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ACTIVATION OF C—H BONDS BY TRANSITION METALS

I. METALLATION OF ALLYLPHOSPHINES COORDINATED TO IRIDIUM(I)

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Summary

The reaction of the olefinic phosphines, $R_2P(allyl)$ (R = t-butyl, cyclohexyl), with $[(COT)_2IrCl]_2$ (COT = cyclo-octene) in the presence of γ-picoline at room temperature yields the six coordinated, metallated complexes $[(R_2PCH_2CH{=}\overline{CH})IrHCl(R_2PCHCH{=}CH_2)NC_6H_7]$. In the case of (t-butyl)$_2$allylphosphine and without γ-picoline a five coordinated metallated compound is formed. The stereochemistries of the products were deduced from ^1H, ^{31}P NMR and IR data.

Reaction of $[(COT)_2RhCl]_2$ with the same phosphines yields an oily product, probably $[(COT)RhClL_2]$ (L = phosphine) while [dibenzonitrileMCl_2] (M = Pd(II), Pt(II)) reacted with these phosphines to give L_2MCl_2.

Introduction

Since 1963, when the first example was reported [1], much attention has been given to *ortho* metallations in transition metal complexes [2,3]. Most of the cyclometallation reactions involve activation of aromatic C—H bonds, but similar reactions involving olefinic C—H bonds were recently found [4—7]. As an extension of this work we describe below the first metallations of allylphosphines involving reactions with $[(COT)_2IrCl]_2$.

Experimental

All operations were carried out under purified nitrogen.

Preparation of the phosphines

The new phosphines di-t-butylallylphosphine and dicyclohexylmethallyl-

TABLE 1

ANALYTICAL DATA FOR THE METALLATED COMPLEXES

Compound		Analysis found (calcd.) (%)			Colour
		C	H	Cl	
$\{(t\text{-}C_4H_9)_2PCH_2CH{=}CH\}IrHCl\{P(t\text{-}C_4H_9)_2CH_2CH{=}CH_2\}NC_6H_7$	I	48.07 (48.50)	7.69 (7.65)	5.22 (5.12)	cream
$\{(t\text{-}C_4H_9)_2PCH_2CH{=}CH\}IrHCl\{P(t\text{-}C_4H_9)_2CH_2CH{=}CH_2\}CO$	Ia	43.85 (43.96)	7.42 (7.33)	5.54 (5.65)	white
$\{(t\text{-}C_4H_9)_2PCH_2CH{=}CH\}IrHCl\{P(t\text{-}C_4H_9)_2CH_2CH{=}CH_2\}C{\equiv}NC_6H_{11}$	Ib	48.72 (49.10)	8.12 (8.04)	4.92 (5.01)	white
$\{(t\text{-}C_4H_9)_2PCH_2CH{=}CH\}IrHCl\{P(t\text{-}C_4H_9)_2CH_2CH{=}CH_2\}N{\equiv}CCH_3$	Ic	44.56 (44.94)	7.76 (7.65)	5.62 (5.54)	white
$\{(t\text{-}C_4H_9)_2PCH_2CH{=}CH\}IrHCl\{P(t\text{-}C_4H_9)_2CH_2CH{=}CH_2\}$	III	43.59 (44.01)	7.62 (7.67)	5.82 (5.92)	orange-red
$\{(C_6H_{11})_2PCH_2C(CH_3){=}CH\}IrHCl\{P(C_6H_{11})_2CH_2C(CH_3){=}CH_2\}NC_6H_7$	II	55.19 (55.29)	7.23 (7.15)	4.41 (4.30)	white
$\{(C_6H_{11})_2PCH_2C(CH_3){=}CH\}IrHCl\{P(C_6H_{11})_2CH_2C(CH_3){=}CH_2\}CO$	IIa	51.82 (52.12)	6.95 (6.84)	4.52 (4.66)	white

TABLE 2

IR AND ^1H NMR DATA (ppm (δ) RELATIVE TO TMS) OF THE FREE PHOSPHINES AND OF THE UNMETALLATED COMPLEXES

Compound	Solvent	t-butyl	^3J(P—H) (Hz)	Allyl			C=C [a] (cm^{-1})
				H_1H_2	$H_3(CH_3)$	$H_{4,5}$	
$(t\text{-}C_4H_9)_2PCH_2CH{=}CH_2$	C_6D_6	1.2d [b]	11.0	5.0m [c]	6.0m	2.3m	1635
$(C_6H_{11})_2PCH_2C(CH_3){=}CH_2$ [d]	C_6D_6			4.6m	1.7	2.2m	1645
$\{(t\text{-}C_4H_9)_2PCH_2CH{=}CH_2\}_2PdCl_2$	$CDCl_3$	1.4t [e]	6.5	5.0m	6.2m	3.0m	1635
$\{(t\text{-}C_4H_9)_2PCH_2CH{=}CH_2\}_2PtCl_2$	$CDCl_3$	1.4t	6.5	5.0m	6.2m	3.0m	1635
$\{(t\text{-}C_4H_9)_2PCH_2CH{=}CH_2\}_2RhClCOT$	$CDCl_3$	broad					1635
$\{(t\text{-}C_4H_9)_2PCH_2CH{=}CH_2\}_2RhClC_2H_4$	$CDCl_3$	broad					1635
$\{(t\text{-}C_4H_9)_2PCH_2CH{=}CH_2\}_2RhClCO$	$CDCl_3$	1.4t	6.0	5.0m	6.2m	3.0m	1635

[a] The IR spectra were recorded as nujol mulls except for the phosphines, which were recorded as pure liquids. [b] d = doublet. [c] m = multiplet. [d] The cyclohexyl protons appear as a broad signal around 1.5 ppm. [e] t = triplet.

phosphine were prepared by the method decribed below for di-t-butylallylphosphine.

Di-t-butylphosphinous chloride (20 g, 0.11 mmol) was added slowly to a solution of allylmagnesium chloride (0.12 mmol) in THF. The mixture was refluxed until $MgCl_2$ separated and the THF was then distilled off under reduced pressure. The fraction boiling at 40—60°C/0.5 mmHg was collected. Redistillation gave the pure liquid (b.p. 56°C/0.3 mmHg) which was identified by ^1H NMR (yield 70%). The free phosphines are very air-sensitive.

Preparations of the complexes

$[\{(t\text{-}C_4H_9)_2PCH_2CH{=}\overline{CH}\}IrHCl\{(t\text{-}C_4H_9)_2PCH_2CH{=}CH_2\}NC_6H_7]$ (I). $[(COT)_2IrCl]_2$ (300 mg, 0.33 mmol) was suspended in 15 ml hexane. The complex dissolved upon addition of 0.5 ml γ-picoline. On dropwise addition of di-t-butylallylphosphine (227 mg, 1.22 mmol) at room temperature the colour changed quickly from orange-red to yellow. After stirring for 15 min the solution was filtered and cooled to —30°C. Air-stable crystals were filtered off, washed with cold hexane, and dried under vacuum (yield 80% of cream crystals).

The complex $[\{(C_6H_{11})_2PCH_2C(CH_3){=}\overline{CH}\}IrHCl\{P(C_6H_{11})_2CH_2C(CH_3){=}CH_2\}(NC_6H_7)]$ (II) was prepared similarly.

$[\{(t\text{-}C_4H_9)_2PCH_2CH{=}\overline{CH}\}IrHCl\{(t\text{-}C_4H_9)_2PCH_2CH{=}CH_2\}CO]$ (Ia). Complex I (200 mg, 0.29 mmol) was dissolved in 15 ml hexane and CO was bubbled through for 5 min. The product was isolated as white crystals and recrystallized from hexane (yield 90%). The CO analogue of complex II was prepared similarly.

$[\{(t\text{-}C_4H_9)_2PCH_2CH{=}\overline{CH}\}IrHCl\{(t\text{-}C_4H_9)_2PCH_2CH{=}CH_2\}(C{\equiv}NC_6H_{11})]$ (Ib). Complex I (200 mg, 0.29 mmol) was dissolved in 15 ml hexane and an excess of cyclohexylisocyanonitrile was added. After stirring for 2 h the product separated as white microcrystals (yield 80%).

$[\{(t\text{-}C_4H_9)_2PCH_2CH{=}\overline{CH}\}IrHCl\{(t\text{-}C_4H_9)_2PCH_2CH{=}CH_2\}]$ (III). $[(COT)_2IrCl]_2$ (300 mg, 0.33 mmol) was suspended in 10 ml hexane and di-t-butylallylphosphine (227 mg, 1.22 mmol) was added dropwise. The solution turned red and after 30 min the solution was filtered and cooled to —30°C. The red product was recrystallized from hexane (yield 65%).

The acetonitrile adduct of compound III was prepared by adding the ligand to a solution of III in hexane and recrystallizing the product from hexane (yield 85%) (Ic).

The diethyl sulphide (Id) and pyridine *N*-oxide (Ie) complexes were prepared in a similar way but could not be isolated. The analytical data for the metallated complexes are listed in Table 1.

Reactions with complexes of rhodium(I), palladium(II) and platinum(II)

$[(COT)_2RhCl]_2$ (300 mg, 0.42 mmol) was suspended in heptane and an excess of γ-picoline was added. A rapid reaction occurred to give a yellowish insoluble compound, probably $[(COT)_2RhCl(NC_6H_7)]$. The solution became clear orange after dropwise addition of di-t-butylallylphosphine (330 mg, 1.78 mmol). After refluxing for 15 h the solvent was removed. The IR spectrum of the oily orange product showed that no metal-bonded hydrogen atom was present. In the ^1H NMR spectrum all the resonances are very broad, probably because of

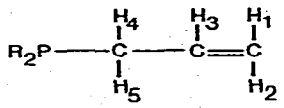

Fig. 1. Assignment of the hydrogen atoms of the allyl group.

hindered rotation around a Rh—P bond. We suggest that the compound is [(COT){(t-butyl)$_2$allylP}$_2$RhCl]. Upon reaction with CO the t-butyl resonances appear as a triplet which means that the COT ligand has exchanged with CO with formation of the Vaska analogue, [RhClCOL$_2$] (Table 2).

The same reactions with [$(C_2H_4)_2$RhCl]$_2$ gave the same CO adduct.

In the case of palladium and platinum, essentially the same procedure was followed, the starting materials being di-benzonitrilepalladium dichloride and di-benzonitrileplatinum dichloride, and *trans*-[{(t-butyl)$_2$allylP}MCl$_2$] was isolated. The IR and ^{1}H NMR data of the free phosphines and of the unmetallated complexes are listed in Table 2. The numbering of the hydrogen atoms of the allylgroup used in Table 2 is shown in Fig. 1.

Spectroscopic measurements

The ^{1}H NMR spectra were recorded on a Varian T-60 apparatus, the ^{31}P NMR spectra on a Varian XL-100 with Fourier transform and with broad band proton noise decoupling. The infrared spectra were recorded with a Beckman 4250 spectrophotometer, between 4000 and 200 cm^{-1}.

Results and discussion

Structural characterization of the compounds

The compounds [(PR$_2$allyl)(PR$_2$allyl)IrHClL] (I, II) and [(PR$_2$allyl)(PR$_2$allyl)IrHCl] (III) (R = t-butyl, cyclohexyl and L = γ-picoline, CO, C≡NC$_6$H$_{11}$, N≡CCH$_3$, S(CH$_2$CH$_3$)$_2$ and ONC$_6$H$_5$) were characterized by means of their infrared and ^{1}H and ^{31}P NMR spectra.

Infrared spectra (Table 3)

The presence of a hydrido ligand in these complexes is shown by the appearance of ν(M—H) in the region 2100—2350 cm^{-1} [3]. In the complexes with a strong *trans* directing ligand L (CO and C≡NC$_6$H$_{11}$) a shift to lower frequency of the metal—hydrogen vibration (Table 3) is found [8], indicating that the ligand L lies *trans* to the hydride. The assignment of the carbonyl peaks at 1995 and 1985 cm^{-1} (Table 3) is straightforward. The ν(C≡N) of complex Ib at 2200 cm^{-1} is assigned by comparison with isonitrile complexes of iron(II) [8], all showing a shift to higher frequency with respect to the free ligand frequency (2146 cm^{-1}). A definite choice cannot be made between the ν(N≡C) and the ν(Ir—H) in complex Ic for the bands at 2295 cm^{-1} and 2260 cm^{-1}, although most of the nitrile complexes have bands shifted to higher frequency compared with the free ligand [8]. Obviously the acetonitrile ligand has only a small *trans* influence.

In the region of 1500—1600 cm^{-1} two frequencies are found which belong

TABLE 3

IMPORTANT IR FREQUENCIES OF THE METALLATED PRODUCTS (in cm^{-1})

All spectra are recorded as nujol mulls

Compound	ν(Ir—H)	ν(Ir—Cl)	ν(C=C)		Other frequencies
I	2310	235	1630	1545	
Ia	2160	260	1640	1575	1955 ν(CO)
Ib	2135	240	1635	1580	2200 ν(C≡N)
Ic	2260	240	1635	1560	2295 ν(N≡C)
III	2340	220	1570	1525	
II	2250	245	1635	1590	
IIa	2200	265	1640	1610	1985 ν(CO)

to ν(C=C) of the allyl group (when L = γ-picoline there are two additional frequencies belonging to the ring vibrations of this ligand). One of these bands, which has about the same frequency as the uncoordinated phosphine, is assinged to an unmetallated allyl group. The other is shifted to lower frequency (about 80 cm^{-1}) and must originate from the ν(C=C) of a metallated phosphine. Such lowering of the ν(C=C) stretching vibration in the metallocyclic ring can have various causes. It is well known that ν(C=C) is lowered in frequency on ring formation [9] and further lowering will occur if a hydrogen atom is replaced by a heavy metal atom. Finally, back-donating from the metal to the antibonding orbital of the olefin will also cause a lowering of ν(C=C). The only difference between these metallated compounds will be in the amount of back donation from the metal, which will increase when the π-acceptor ability of L is decreased in the series $CO > C{\equiv}NR > N{\equiv}CCH_3 \sim NC_6H_7 > S(CH_2CH_3)_2 \sim ONC_6H_5$. In fact a decrease of ν(C=C) is found when L is varied in this order. The small influence of the different ligands L on the metal—chlorine stretching vibration together with the low value of this frequency indicates that the chlorine atom must lie *trans* to the metallated carbon atom, which has a high *trans* influence [10].

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

The ^1H NMR spectra of all the compounds show a high field pseudo-triplet, which clearly indicates the presence of a hydrogen atom directly bonded to iridium. The chemical shift of this signal is strongly dependent on the ligand L [11], just as ν(M—H), in agreement with a *trans* position of L with respect to H. The *trans* influence of L diminishes in the series $CO > C{\equiv}NC_6H_{11} > N{\equiv}CCH_3 \sim NC_6H_7 > S(CH_2CH_3)_2 \sim ONC_6H_5$.

The small phosphorus coupling of 10—20 Hz [12,13] with the high field proton indicates that this hydrogen atom lies *cis* to both phosphorus atoms. The resonance is not a pure triplet but the *X* part of an *XAB* spectrum in which *X* is the hydrogen atom and *A* and *B* are two non-equivalent phosphorus atoms (see Fig. 2).

The very complicated pattern of the t-butyl resonances is due to the non-equivalence of these groups.

In compound I the resonances of the α and β protons of γ-picoline are broadened; on adding free ligand these resonances are shifted towards the free ligand

TABLE 4

^1H NMR DATA FOR THE METALLATED COMPLEXES

The spectra were recorded in C_6D_6

Only the resonances of the metal bonded hydrogen atom are reported

Compound	Chemical shift δ (ppm) relative to TMS	$^2J(^1H—^{31}P)$ (Hz)
I	−24 t [a]	16
Ia	−8 t	16
Ib	−12 t	18
Ic	−23 t	14
Id	−24 t	14
Ie	−30 t	16
III	−32 t	14
II	−22 t	16
IIa	−8 t	16

[a] The middle peak of the triplets is more or less split up (see Fig. 2).

value, which indicates intermolecular exchange of γ-picoline.

On the basis of these spectral results and in accordance with analogous metallated compounds of the type $[(Ph_3)_2Ph_2P\overrightarrow{PPhI}rHCl]$ [11] and $[(PPh_3)_2Ph\text{-}NN\overrightarrow{PhI}rHCl]$ [4,5] a structure is proposed (see Fig. 3) in which the hydrogen

TABLE 5

^{31}P NMR DATA

Compound	Solvent	T (°C)	P_1 [a]	P_2 [a]	$^2J(P—P)$ (Hz)
I	C_7D_8	35	−57.657	−16.849	365.0
		0	−57.921	−16.815	369.0
		−30	−55.831	−16.882	369.0
		−80	−55.709, −53.730	−16.668	362.0, 362.6
	$CDCl_3$	+35	−58.5 [b]	collapsed	345 [b]
		0	−56.120	−16.661	362.5
		−35	−55.547	−16.325	360.2
Ia	C_7D_8	+35	−70.975		305.0
		0	broad	broad	
		−30	−68.358, −62.358	−22.433, −18.576	302.0, 302.0
Ib	$CDCl_3$	+35	−65.557	−20.518	340.8
		0	−65.3 [b]	−17.4 [b]	340 [b]
		−30	−67.377, −68.509	−27.988, −26.499	329.0, 355.8
			−62.288	−14.847	332.0
III	C_7D_8	+35	collapsed		
		0	broad		
		−30	−69.2 [b]	broad	335 [b]
		−50	−66.2 [b]	broad	337 [b]
		−60	−64.241	+48.0 [b]	357 [b]
		−70	−67.057, −63.901	+81.923, +47.689	287.0, 356.0
		−80	−67.136, −63.923	+81.906, +47.519	285.8, 355.2

[a] ^{31}P chemical shift with reference to 85% H_3PO_4; recorded at 40.5 MHz; [b] Too broad to be determined more accurately.

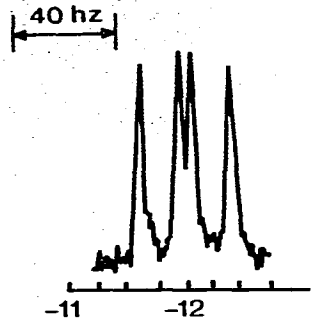

Fig. 2. High field ^1H NMR spectrum of compound Ib.

atom is located *cis* to both phosphorus atoms and *trans* to the ligand L, with the chloride located *trans* to the carbon atom (Fig. 3).

The ^{31}P NMR spectra of all the compounds show *AB* patterns at low temperature, with a large phosphorus—phosphorus coupling, which indicates the presence of two non-equivalent *trans* phosphorus atoms. It is not known whether the high-field resonance belongs to the phosphorus atom of the metallated or that of the unmetallated phosphine and so the phosphorus atoms are assigned arbitrarily (Fig. 4, Table 5).

In toluene-d_8 at −80°C compound I shows two *AB* spectra, indicating the presence of two conformations at this temperature. The peaks broaden when the temperature is raised, and at −50°C one quartet remains, showing that the two conformations interconvert at that temperature. On further warming the chemical shifts of the peaks change, showing that different amounts of the possible conformations are present at different temperatures [19] (Fig. 3). At temperatures above 40°C the peaks broaden and at 80°C they collapse, while decomposition partly occurs.

In $CDCl_3$ below 0°C the spectrum is the same as in toluene-d_8. At room temperature compound I shows only two broadened resonances. It is assumed that the resonance of one phosphorus atom is not observed at room temperature because it is too broad. Such a broad line arises when compound I is partly dissociated according to the following equilibrium (Fig. 5). Compound Ia shows,

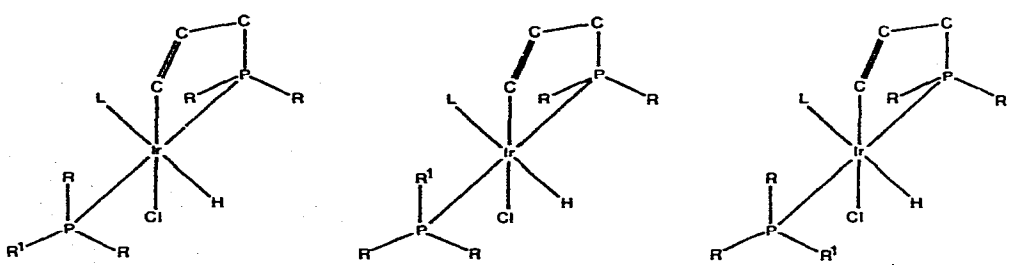

Fig. 3. Proposed stereochemistry of the complexes. The three possible conformers are shown.

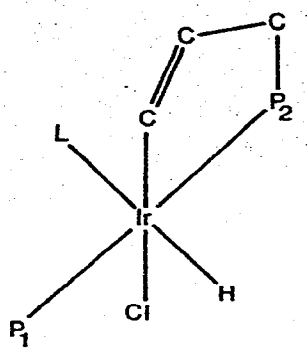

Fig. 4. Structure of [$\{R_2PCH_2CH{=}\overline{CH}\}IrHCl\{PR_2CH_2CH{=}CH_2\}L$] (R = t-butyl) necessary for the assignment in Table 5. P_1 and P_2 are numbered arbitrarily.

in toluene-d_8 at −30°C, two *AB* patterns with about equal intensity, indicating the presence of two conformations. At 0°C the peaks collapse and at +35°C one *AB* pattern remains.

In $CDCl_3$, the spectrum of compound Ib is split at −30°C into three *AB* patterns (see Fig. 6). Thus all three possible conformations exist. At room temperature the three conformations are again in fast exchange.

Compound III shows a different behaviour. At −70°C there are two *AB* patterns, one phosphorus atom showing a very large upfield shift in both conformations. The nature of this large shift is not yet understood. When the temperature is raised, the peaks at high field collapse first, so that at 0°C only one broadened doublet is found at low field. The reason for this is that the chemical shift difference between the high-field peaks is larger than the shift difference between the low-field peaks. At still higher temperatures all the peaks collapse.

A mixture of I and III in toluene-d_8 did not show sharp signals at room temperature, which means that γ-picoline exchanges between the two compounds. At −30°C the resonance of I appears as the normal quartet showing that the exchange of γ-picoline has stopped at this temperature.

Two possible mechanisms have been proposed for cyclometallation reactions;

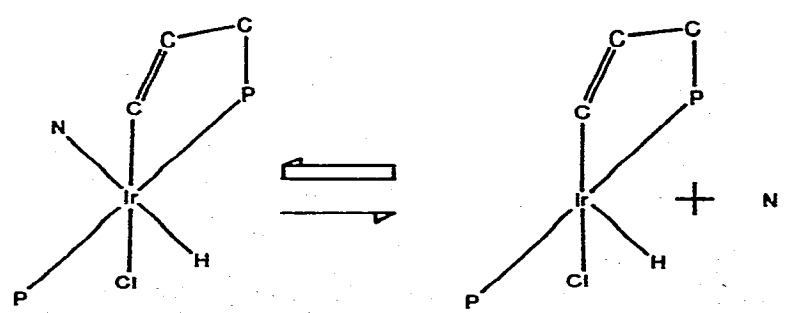

Fig. 5. Partly dissociation of compound I in $CHCl_3$.

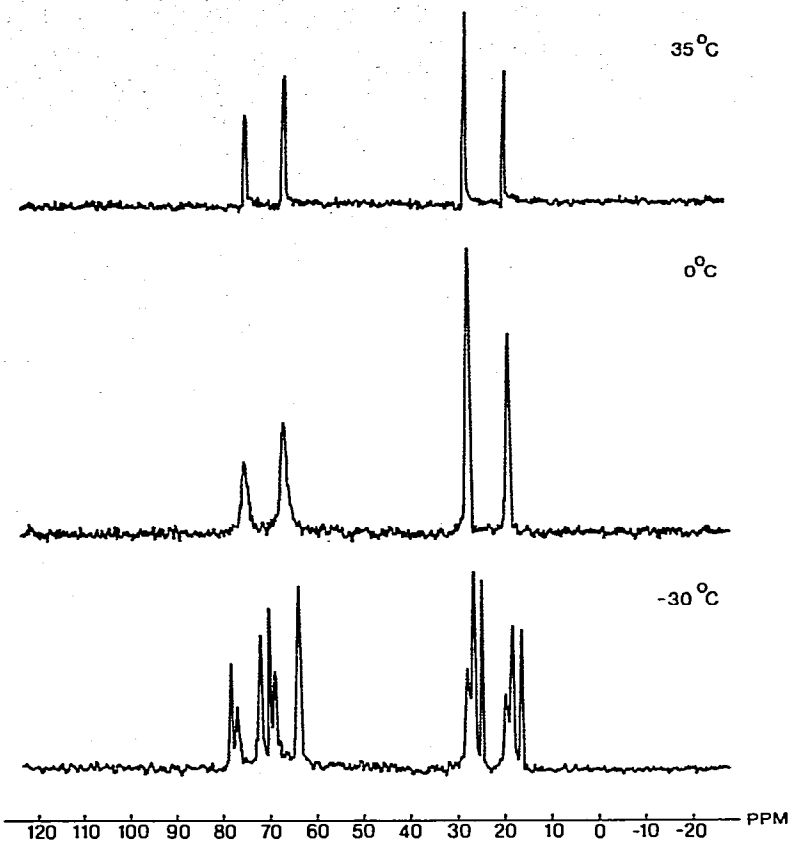

Fig. 6. Temperature dependent ^{31}P NMR spectrum of compound Ib.

an electrophilic mechanism for compounds of palladium(II), platinum(II), iridium(III) and rhodium(III) [2,15—17] when the ligand contains nitrogen as a donor atom, and a nucleophilic mechanism for the reactions of compounds of iridium(I) and rhodium(I) [4,5] with azo and imine compounds. Formation of cyclometallated complexes containing a donor phosphorus atom probably also occurs by a nucleophilic mechanism, at least when the metal is very basic. In the light of this, aliphatic phosphines were used to create a high negative charge on the metal. Surprisingly, however, rhodium(I) did not give metallation compounds with our phosphines although dehydrogenation of phosphines with rhodium(I) complexes is known [6,18].

Apart from electronic effects, the steric requirements are very strict. It is well known [2] that the best results for metallation reactions are obtained when a five-membered ring can be formed. Models show that the least strain occurs in such a ring. This strain is even lower when the ring contains one or two double bonds, which may account for the fact that unsaturated ligands are so easily metallated. Furthermore, it is well known that bulky groups promote metallation [19,20] reactions by forcing the olefinic group into the right orientation for reaction [21].

Another important condition for high reactivity of a metal atom is the presence of a loosely bonded ligand or an incompletely filled coordination sphere. In our complexes two bulky phosphines and one chloride atom are initially bonded to the metal, while the fourth coordination site is occupied by the loosely bonded γ-picoline or is not unoccupied (compound III). It is not possible to coordinate more than two of the very bulky di-t-butylallylphosphines to a metal, and this leaves one coordination site open for reaction. When dicyclohexylmethallylphosphine is used as a ligand $IrCl(PR_3)_3$ is presumably formed. This is possibly the reason why a cyclometallated compound was formed with di-t-butylallylphosphine as ligand even in the absence of γ-picoline, while in the case of dicyclohexylmethallylphosphine these reactions did not occur.

Neither complexes of palladium(II) nor platinum(II) underwent metallation with these phosphines. This result may be due to the high basicity of the ligands which may make an electrophilic mechanism impossible.

Further studies are in progress to obtain a better insight in the steric and electronic factors which determine the reactivity of these metals in metallation reactions.

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