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ACTIVATION OF C—H BONDS BY TRANSITION METALS

II *. METALLATION OF ALLYLPHOSPHINES BY $(acac)Ir(C_2H_4)_2$

S. HIETKAMP, D.J. STUFKENS and K. VRIEZE *
Anorganisch Chemisch Laboratorium, University of Amsterdam, J.H. van 't Hoff Instituut, Nieuwe Achtergracht 166, Amsterdam (The Netherlands)

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Summary

Reaction of the olefinic phosphines R_2P-allyl (R = t-butyl, cyclohexyl) with $[(acac)Ir(C_2H_4)_2]$ (acac = acetylacetonate) in the presence of γ-picoline and acetonitrile, yields the six-coordinated metallated iridium(III) complexes $[(acac)R_2P(CH_2CH{=}CH)IrHL]$ (L = γ-picoline, acetonitrile). CO, CNR and $P(OMe)_3$ displace the ligand L from these complexes; in the case of CO and of $P(OMe)_3$ several isomers are formed. A very large phosphorus—hydrogen coupling was found in the metallocyclic rings (J(PCCH) = 34—38 Hz). (Acac)Rh-$(C_2H_4)_2$ does not give metallated complexes with these phosphines under the same conditions, and at higher temperature only decomposition occurs.

Introduction

It is well known, that both steric and electronic factors are important in influencing metallation reactions [1—4]. According to earlier observations in this laboratory basic iridium(I), compounds can activate not only aromatic C—H bonds, but also olefinic C—H bonds of N- and P-donor ligands under very mild conditions [5—7]. We now report some metallation reactions of the olefinic phosphines $[R_2PCH_2CH{=}CH_2]$ (R = t-butyl, cyclohexyl) with the complex $[(acac)Ir(C_2H_4)_2]$. The latter complex is chosen because its steric features differ from that of the previously used iridium(I) compounds due to the bidentate character of the acac-group.

Experimental

All operations were carried out under purified nitrogen.

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* For part I, see ref. 7.

Preparation of the complexes

$[(acac)\{(t\text{-}C_4H_9)_2PCH_2CH{=}\overline{CH\}Ir}H(NC_6H_7)]$ (IA). $[(acac)Ir(C_2H_4)_2]$ (0.80 mmol) was dissolved in 10 ml hexane. To this solution was added γ-picoline (0.80 mmol) followed by di-t-butylallylphosphine (0.80 mmol). After stirring for 30 min at 60°C, the yellow solution was filtered, concentrated, and cooled to —30°C. Air-stable yellow crystals were collected on a filter, washed with cold hexane, and dried under vacuum (yield 70%) $[(acac)\{(t\text{-}C_4H_9)_2PCH_2CCH_3{=}\overline{CH\}Ir}(NC_6H_7)]$ (IB) and $[(acac)\{(C_6H_{11})_2PCH_2CCH_3{=}\overline{CH\}Ir}H(NC_6H_7)]$ (IC) were prepared similarly. When the reactions were carried out without γ-picoline a non-crystallizable mixture of metallated compounds was obtained.

$[(acac)\{(t\text{-}C_4H_9)_2PCH_2CH{=}\overline{CH\}Ir}H(N{\equiv}CCH_3)]$ (II). The procedure used for compound IA gave the product II as white microcrystals (yield 50%).

$[(acac)\{(t\text{-}C_4H_9)_2PCH_2CH{=}\overline{CH\}Ir}HCO]$ (isomers IIIA, IIIB and IIIC). A solution of compound IA (0.35 mmol) in 20 ml hexane was stirred overnight at 40°C under carbon monoxide. A mixture of two isomers (IIIB and IIIC) resulted, only one of which (IIIB) crystallized out when the solution was cooled to —30°C (yield 40% cream crystals). Isomer IIIA was obtained after stirring a solution of II in hexane for 10 min in a carbon monoxide atmosphere at 0°C. Evaporation of the solvent yielded the impure product, which slowly isomerized on standing.

$[(acac)\{(t\text{-}C_4H_9)_2PCH_2CH{=}\overline{CH\}Ir}H(C{\equiv}NC_6H_{11})]$ (IV). Cyclohexylisocyanide (0.35 mmol) was added to a solution of compound IA (0.35 mmol) in 15 ml hexane. After evaporation of the solvent the crude product remained as an orange oil.

$[(acac)\{(t\text{-}C_4H_9)_2PCH_2CH{=}\overline{CH\}Ir}H\,P(OMe)_3]$ (isomer mixture VA and VB). These complexes, which were obtained in the same way as complex IV, were non-crystallizable oils.

Reaction of tri-methallylphosphine with $[(acac)Ir(C_2H_4)_2]$ yielded a complex mixture of metallated compounds, which could not be separated. There is spectral evidence (^1H NMR, ^{31}P NMR) that the products were structurally similar to those from the reaction of compound IA with $P(OMe)_3$.

Several attempts to prepare the Rh-analogue of compound IA were unsuccessfull, even at elevated temperatures.

The C and H analyses (Table 1) were carried out in this laboratory. For com-

TABLE 1

ANALYTICAL DATA OF THE COMPOUNDS $[(acac)R_2P(CH_2CH{=}\overline{CH)Ir}HL]$

Compound	Colour	Analysis found (calcd.) (%)	
		C	H
$(acac)\{t\text{-}C_4H_9)_2PCH_2CH{=}\overline{CH\}Ir}HNC_6H_7$ (IA) [a]	yellow	46.26 (46.29)	6.68 (6.49)
$(acac)\{(t\text{-}C_4H_9)_2PCH_2CCH_3{=}\overline{CH\}Ir}HNC_6H_7$ (IB)	yellow	47.13 (47.23)	6.72 (6.76)
$(acac)\{(C_6H_{11})_2PCH_2CCH_3{=}\overline{CH\}Ir}HNC_6H_7$ (IC)	yellow	49.95 (50.14)	6.63 (6.59)
$(acac)\{(t\text{-}C_4H_9)_2PCH_2CH{=}\overline{CH\}Ir}HN{\equiv}CCH_3$ (II)	cream	41.52 (41.67)	6.48 (6.35)
$(acac)\{(t\text{-}C_4H_9)_2PCH_2CH{=}\overline{CH\}Ir}HCO$ (IIIB) [b]	cream	40.42 (40.37)	6.02 (5.94)

[a] Compound IA is monomeric in C_6H_6 as measured by VPO. As the other compounds have analogous spectroscopic properties they are assumed to be also monomeric. [b] Other compounds are oils and could not be obtained pure.

pound IA the molecular weight was determinated by the vapour pressure osmometer method in benzene, showing it to be monomeric. It was assumed that the other compounds are also monomeric.

Spectroscopic measurements

The ^{1}H NMR spectra were recorded on Varian T-60 and Varian XL-100 instruments, the ^{31}P NMR spectra on a Varian XL-100 with Fourier transform and with a proton noise decoupler with variable bandwidth and the ^{13}C NMR spectra on a Varian CFT-20 apparatus. The IR spectra were recorded as Nujol mulls on a Beckmann 4250 spectrophotometer, between 4000 and 200 cm^{-1}.

Results and discussion

The compounds $[(\text{acac})(\text{R}_2\text{Pall}\overline{\text{yl})\text{Ir}}\text{HL}]$ (I—V) (R = t-butyl, cyclohexyl, L = γ-picoline, $N{\equiv}CCH_3$, $C{\equiv}NC_6H_{11}$, CO and $P(OMe)_3$) were characterized by C and H analysis and by their IR, ^{1}H, ^{31}P and ^{13}C NMR spectra.

Infrared spectra (Table 2)

Of the very complicated spectra only the most relevant bands will be discussed. The hydrido ligand is shown to be present in all complexes by the appearance of the ν(Ir—H) vibration as a medium to strong band in the region 2100—2250 cm^{-1} [8]. When a strong *trans*-directing group is located *trans* to the hydrogen atom, this band is shifted to lower frequency [9]. ν(C=C) of the phosphines, which is located at 1635—1640 cm^{-1} in the free ligands is shifted to lower frequencies upon complexation just as in $[(\text{R}_2\text{Pall}\overline{\text{yl})\text{Ir}}\text{HClL}(\text{R}_2\text{Pallyl})]$ [7], and is obscured by the vibrations of the acac group. The ν(CO), ν(C≡N) and ν(N≡C) are located at about the same frequencies as in similar compounds [10,11].

^{13}C NMR spectra (Table 3)

In order to assign the ^{13}C NMR spectra of the complexes correctly, the off-resonance spectra of the compounds IA, IB and IC were compared with the completely proton-decoupled spectra. In the off-resonance spectra C_1 appears as a doublet. which indicates the loss of a proton (for the numbering of the carbon atoms, see Fig. 1). In compound IA two tertiary carbon atoms form

TABLE 2

IR DATA FOR THE COMPOUNDS $[(\text{acac})\{\text{R}_2\text{PCH}_2\text{CH{=}}\overline{\text{CH}\}\text{Ir}}\text{HL}]$. (The spectra were recorded as nujol mulls.)

Compound [a]	ν(Ir—H) (cm^{-1})	Other frequencies
IA	2225	
IB	2250	
IC	2200	
II	2205	ν(N≡C) 2295
IIIA	2118	ν(CO) 2010
IIIB, IIIC	2255	ν(CO) 1970—2015
IV	2125	ν(C≡N) 2210

[a] Only ν(Ir—H) and ν(C≡O) ν(C≡N) and ν(N≡C) are reported.

TABLE 3

^{13}C SPECTRA OF THE COMPOUNDS [acac$\{R_2PCH_2CH{=}CH\}$IrHL]. (Spectra recorded in C_6D_6: only the resonances of the olefinic carbon atoms are shown)

Compound	C_1	$J(^{31}P-^{13}C)$	Δ [a]	C_2	$J(^{31}P-^{13}C)$	Δ [a]
IA	131.63 d [b]	[c]	+15.68	130.00 d [b]	9.0	−8.88
IB	122.38 d [b]	1.0	+10.85	136.34 s [b]	10.2	−8.95
IC	122.17 d [b]	[c]	+10.65	135.62 s [b]	9.5	−9.14
IIIB [d]	157.23	[c]	+41.28	133.33	8.1	−5.50

[a] Shift difference between free phosphine and complex. [b] Splitting found when recording the off-resonance spectra, d = doublet, s = singlet. [c] Too small to detect. [d] No off-resonance spectrum was recorded.

the double bond and, therefore, it is not possible to assign the metallated carbon atom on the basis of this off-resonance experiment alone. For compounds IB and IC, however, the carbon atoms C_1 and C_2 can be distinguished because C_1 is a tertiary carbon atom whereas C_2 is quaternary. It appears that C_2 shows the larger coupling with the phosphorus nucleus. So, in all the compounds the resonance with the small phosphorus coupling is assigned to the metallated carbon atom (C_1). In all the compounds this resonance is shifted downfield, whereas the resonance of C_2 is shifted upfield [12]. For C_1 in compound IIIB a much larger downfield shift was found. A similar downfield shift was found for the carbonyl compounds *trans*-$[(CH_3)Pt\{As(CH_3)_3\}_2CO]^+PF_6^-$ [13] and *trans*-$[(C_6H_5)Pt\{As(CH_3)_3\}_2CO]^+PF_6^-$ [14] indicating a *trans* position of carbon monoxide with respect to C_1.

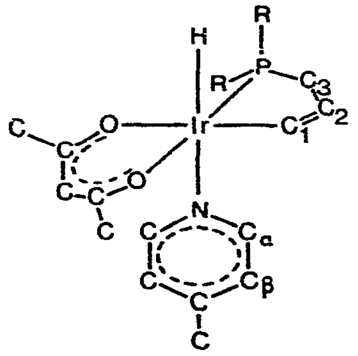
^1H and ^{31}P NMR spectra (Tables 4 and 5)

The ^1H NMR spectra of the compounds show a large downfield shift (2.5 ppm) for the resonance of the proton at C_1 ($\delta = 7.6$ ppm). A similar downfield shift was found for the square-planar compound [*trans*-$(PPh_3)_2Pt(HC{=}CH_2)Br$] ($\delta = 6.25$ ppm) [15] and for the octahedral compound [$RuHCH{=}CCH_3C(O)$-$OEt(PPh_3)_3$] ($\delta = 8.20$ ppm) [16]. However, an upfield shift for the resonance of such a proton was found for the square planar compound [$(PPh_3)PtCl$-$\{N(CH_3)_2CH_2CCH_3{=}CH\}$] ($\delta = 4.86$ ppm) [17] and also for the octahedral compound [$(PPh_3)_2IrHCl(CH{=}CCH_3{-}N{=}NCH_3)$] ($\delta = 1.58$ ppm) [5]. From

TABLE 4

^1H NMR SPECTRA OF THE COMPOUNDS (acac) $\{(t\text{-}C_4H_9)_2PCH_2CH{=}CH\}$IrHL in C_7D_8 (δ relative to TMS). Only the important resonances are shown.

Compound	Ir—H (J(P—H)) (Hz)	$H_1(J(H_1H_2))$ (Hz)	$H_2(J(P{-}H))$ (Hz)
IA	−26.6(24)	7.6(8.6)	6.1(34)
II	−26.3(26)	7.6(8.6)	6.1(34)
IIIA	−5.8(19)	7.6(8.8)	6.1(36)
IIIB	−22.75(22)	7.9(9.0)	6.3(38)
IIIC	−22.80(20)	7.5(8.8)	~6.2(37)
IV	−8.5(20)	8.0(8.7)	5.9(32)
VA, VB	−25(18.16), −25.6(20,24)	7.8, 7.4 (~9)	6.1(~32)



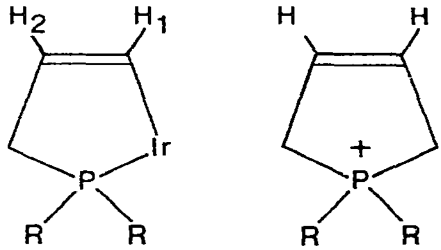


Fig. 1. Structure and numbering of the important atoms of compound IA.

Fig. 2. Comparison of the metallocyclic ring with $^{+}$phosphorus(IV) phospholene.

these data it is not possible to define the factors which contribute to the observed shifts.

In all the complexes the proton at C_2 shows a very large phosphorus coupling ($J(^{31}P—^{1}H)$ = 32—38 Hz) with respect to the free ligand ($J(^{31}P—^{1}H)$ = 12 Hz). This coupling can be compared with the phosphorus—hydrogen coupling in 3-phospholenes (Fig. 2). In phosphorus(V) 3-phospholenes $J(^{31}P—^{1}H)$ = 20—45 Hz; in phosphorus(IV) 3-phospholenes $J(^{31}P—^{1}H)$ = 25—38 Hz and in phosphorus(III) 3-phospholenes $J(^{31}P—^{1}H)$ = 5—8 Hz [18]. In our compounds the hybridisation of the phosphorus atom is most like that of the phosphorus in $^{+}$phosphorus(IV) 3-phospholenes (sp^3 hybridisation). The coupling $J(^{31}P—^{1}H)$ with H_1 is very small ($J(^{31}P—^{1}H)$ = 1 Hz) although the number of bonds between this proton and the phosphorus atom is the same as between atom H_2 and the phosphorus atom, clearly indicating the large influence of the iridium atom on this coupling. The resonance of the t-butyl groups appears as two doublets ($J(^{31}P—^{1}H)$ = 12 Hz), showing the inequivalence of these groups.

The downfield shift of +0.2 ppm of the α protons and the upfield shift of —0.2 ppm of the β-protons of γ-picoline in compound IA indicates that this ligand is bonded to the metal [19]. No exchange with free γ-picoline was observed

TABLE 5

^{31}P NMR DATA FOR THE COMPOUNDS [acac$\{R_2PCH_2\overline{CH{=}CH}\}$IrHL]. The resonance of $(t\text{-}C_4H_9)_2PCH_2CH{=}CH_2$ is at —32.14 ppm, the resonance of $P(OMe)_3$ is at —141.00 ppm.

Compound	P (Metallated)	J(P—H) [a] (Hz)	P (unmetallated)
IA	—63.99	16.5	
II	—67.26	15.8	
IIIA	—68.64	b	
IIIC	—73.83	9.6	
IIIB	—66.15	11.4	
IV	—72.35	b	
VA (*trans*)	—73.2 (J(PP) = 586 Hz)	13.0	—114.7 J(PH) = 10.0, J(PP) = 586 Hz
VB (*cis*)	—56.9 (J(PP) = 10 Hz)	17.1	—126.2 J(PH) = 13.15, J(PP) = 10 Hz

[a] J(PH) is actually larger because partly decoupling occurs. [b] Complete decoupling occurs.

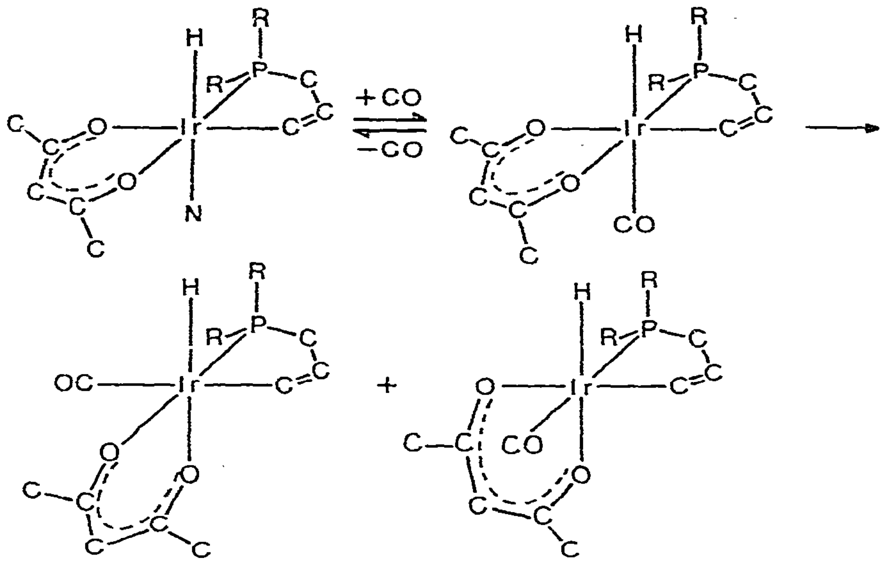


Fig. 3. Scheme of the reaction of carbon monoxide with compound IA.

at room temperature. This ligand is therefore more strongly bound than in the complex $\{(t\text{-}C_4H_9)_2PCH_2CH{=}CH\}IrHCl\}(t\text{-}C_4H_9)_2PCH_2CH{=}CH_2[\ (NC_6H_7)$ [7]. This is probably due to steric factors because the two bulky phosphines will give a large increase of crowding around the metal atom.

The resonance of the metal-bonded hydrogen atom in complex IA is found at −26.6 ppm ($J(^{31}P{-}^{1}H) = 24$ Hz), which shows that the proton is in a *cis*-position with respect to the phosphorus atom. The proton is believed to be situated in a *trans*-position with respect to γ-picoline (Fig. 1) because the following reactions with carbon monoxide occur (Fig. 3).

$$\text{IA} + \text{CO} \rightleftharpoons \text{IIIA} \xrightarrow{\Delta T} \text{IIIB} + \text{IIIC}$$

After bubbling CO through a solution of IA in hexane between 0°C and room temperature a doublet resonance appears in the ^{1}H NMR spectrum at $\delta = -5.8$ ppm ($J(^{31}P{-}^{1}H) = 19$ Hz). This small negative value of δ shows that the metal-bonded hydrogen atom is *trans* to CO. The reaction does not go to completion, and after flushing the solution with nitrogen the resonances of the CO-adduct disappear and compound IA is regenerated. When, however, compound IA is kept overnight under a CO atmosphere at 40°C, two doublets appear in the ^{1}H NMR spectrum, at $\delta = -22.75$ ppm ($J(^{31}P{-}^{1}H) = 22$ Hz) and at $\delta = -22.80$ ppm ($J(^{31}P{-}^{1}H) = 20$ Hz) indicating the formation of two isomers. The high negative δ-values show that in both compounds a weak *trans*-directing ligand is situated *trans* to the hydrogen atom. Furthermore, the resonances of the α and β protons of γ-picoline have the free ligand value, so the only possible structures are IIIB and IIIC.

A proton noise-decoupler with variable bandwidth was used during the recording of the ^{31}P NMR spectra. In the cases where the resonance of the metal-bonded proton is more than 10 ppm upfield from TMS, all protons could

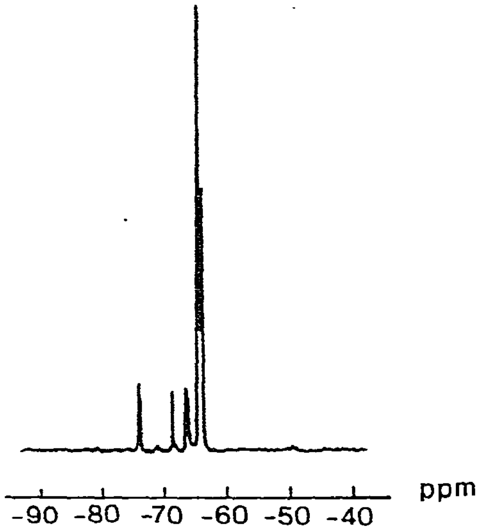


Fig. 4. ^{31}P NMR spectrum of the mixture IA, IIIA, IIIB and IIIC.

be decoupled except the metal-bonded one, which was only partly decoupled. As a result the ^{31}P NMR resonance appeared as a doublet. When the bandwidth of the noise decoupler was increased or the offset of the decoupler was shifted to higher field, the coupling $J(^{31}P-^{1}H)$ decreased, giving rise to a singlet resonance.

The above conclusions are confirmed by the ^{31}P-NMR spectra of the products of the reaction of compound IA with CO between 0°C and room temperature. These show a singlet at −68.64 ppm and a doublet of the starting material at −63.99 ppm. This indicates that the resonance of the metal-bonded hydrogen atom in the product (IIIA) is less than 10 ppm upfield from TMS, agreeing with the ^{1}H NMR ($\delta = -5.8$ ppm). When this reaction mixture is allowed to warm up two new doublets appear in the ^{31}P NMR spectrum, one at −73.83 ppm, the other at −66.15 ppm, while the singlet becomes much smaller (Fig. 4). That the two new resonances appear as doublets again agrees with the large upfield shift of the resonance of the metal-bonded hydrogen atom in the ^{1}H NMR spectra of these two compounds (IIIB, IIIC).

The ^{31}P NMR spectrum obtained after reaction of $P(OMe)_3$ with compound IA is shown in Fig. 5. A decoupler bandwidth of approximately 1 kHz was used. The product shows an *AB* spectrum with a large coupling ($J(PP) = 586$ Hz), clearly indicating that the phosphorus atoms are in a *trans* position. Each signal shows a small phosphorus—hydrogen coupling. This *AB* spectrum is assigned to compound IA. Apart from the resonance of free $P(OMe)_3$ at −141.00 ppm, two more complex signals are found at −126.2 and at −56.9 ppm. When the spectrum is recorded with a decoupler bandwidth of approximately 3 kHz, the phosphorus—hydrogen coupling disappears. The signals at −126.2 and at −56.9 ppm remain as doublets with a phosphorus—phosphorus coupling of 10 Hz, indicating a *cis*-arrangement. The structure Vb is assigned to this compound.

In both compounds the most deshielded signal arises from the bonded $P(OMe)_3$

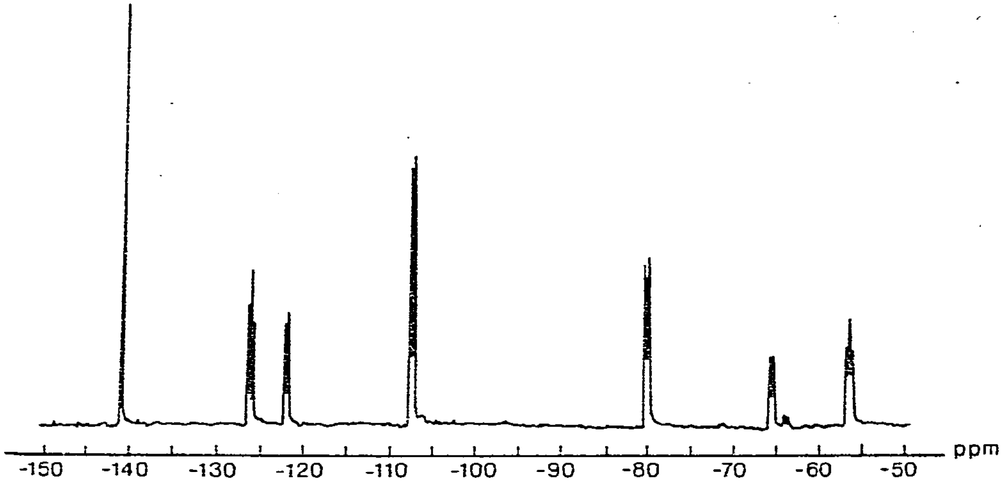


Fig. 5. ^{31}P NMR spectrum (not completely decoupled) of the mixture $P(OMe)_3$, VA and VB.

ligand, which was shown by recording a non-decoupled spectrum of the compounds. The most downfield peaks showed a regular coupling caused by the methyl groups, while the upfield peaks appeared as an irregular broadened signal, showing the different couplings with the hydrogen atoms in the phosphinic part of the molecule.

The upfield part of the ^1H NMR spectrum of the same product shows a four line pattern at $\delta = -25$ ppm (Fig. 6). This is the *X* part of an *XAB* spectrum, where *X* is the metal-bonded hydrogen atom and *A* and *B* are the two nonequivalent phosphorus atoms, which are strongly coupled. At $\delta = -25.5$ ppm another four line pattern is found, showing a slightly larger difference in coupling constants with the two phosphorus nuclei. For the same sample the ^{31}P NMR spectrum shows that the ratio Va/Vb is larger than one; and since in the ^1H NMR spectrum the second four line pattern is the weaker, this pattern belongs to complex Vb. The difference in chemical shift of the hydrogen atom in the two compounds is small, so in both cases the hydrogen atom is located *trans* to the acac-group.

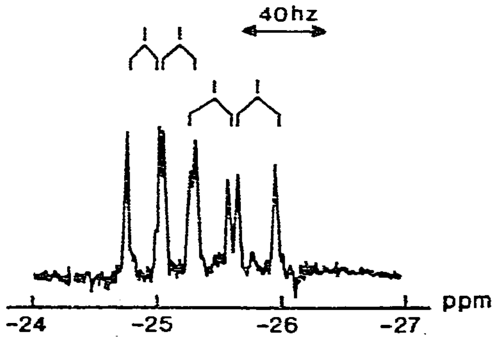


Fig. 6. ^1H NMR spectrum (only the high field part is shown) of the compounds VA and VB.

In conclusion the most important difference between the reaction of olefinic phosphines with [[IrCl(C_8H_{14})$_2$]$_2$] and [(acac)Ir(C_2H_4)$_2$] is that, when the bidentate acac group is used, one bulky phosphine is sufficient to cause metallation. Apparently after coordinating one phosphine, the metal is sufficiently basic to react with an olefinic C—H bond.

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