorus which is now partly compensated by $(p\text{–}d)\pi$ delocalization from the ring towards the phosphorus resulting in a positive δ' value. However, a comparison with the corresponding halide derivatives [1], shows that the variation on substitution is minimal. The $(p\text{–}d)\pi$ effect is mainly dependent on the high electronegativity of the substituents on the phosphorus in the halides.

Table 3. ^{31}P NMR data of $(C_6H_5)_{3-n}PH_n$ and $(C_6H_5)_{3-n}PH_nCr(CO)_5$ derivatives ($n = 0$–3)

Ligand	θ[a]	$\Sigma\sigma^*$	$\delta 31_P$ (ppm)	J_{P-H} (Hz)	Complex	$\delta 31_P$ (ppm)	J_{P-H} (Hz)
PH_3	87	0	-379.3	189.2	$PH_3Cr(CO)_5$	-264.6	327.2
$C_6H_5PH_2$	101	0.215	-263.2	200.7	$C_6H_5PH_2Cr(CO)_5$	-175.1	332.0
$(C_6H_5)_2PH$	128	0.430	-180.7	217.3	$(C_6H_5)_2PHCr(CO)_5$	-107.9	338.8
$(C_6H_5)_3P$	145	0.645	-146.1	-	$(C_6H_5)_3PCr(CO)_5$	- 85.6	-

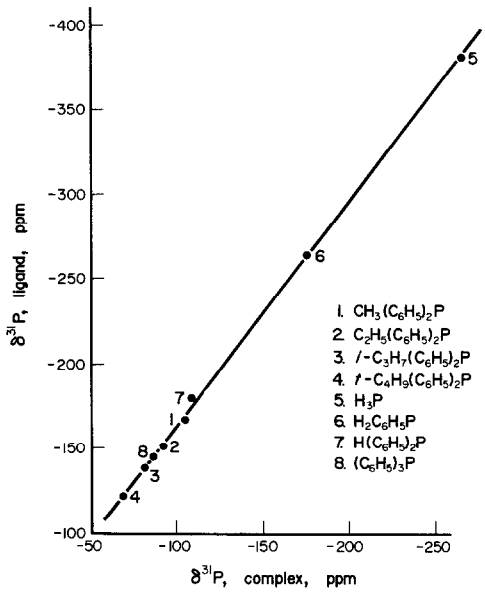

Fig. 2. Plot of $\delta^{31}P$ of the ligands L vs $\delta^{31}P$ of the complexes $LCr(CO)_5$.

^{13}C *NMR of the phenyl carbon atoms in* $(C_6H_5)_2PCH_{3-n}$ ($n = 0$–3) *and the corresponding* $LCr(Co)_5$ *derivatives*

The experimental δ' data (Table 4) indicate an increasing $(p-d)\pi$ electron delocalization from the phenyl ring to the phosphorus with branching. This is in contradiction to the Taft σ^* induction constants of the alkyl groups. On the other hand the δ' data display a good correlation with the cone angle θ (Fig. 3). This can be rationalized in the following way: an increasing number of methyl groups on the α-C atom causes a distortion of the R—P—Ph angle followed by a rehybridization resulting in increased s-character in the phosphorus orbitals and a higher orbital electronegativity of the phosphorus as the number of methyl groups on the α-carbon atom increases.

The phenyl group reacts to this increased orbital electronegativity with an increased electron delocalization towards the phosphorus. However, the absolute value and the variation in the δ' data are small, so $(p-d)\pi$ electron delocalization seems rather unimportant for this group of compounds.

Table 4. ^{13}C NMR data of the phenyl carbon atoms in $(C_6H_5)_{3-n}PH_n$ and $(C_6H_5)_{3-n}PH_nCr(CO)_5$ ($n = 0$–2), and in $(C_6H_5)_2PR$ and $(C_6H_5)_2PRCr(CO)_5$

Compound	$C_{(1)}$		$C_{(2,6)}$		$C_{(3,5)}$		$C_{(4)}$		δ'[a]	$\Delta\delta'$[b]
	δ	J	δ	J	δ	J	δ	J		
$(C_6H_5)_3P$	139.2	12.0	135.5	19.8	130.2	7.3	130.4	0	0.2	-
$(C_6H_5)_2PH$	136.8	10.4	135.9	17.0	130.5	6.7	130.4	0	-0.1	-
$C_6H_5PH_2$	130.4	8.4	136.5	15.4	130.1	6.0	129.7	0	-0.4	-
$(C_6H_5)_3PCr(CO)_5$	136.9	36.1	134.4	11.5	130.2	9.5	131.8	2.4	1.6	1.4
$(C_6H_5)_2PHCr(CO)_5$	134.4	38.7	133.6	10.6	130.7	9.6	132.0	2.2	1.3	1.4
$C_6H_5PH_2Cr(CO)_5$	127.7	42.7	133.8	10.6	130.8	10.0	132.1	2.6	1.3	1.7
$(C_6H_5)_2PCH_3$	142.3	13.2	134.0	18.8	130.3	5.6	130.1	0	-0.2	-
$(C_6H_5)_2PCH_2CH_3$	140.9	14.2	134.6	18.3	130.2	6.6	130.2	0	0.0	-
$(C_6H_5)_2PCH(CH_3)_2$	139.6	15.1	135.3	19.3	130.1	6.8	130.4	0	0.3	-
$(C_6H_5)_2PC(CH_3)_3$	138.6	17.8	136.2	19.8	129.6	6.8	130.0	0	0.4	-
$(C_6H_5)_2PCH_3Cr(CO)_5$	138.8	36.6	132.6	11.0	130.3	9.5	131.6	2.2	1.3	1.5
$(C_6H_5)_2PCH_2CH_3Cr(CO)_5$	137.6	35.4	133.4	10.3	130.3	9.0	131.6	2.0	1.3	1.3
$(C_6H_5)_2PCH(CH_3)_2Cr(CO)_5$	135.5	33.0	134.3	9.5	130.0	8.8	131.5	2.0	1.5	1.2
$(C_6H_5)_2PC(CH_3)_3Cr(CO)_5$	137.5	29.1	135.2	9.3	129.6	8.6	131.2	2.0	1.6	1.2

[a] $\delta' = \delta^{13}C(4) - \delta^{13}C(3,5)$.
[b] $\delta' = \delta'(\text{complex}) - \delta'(\text{ligand})$.

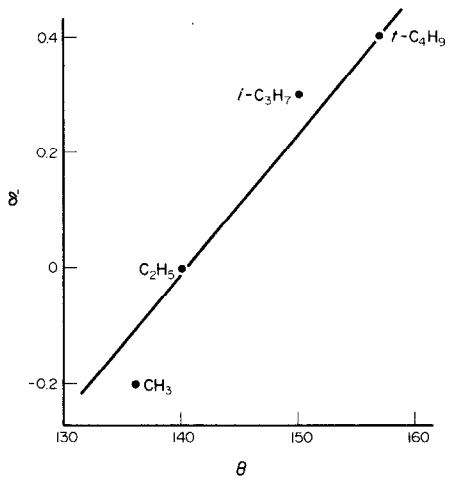

Fig. 3. Plot of δ' vs θ for the ligands $(C_6H_5)_2PR$.

The parameter, $\Delta\delta'$, is almost invariant, indicating a constant $(d_{Cr}\rightarrow d_P)\pi$ contribution in these series.

^{13}C NMR of the carbonyl carbon atoms in $(C_6H_5)_2PRCr(CO)_5$ and $(C_6H_5)_{3-n}PH_nCr(CO)_5$ ($n = 0$–3)

As stated in a previous report [1] the $\delta^{13}CO$ is mainly governed by the ΔE^{-1} factor which is very sensitive to the distribution of the π-electron density between the Cr—P and Cr—CO bonds. The small experimental ^{13}CO chemical shifts in this series of products (see Table 5) indicate a negligible π-electron redistribution on substitution. This confirms the conclusion reached from the study of the ^{31}P and the ^{13}C(ring) chemical shift, that there are no notable changes in $(d_{Cr}\rightarrow d_P)\pi$ back-bonding in this series of compounds.

^{13}C NMR of the alkyl carbon atoms in $(C_6H_5)_2PCH_{3-n}(CH_3)_n$ ($n = 0$–3) and the corresponding $LCr(CO)_5$ derivatives

Substitution of a hydrogen atom by the more electronegative [11] methyl group causes deshielding (Table 6). However, the deshielding effect is not additive (Fig. 4) because of two other effects:

(1) On substitution steric hindrance forces the phosphorus to rehybridize affecting the orbital electronegativity.

Table 6. ^{13}C NMR data of the alkyl carbon atoms in the $(C_6H_5)_2PR$ and $(C_6H_5)_2PRCr(CO)_5$ derivatives

Compound	δC_α	$^1J_{P-C_\alpha}$ (Hz)	δC_β	$^2J_{P-C_\beta}$ (Hz)
$(C_6H_5)_2PCH_3$	14.5	14.4	-	-
$(C_6H_5)_2PCH_2CH_3$	22.6	11.2	12.0	17.1
$(C_6H_5)_2PCH(CH_3)_2$	26.9	10.4	21.5	18.8
$(C_6H_5)_2PC(CH_3)_3$	32.3	13.9	30.3	14.2
$(C_6H_5)_2PCH_3Cr(CO)_5$	20.8	25.9	-	-
$(C_6H_5)_2PCH_2CH_3Cr(CO)_5$	27.1	23.3	9.5	0
$(C_6H_5)_2PCH(CH_3)_2Cr(CO)_5$	30.2	19.5	19.6	0
$(C_6H_5)_2PC(CH_3)_3Cr(CO)_5$	38.7	14.2	30.1	5.6

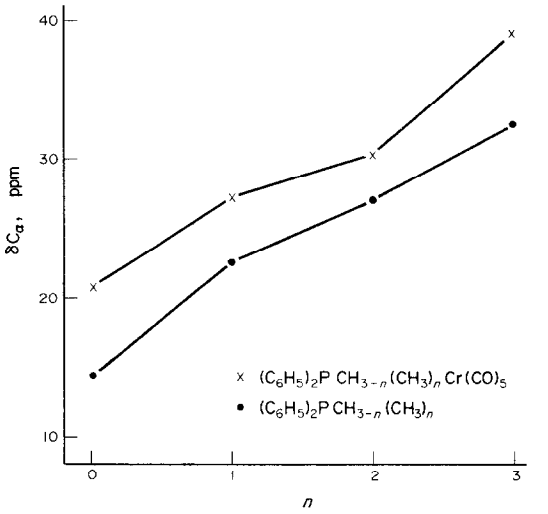

Fig. 4. Plot of δC_α vs n for the ligands $(C_6H_5)_2PCH_{3-n}(CH_3)_n$ and the corresponding $LCr(CO)_5$ derivatives.

Table 5. ^{13}C NMR data of the carbonyl moiety in $(C_6H_5)_2PRCr(CO)_5$ and $(C_6H_5)_{3-n}PH_nCr(CO)_5$ ($n = 0$–3)

Compound	$\delta_{CO(eq.)}$ (ppm)	$J_{P-C(eq.)}$ (Hz)	$\delta_{CO(ax.)}$ (ppm)	$J_{P-C(ax.)}$ (Hz)
$(C_6H_5)_2PCH_3Cr(CO)_5$	218.4	13.4	223.0	7.3
$(C_6H_5)_2PCH_2CH_3Cr(CO)_5$	218.5	13.2	223.1	6.8
$(C_6H_5)_2PCH(CH_3)_2Cr(CO)_5$	218.6	12.9	223.3	6.4
$(C_6H_5)_2PC(CH_3)_3Cr(CO)_5$	218.7	12.2	223.3	5.9
$PH_3Cr(CO)_5$	216.8	13.7	221.3	6.8
$C_6H_5PH_2Cr(CO)_5$	217.4	13.7	222.1	7.3
$(C_6H_5)_2PHCr(CO)_5$	217.9	13.2	222.7	7.2
$(C_6H_5)_3PCr(CO)_5$	218.4	13.2	223.1	7.1

$Cr(CO)_6 = \delta^{13}_{CO} = 211.9$ ppm

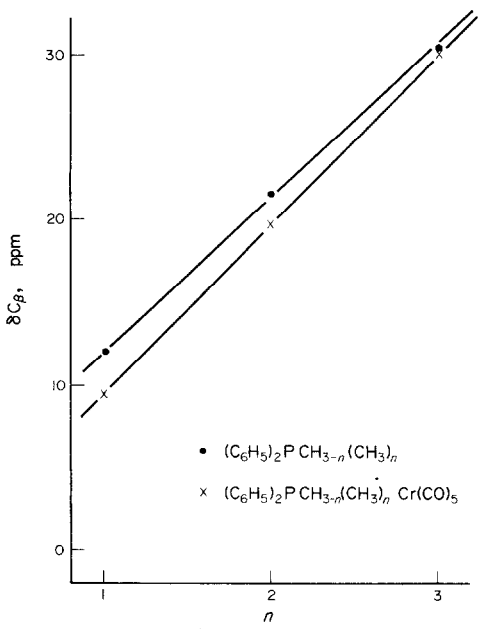

FIG. 5. Plot of δC_β vs n for the ligands $(C_6H_5)_2PCH_{3-n}(CH_3)_n$ and the corresponding $LCr(CO)_5$ derivatives.

Table 7. ^{1}H NMR data of $(C_6H_5)_{3-n}PH_n$ and $(C_6H_5)_{3-n}PH_nCr(CO)_5$ derivatives

Compound	δ^1H (ppm)	$^1J_{H-^{31}P}$ (Hz)
PH_3	1.81	188.0
$C_6H_5PH_2$	3.91	200.0
$(C_6H_5)_2PH$	5.69	217.0
$PH_3Cr(CO)_5$	3.74	326.0
$C_6H_5PH_2Cr(CO)_5$	5.42	330.0
$(C_6H_5)_2PHCr(CO)_5$	6.35	337.0

(2) The electronic population of the different carbon orbitals is altered which influences the asymmetry parameter P in the paramagnetic term [1] of the magnetic screening of the ^{13}C nuclei.

In turn, the additivity for the $\delta^{13}C\beta$ (Fig. 5) is due to the fact that the influence of both effects on the electron distribution of the β-carbon atom is negligible.

^{1}H chemical shift of the ligands $(C_6H_5)_{3-n}PH_n$ (n = 1–3) and the $(C_6H_5)_{3-n}PH_nCr(CO)_5$ complexes

Progressive substitution of a hydrogen atom by the more electronegative phenyl group in PH_3 has a deshielding effect (Table 7).

However, the chemical shifts are not additive. This is probably because the deshielding effect is reinforced by the $(p_{ring} \leftarrow d_P)\pi$ electron delocalization, which is stronger for $C_6H_5PH_2$ than for $(C_6H_5)_2PH$ (see δ' parameter in Table 4).

On complexation the electron drain towards Cr lowers the electron density around hydrogen. On substitution the deshielding effect of the phenyl groups is then partly compensated by a $(p_{ring} \rightarrow d_P)\pi$ bonding (see Table 4) and so the chemical shift changes for the complexes are smaller than for the ligands.

^{1}H chemical shift of the ligands $(C_6H_5)_2PCH_{3-n}(CH_3)_n$ (n = 0–3) and the $(C_6H_5)_2PCH_{3-n}(CH_3)_nCr(CO)_5$ complexes

Substitution of a hydrogen atom by the more electronegative [11] methyl group lowers the electron density around the α-hydrogen atoms. Since the ^{1}H chemical shift is mainly dominated by the diamagnetic term, the result is deshielding (Table 8). Indeed, the neighboring anisotropy effect and the ring current effect can be considered to be almost constant in these series of compounds. The deshielding influence is clearly much smaller for the β-hydrogen atoms which are more distant from the substitution center. The resonance positions of the α and β protons both move downfield upon coordination as is expected from the greater electronegativity of phosphorus in the complex than in the free ligand [12].

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Table 8. ^{1}H NMR data of $(C_6H_5)_2PCH_{3-n}(CH_3)_n$ and $(C_6H_5)_2PCH_{3-n}(CH_3)_nCr(CO)_5$ derivatives

Compound	δ^1H_α (ppm)	$^2J_{H_\alpha-P}$ (Hz)	δ^1H_β (ppm)	$^3J_{H_\beta-P}$ (Hz)
$(C_6H_5)_2PCH_3$	1.43	3.9	-	-
$(C_6H_5)_2PCH_2CH_3$	1.90	<1.0	0.97	16.8
$(C_6H_5)_2PCH(CH_3)_2$	2.30	<1.0	1.03	15.3
$(C_6H_5)_2PC(CH_3)_3$	-	-	1.15	12.4
$(C_6H_5)_2PCH_3Cr(CO)_5$	2.00	6.7	-	-
$(C_6H_5)_2PCH_2CH_3Cr(CO)_5$	2.39	7.0	0.97	17.5
$(C_6H_5)_2PCH(CH_3)_2Cr(CO)_5$	2.75	a.	1.15	15.2
$(C_6H_5)_2PC(CH_3)_3Cr(CO)_5$	-	-	1.30	14.3

[a] Cannot be determined because of the higher order of the spectrum.

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