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## ACTIVATION OF C—H BONDS BY TRANSITION METALS

### V \*. A STUDY OF THE MECHANISM OF METALLATION REACTIONS OF BENZYL- AND *meta*-FLUOROBENZYLPHOSPHINES WITH $Rh^I$ , $Ir^I$ , $Pd^{II}$ AND $Pt^{II}$ COMPOUNDS

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#### Summary

Reaction of  $R_2PCH_2C_6H_5$  ( $R = \text{cyclohexyl}$  or  $t\text{-butyl}$ ) with  $[(COT)_2RhCl]_2$ ,  $[(COT)_2IrCl]_2$ ,  $PdCl_2$  or  $PtCl_2(\text{benzotrile})_2$  yields cyclometallated compounds. The reactivity appears to decrease in the order  $Ir^I > Rh^I \gg Pd^{II} \sim Pt^{II}$ , suggesting a different reaction mechanism for univalent and bivalent  $d^8$  metal atoms. Reaction of *meta*- $FC_6H_4CH_2PR_2$  with the same metal chlorides shows that for  $Rh^I$  and  $Ir^I$  a nucleophilic mechanism operates and for  $Pd^{II}$  an electrophilic one. For  $Pt^{II}$  no decision could be made on the basis of these experiments. Steric effects have a large influence on the rates of the reactions.

#### Introduction

Although many intramolecular reactions involving C—H bond cleavage together with metal—carbon bond formation are known, only few studies have appeared which deal with the mechanism of this process [1–3]. In the case of relatively electron poor metal compounds such as  $PdX_2$  ( $X = \text{halogen}$ ), it has been shown by varying the *para* substituent in the aromatic ring of azobenzenes that an electrophilic mechanism is most likely. The metal atom acts as an electrophilic center, attacking the aromatic ring [4]. A nucleophilic mechanism has been proposed for the reaction of *meta*-fluoro substituted azobenzene with  $Mn(CH_3)(CO)_5$  [5,6] and also for the reactions of *ortho*-chloroazobenzene with nickelocene [7] and of decafluoroazobenzene with ruthenium complexes [8]. The metal atom is regarded as a negative center which is oxidized from  $n+$  to

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$(n + 2)^+$ ; sometimes reductive elimination takes place afterwards, so that the metal ends up with the valency  $n^+$ .

Van Baar [9] found that the metallations of azo and imine compounds with  $Rh^I$  and  $Ir^I$  have a nucleophilic character. The more electron-rich iridium compounds were more easily metallated than the corresponding rhodium complexes. It was also found that rhodium only gave metallated products when aliphatic phosphines were used as co-ligands. With the less basic triphenylphosphine only coordination of the azo or imine ligand occurred.

Less is known about the mechanism of the reactions of P-donor ligands such as phosphines and phosphites. In the case of the *ortho* metallation of  $IrCl[P(\text{Aryl})_3]_3$  a nucleophilic mechanism was proposed on the basis of the influence of the *para* substituent on the rate of the intramolecular C-H bond breaking reaction [10]. A three center mechanism appeared likely, since no kinetic isotope effect was observed. The metallation reaction of  $PtX_2(PR_3)_2$  seemed to be of nucleophilic origin, since the rate of the reaction decreased in the order  $I > Br > Cl$  [11]. On the other hand, the sequence  $Cl > Br > I$  was found for  $PtX_2[P(OR)_3]_2$  [12], suggesting an electrophilic mechanism. An important difference between phosphines and phosphites is the small cone angle of the latter [13]. Thus steric influences are more important for reactions of phosphines than for those of phosphites. The smaller steric influence for the latter complexes is illustrated by the fact that in phosphite complexes the *cis* isomer is always found, while with bulky phosphines the *trans* isomer is preferred. Therefore, for phosphine complexes the size of the halogen atom and its leaving group ability might be more important than its electronegativity. Thus, dissociation of the molecule could be the rate determining step. For phosphite complexes the electronic effects are likely to dominate, making an electrophilic mechanism more probable. In order to obtain more insight into the nature of the mechanism we have studied the metallation reactions of  $C_6H_5CH_2PR_2$  and of *m*- $FC_6H_4CH_2PR_2$  with complexes of  $Rh^I$ ,  $Ir^I$ ,  $Pd^{II}$  and  $Pt^{II}$ .

## Experimental

All operations were carried out under purified nitrogen.

### Preparation of the phosphines

$(C_6H_{11})_2PCH_2C_6H_5$  and  $(C_6H_{11})_2P(m-FCH_2C_6H_4)$ .  $(C_6H_{11})_2PCl$  (0.1 mol) was dissolved in 300 ml diethyl ether and a solution of  $C_6H_5CH_2MgCl$  or *m*- $FC_6H_4CH_2MgCl$  in 200 ml diethyl ether (0.1 mol) was added dropwise with stirring at  $0^\circ C$ . Afterwards the mixture was refluxed for 15 min. The precipitate was filtered off, the ether was removed under reduced pressure, and the product was distilled under vacuum (b.p.  $160^\circ C/0.1$  mm Hg and  $180^\circ C/0.1$  mm Hg, respectively). The oily products crystallized upon standing at room temperature (m.p.  $70^\circ$  and  $50^\circ C$ , respectively). Yield 65%.

$(t-C_4H_9)_2P(m-FCH_2C_6H_4)$ .  $(m-FC_6H_4CH_2)_3SnCl$  (0.03 mol) was dissolved in 300 ml diethyl ether and a solution of  $CH_3Li$  (0.12 mol) in diethyl ether (200 ml) was added dropwise with stirring at  $0^\circ C$ . A solution of  $(t-C_4H_9)_2PCl$  (0.09 mol) in diethyl ether (100 ml) was then added dropwise with stirring. After refluxing for 15 min, the precipitate was filtered off and the ether was removed

under reduced pressure. The resulting oily substance was extracted twice with hexane. The hexane layer was distilled under vacuum, yielding the product, b.p. 140°C/0.1 mm Hg as a viscous oil.

#### Preparation of the complexes

$\{(C_6H_{11})_2PCH_2C_6H_4\}RhHCl(NC_6H_7)_2$  (Ia) and  $\{(C_6H_{11})_2PCH_2C_6H_3F\}RhHCl(NC_6H_7)_2$  (*ortho-F* (Ib) and *para-F* (Ic) with respect to the metallated carbon atom).  $[(COT)_2RhCl]_2$  (0.33 mmol) was suspended in 15 ml hexane and 0.2 ml  $\gamma$ -picoline was added. Addition of the phosphine (0.66 mmol) followed by stirring gave a clear yellow solution. After refluxing for 30 min the product separated as a yellow precipitate (yield 80%).

$\{(C_6H_{11})_2P(CH_2C_6H_4)\}IrHCl\{P(C_6H_{11})_2(CH_2C_6H_5)\}(NC_6H_7)$  (IIa) and  $\{(C_6H_{11})_2P(CH_2C_6H_3F)\}IrHCl\{P(C_6H_{11})_2(m-FCH_2C_6H_4F)\}(NC_6H_7)$  (*ortho-F* (IIb), *para-F* (IIc)).  $[(COT)_2IrCl]_2$  (0.33 mmol) was suspended in 15 ml hexane and 0.2 ml  $\gamma$ -picoline was added. After addition of the phosphine (1.32 mmol) a nearly colorless solution was immediately formed upon stirring. This solution was kept for 15 min at 50°C, then the solution was filtered and cooled to -30°C. The white crystals were washed with cold hexane and dried under vacuum (yield 80%).

$[\{(t-C_4H_9)_2P(CH_2C_6H_3F)\}PdCl]_2$  (III). The product was prepared as described for the analogous compound  $[\{t-C_4H_9\}_2P(CH_2C_6H_4)\}PdCl]_2$  by Shaw and coworkers [14].

$\{(C_6H_{11})_2P(CH_2C_6H_4)\}PtBr\{P(C_6H_{11})_2(CH_2C_6H_5)\}$ ;  $\{(C_6H_{11})_2P(CH_2C_6H_3F)\}PtBr\{P(C_6H_{11})_2(m-FCH_2C_6H_4F)\}$  (*ortho-F* (IVb), *para-F* (IVc));  $\{(C_6H_{11})_2P(CH_2C_6H_3F)\}_2Pt$  (*ortho-ortho'-diF* (IVd), *ortho-para'-diF* (IVe));  $\{(C_6H_{11})_2P(CH_2C_6H_3F)\}_2PtHBr$  (IVf);  $\{(C_6H_{11})_2P(m-FCH_2C_6H_4F)\}_2PtHBr$  (IVg).  $Pt(C_6H_5CN)_2Cl_2$  (2 mmol) was suspended in ethoxyethanol, excess LiBr (10 mmol) and the appropriate phosphine (4 mmol) were added. After refluxing 4 days at 180°C the hot solution was filtered and cooled. The crystals were collected and washed with chloroform, leaving the not very soluble yellow products IVf or IVg (50% yield). The chloroform layer was evaporated and the white products IVd and IVe were obtained together in 20% yield.

The ethoxyethanol layer was evaporated under vacuum. The residue was washed with diethyl ether. The solvent was evaporated and the white products IVa or IVb and IVc were obtained impure in low yield (10%). The C and H analyses (Table 1) were carried out by the elemental analysis section of the Institute of Organic Chemistry TNO, Utrecht (Table 1).

#### Spectroscopic measurements

The  $^1H$  NMR spectra were recorded on a Varian T-60 instrument. The  $^{31}P$  and  $^{19}F$  NMR spectra on a Varian XL-100;  $^{31}P$  NMR with Fourier transform;  $^{19}F$  NMR continuous wave; both with proton noise decoupling. The IR spectra were recorded as Nujol mulls on a Beckmann 4250 spectrophotometer between 4000 and 200  $cm^{-1}$ .

#### Results

$(C_6H_{11})_2PCH_2C_6H_5$  readily reacts at room temperature with  $[(COT)_2IrCl]_2$  in the presence of  $\gamma$ -picoline in hexane, giving the cyclometallated compound IIa

TABLE 1  
ANALYTICAL DATA

Compound	Color	Anal. (found (calcd.)) (%)	
		C	H
$\{(\text{C}_6\text{H}_{11})_2\text{P}(\text{CH}_2\text{C}_6\text{H}_4)\}_2\text{RhHCl}(\text{NC}_6\text{H}_7)_2$ (Ia)	yellow	60.22(60.73)	6.51(6.69)
$\{(\text{C}_6\text{H}_{11})_2\text{PCH}_2\text{C}_6\text{H}_3\text{F}\}_2\text{RhHCl}(\text{NC}_6\text{H}_7)_2$ (Ib/Ic)	yellow	58.54(59.00)	6.32(6.35)
$\{(\text{C}_6\text{H}_{11})_2\text{P}(\text{CH}_2\text{C}_6\text{H}_4)\}_2\text{IrHCl}(\text{C}_6\text{H}_5\text{CH}_2)\text{P}(\text{C}_6\text{H}_{11})_2(\text{NC}_6\text{H}_7)$ (IIa)	white	60.23(60.45)	7.12(7.24)
$\{(\text{C}_6\text{H}_{11})_2\text{P}(\text{CH}_2\text{C}_6\text{H}_3\text{F})\}_2\text{IrHCl}(\text{m-FC}_6\text{H}_4\text{CH}_2)\text{P}(\text{C}_6\text{H}_{11})_2\text{NC}_6\text{H}_7$ (IIb/IIc)	white	56.72(56.56)	6.82(6.75)
$[\{(\text{t-C}_4\text{H}_9)_2\text{PCH}_2\text{C}_6\text{H}_3\text{F}\}_2\text{PdBr}]_2$ (IIIb)	white	39.26(40.87)	5.02(5.45)
$\{(\text{C}_6\text{H}_{11})_2\text{P}(\text{CH}_2\text{C}_6\text{H}_3\text{F})_2\text{Pt}\}$ (IVa/IVe)	white	56.34(56.51)	6.89(6.94)
$\{(\text{C}_6\text{H}_{11})_2\text{P}(\text{m-FC}_6\text{H}_4\text{CH}_2)\}_2\text{PtHBr}$ (IVf)	yellow	56.21(56.44)	7.18(7.32)

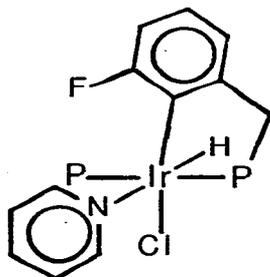


Fig. 1. Structure of compound IIb.

(cf. Fig. 1).  $[(\text{COT})_2\text{RhCl}]_2$  reacts equally well in boiling hexane to give  $(\text{C}_6\text{H}_{11})_2\text{-PCH}_2\text{C}_6\text{H}_4\text{RhHCl}(\text{NC}_6\text{H}_7)_2$ . However, under mild conditions no metallation was observed for  $\text{PdCl}_2(\text{NCC}_6\text{H}_5)_2$  or  $\text{PtCl}_2(\text{NCC}_6\text{H}_5)_2$  with this phosphine. At  $140^\circ\text{C}$ , in ethoxyethanol, the initially formed  $[\text{P}(\text{C}_6\text{H}_{11})_2(\text{CH}_2\text{C}_6\text{H}_5)]_2\text{PdCl}_2$  decomposed. Shaw and coworkers reported that  $(t\text{-C}_4\text{H}_9)_2\text{P}(\text{CH}_2\text{C}_6\text{H}_5)$  yielded the metallated compound III with  $\text{Pd}^{\text{II}}$  salts [14]. Therefore compound III was prepared for comparison. The Pt compound,  $[\text{P}(\text{C}_6\text{H}_{11})_2(\text{CH}_2\text{C}_6\text{H}_5)]_2\text{PtBr}_2$ ,

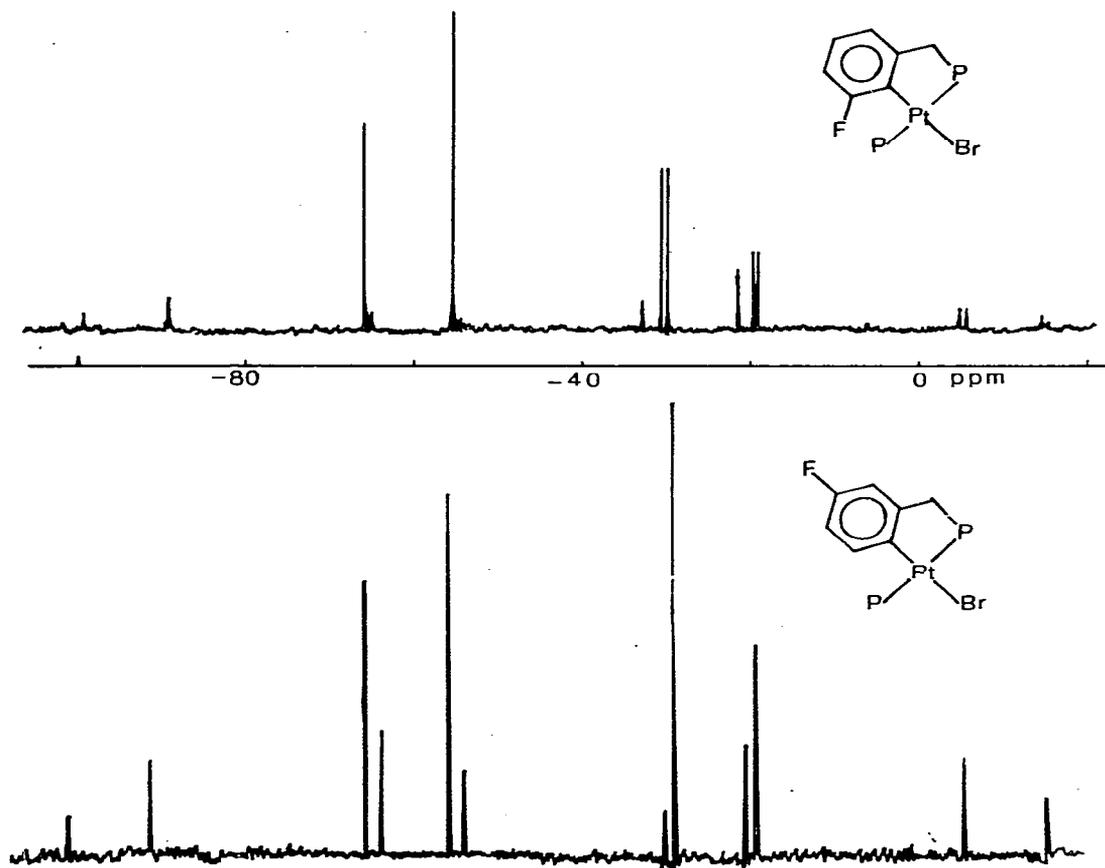


Fig. 2.  $^{31}\text{P}$  NMR spectrum and structures of the monometallated platinum compounds.

TABLE 2  
 $^{31}\text{P}$  NMR data

Compound	$\delta_{1m}^a$	$\delta_{2u}^a$	$J_{PP}$	$J_{PF}$	$J_{P_1M}$	$J_{P_2M}$
Ia	-58.39					119.6
Ib	-56.89					111.8
Ic	-58.14					116.1
IIa	-36.64	-2.46	369			
IIb (35°C)	-35.25	-4.94	377	11.8		
IIc (35°C)	-36.42	-4.37	370			
IIb (-40°C)	-37.62	-7.1	375 ± 5	unresolved		
IIb' (-40°C)	-35.0	-4.5	370 ± 5	~10 Hz		
IIc (-40°C)	-36.7	-5.5	365 ± 5			
IIIa	-96.01					
IIIb	-94.52					
IVa	-58.47	-33.47	395		2885	2812
IVb	-58.37	-24.58	407	1.5/19.2	2689	<sup>b</sup>
IVc	-58.77	-24.19	396		2844	2780
IVd	-63.1			13		2772
IVe	-62.99	-56.87 <sup>c</sup>	403	18.5/5.6	2834	2791

<sup>a</sup> m = metallated, u = unmetallated. <sup>b</sup> The resonance was not resolved. <sup>c</sup> This phosphine is also metallated. For the Rh and Ir compounds the solvent was  $\text{C}_7\text{D}_8$ ; for the Pd and Pt compounds the solvent was  $\text{CDCl}_3$ .

slowly reacted at 180°C yielding mostly  $\text{P}_2\text{PtHBr}$ , although cyclometallated products were found. Thus, for this phosphine the reactivity sequence is  $\text{Ir}^{\text{I}} > \text{Rh}^{\text{I}} \gg \text{Pd}^{\text{II}} \sim \text{Pt}^{\text{II}}$ .

The rates of the reactions of the same metal complexes with the analogous phosphines, possessing *m*-F substituted benzyl groups, did not differ significantly from those for the unsubstituted phosphines. A  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR study,

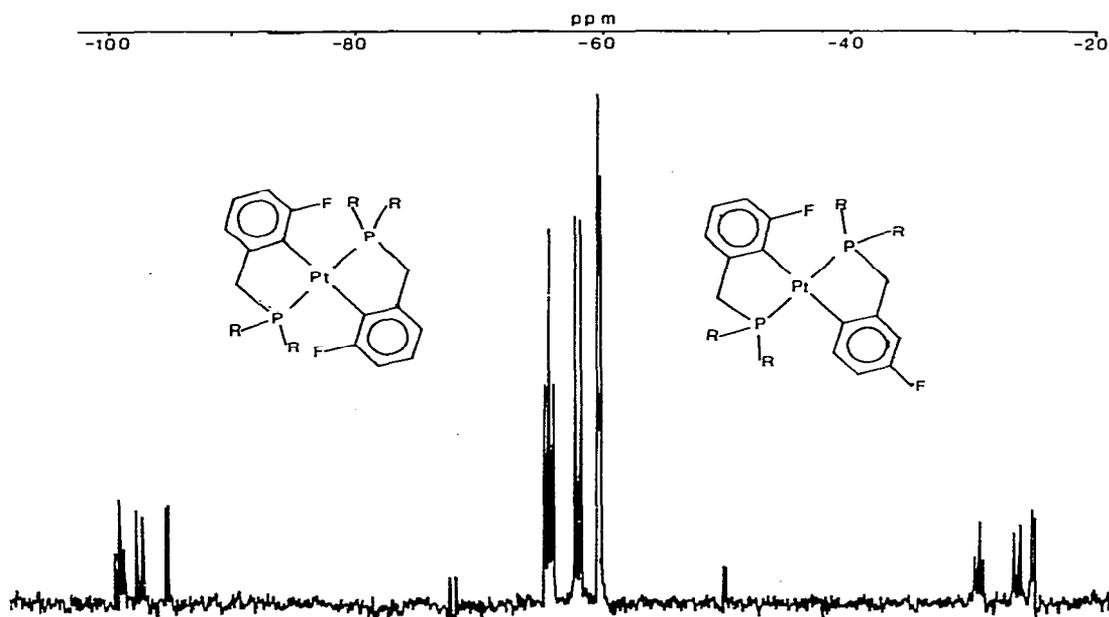


Fig. 3.  $^{31}\text{P}$  NMR spectrum and structures of the dimetallated platinum compounds.

which is discussed in detail below, revealed that for the Ir and Rh complexes the main product (80%) contained the fluoro substituent *ortho* to the metallated carbon atom. The side product (20%) contained the fluorine atom *para* to the metallated carbon atom. In contrast, the metallated Pd complex appeared to be exclusively *para*-substituted, while in the case of platinum the picture is unclear. Apart from large amounts of  $P_2PtHBr$  a mixture of mono- and di-metallated species was found. Two monometallated isomers were obtained, in one of which the fluorine atom occupied the *para* position. In the other the fluorine atom was in the *ortho* position (Fig. 2). For the di-metallated species only two of the three possible isomers were found (Fig. 3). The compound with both fluorine atoms in the *para* position is lacking. The reason for this is not clear.

### Structural characterization of the compounds

The spectra of the products isolated from the reaction of the metal compounds with  $C_6H_5CH_2P(C_6H_{11})_2$  or  $(m-FC_6H_4CH_2)P(C_6H_{11})_2$  are very similar except for the features arising from the presence of fluorine in the molecule. Therefore, only the spectra of the fluoro compounds will be discussed.

The  $^{31}P$  NMR spectrum of the product obtained from the reaction between  $(m-FC_6H_4CH_2)P(C_6H_{11})_2$  and  $[(COT)_2IrCl]_2$  shows that two isomers are present in a 8/1 molar ratio (Table 2). Both isomers show an AB pattern with a large  $^2J(^{31}P-^{31}P)$  coupling, indicating that two inequivalent phosphines are present in a *trans* position. The downfield chemical shift of one doublet is in agreement with the values previously found for five membered phosphorus containing ring systems [15,16]. For the more abundant isomer a doublet coupling is found on the upfield doublet, which is assigned to a  $J(^{19}F-^{31}P)$  coupling with the unmetallated phosphine. No fluorine coupling was, however, observed with the metallated phosphine although these nuclei are also separated by four bonds. Most probably the coupling between fluorine and the unmetallated phosphine is through-space, because the distance between the fluorine and the phosphorus atom of the unmetallated phosphine is very short. Reports of  $J(^{19}F-^{31}P)$  through-space couplings are rare [17], but  $J(^{19}F-^{19}F)$  and  $J(^{19}F-^1H)$  through-space couplings are not uncommon [18].

The  $^{19}F$  chemical shift of this compound (Table 3) is consistent with the proposed *ortho* position of fluorine with respect to the metallated carbon atom

TABLE 3

RELEVANT INFRARED SPECTRAL DATA (NUJOL MULL,  $\nu$   $cm^{-1}$ ) AND  $^{19}F$  NMR DATA  
 $\delta^{19}F$  relative to  $CCl_3F$  (in  $C_6D_6$ ); solvent  $C_7D_8$ .

Compound	$\nu(M-H)$	$\nu(M-hal)$	$\delta_1^{19}F$	$\delta_2^{19}F$
Ia	2080	RhCl 235		
Ib/Ic	2080(br)	RhCl 235	93.5	
IIa	2195	IrCl 240		
IIb/IIc (35°C)	2195(br)	IrCl 240	86.1	114.7
(-40°C)			83.8/89.0	114.5
IIIb				115.5
IVf	2175	PtBr 240		

(Table 2) [5]. The proton decoupled resonance is broad even at room temperature and broadens further on cooling. At  $-40^{\circ}\text{C}$  two new broad resonances are observed, showing that two conformations of the molecule exist on the NMR time scale. The fluorine atom can be situated on both sides of the metallocyclic ring (Fig. 4) as a result of the puckering in the five membered ring.

The resonances of the  $^{31}\text{P}$  NMR spectrum also broaden on lowering the temperature and at  $-40^{\circ}\text{C}$  the resonances due to the metallated phosphorous atom are again rather sharp, showing two doublets arising from  $^2J(^{31}\text{P}-^{31}\text{P})$  coupling. The resonances of the unmetallated phosphine also appear as two doublets. One of these doublets is reasonably sharp (linewidth 15 Hz) while the other is still broad at this temperature. The  $J(^{31}\text{P}-^{19}\text{F})$  coupling is not resolved. The probable reason for this is that, in addition to puckering in the five membered ring, there is also hindered rotation about the iridium-phosphorous bond [19]. Apparently, this rotation is more hindered in one conformation than in the other. The isomer with the fluorine atom in the *para* position does not show such behavior. Only at very low temperature does some broadening occur, and this arises either from hindered rotation or from freezing out of the boat and chair conformations of the cyclohexyl groups for this isomer. Obviously the larger steric interaction of the fluorine group in the *ortho* position with the opposite phosphorous atom when compared with a hydrogen atom causes this different behavior on cooling.

For the Rh complex also two isomers are present in a 8/1 molar ratio, both showing a doublet in the  $^{31}\text{P}$  NMR spectrum due to  $^2J(^{109}\text{Rh}-^{31}\text{P})$  coupling. Thus, only a metallated phosphine is present, agreeing with the weaker bonding of a phosphine to rhodium with respect to iridium. No  $J(^{19}\text{F}-^{31}\text{P})$  coupling was observed in either isomer because no close contact between these two atoms can occur. The  $^{19}\text{F}$  NMR spectrum showed that the most abundant isomer has the fluorine atom *ortho* to the metallated carbon atom.

The metallated palladium complex was only sufficiently soluble when pyridine was present. Apparently, a halogen-bridge had to be broken. The complexed pyridine exchanged fast on the NMR time scale with free pyridine. The product possessed only a metallated phosphine (singlet in  $^{31}\text{P}$  NMR) and the  $^{19}\text{F}$  NMR spectrum showed that the fluorine atom occupied the *para* position.

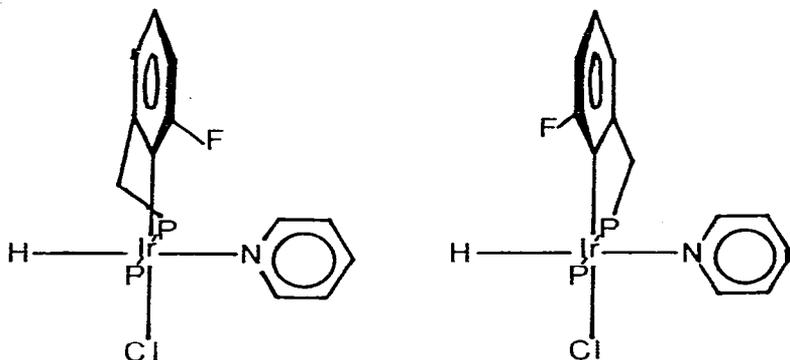


Fig. 4. A view along the P—Ir—P axis of the conformations of compound IIb.

For platinum a mixture of products was formed. One compound, obtained in low yield, showed a  $^{31}\text{P}$  NMR spectrum which involved an AB pattern with platinum satellites and without a  $J(^{19}\text{F}-^{31}\text{P})$  coupling (Fig. 2). Therefore, this compound must possess a metallated and an unmetallated phosphine with the fluorine atom in the *para* position. The other isomer was obtained in slightly better yield. In this product again a  $J(^{19}\text{F}-^{31}\text{P})$  coupling was found on the resonance of the unmetallated phosphine, the magnitude of which was comparable with the  $J(^{19}\text{F}-^{31}\text{P})$  coupling of the iridium complex. A very small  $^4J(^{19}\text{F}-^{31}\text{P})$  coupling was found for the resonance of the metallated phosphine. The resonances of the platinum compounds are all sharp, which means that probably less steric hindrance occurs because of the lower coordination number with respect to rhodium or iridium.

Two bimetallated compounds were found (Fig. 3). The *ortho, ortho'*-bis-F compound showed a triplet in the  $^{31}\text{P}$  NMR spectrum with additional platinum satellites. The main resonances are due to the AA' part of an AA'XX' pattern. Since a deceptively simple triplet is found,  $^2J(^{31}\text{P}-^{31}\text{P})$  must be large with respect to the other couplings and thus the two phosphorous atoms are situated *trans*. The other isomer, the *ortho, para'*-bis-F compound showed an AB pattern with a small chemical shift difference. Again the large value of the  $^2J(^{31}\text{P}-^{31}\text{P})$  coupling indicates a *trans* structure. For one doublet a rather large  $J(^{19}\text{F}-^{31}\text{P})$  coupling was found, for the other a small one. These results are in agreement with the proposed structures.

## Discussion

The higher reactivity of  $\text{Ir}^{\text{I}}$  with respect to metallation reactions with the same phosphines compared with  $\text{Rh}^{\text{I}}$ , is in agreement with the trend observed by van Baar [9] for azo and imine compounds. The considerably different conditions that were necessary to obtain metallated products with  $\text{Pd}^{\text{II}}$  or  $\text{Pt}^{\text{II}}$  prompted us to study metallation reactions with substituted benzylphosphines.

*Para* substituents in coordinated aromatic phosphines not only affect the electronegativity of the metal [13] but also the electron density in the C-H bonds of the rings. In the case of a nucleophilic mechanism it is expected that electron withdrawing groups will decrease the reactivity of the metal while at the same time the reactivity of the C-H bonds will be enhanced. For an electrophilic mechanism the opposite holds. A nucleophilic mechanism was proposed for the metallation reaction of  $[(\text{RPh})_3\text{P}]_3\text{IrCl}$ . On going from  $\text{R}=\text{H}$  to  $\text{R}=\text{F}$  it is not easy to predict whether the increase in reactivity of the C-H bond or the deactivation of the metal will dominate the change in reactivity. Therefore *meta* substituted rings are better suited for this study, because an *ortho* or *para* location of the fluoro substituent in the product with respect to the metallated C atom will indicate the nature of the mechanism. Thus we found with the phosphine  $(m\text{-FC}_6\text{H}_4\text{CH}_2)\text{P}(\text{C}_6\text{H}_{11})_2$  a nucleophilic mechanism for  $\text{Rh}^{\text{I}}$  and for  $\text{Ir}^{\text{I}}$ ,  $\text{Pt}^{\text{II}}$  a borderline situation. With  $(m\text{-FC}_6\text{H}_4\text{CH}_2)\text{P}(\text{t-C}_4\text{H}_9)_2$  an electrophilic mechanism was found for  $\text{Pd}^{\text{II}}$ . Because of the high reaction temperature and long reaction time we cannot completely exclude a radical mechanism for platinum.

The earlier reported metallated products of iridium [15,19,20] reacted with

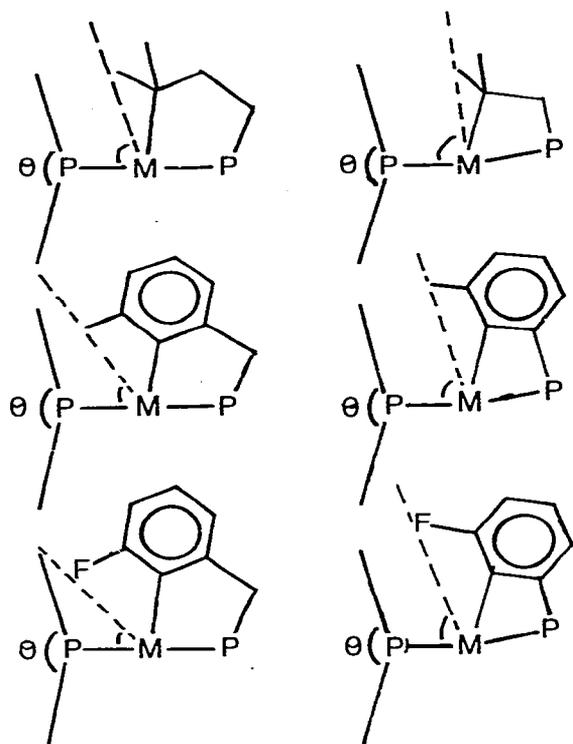


Fig. 5. A comparison of steric hindrance between four- and five-membered rings with an unmetallated phosphine.

CO giving  $[PP\ ClIrHClCO]$ . These products underwent a slow rearrangement even in the solid state at room temperature and finally  $P_2IrCOCl$  was obtained. This result implies that the metallation reaction is reversible. The unmetallated compound is the most stable one when a ligand with large backbonding properties is present. In the metallated compound the *trans* metal–hydrogen bond is destabilized, while in the unmetallated compound the  $d^8$  configuration of the metal is stabilized.

### Steric effects

In addition to electronic influences, steric effects are very important in metallation reactions [21]. The choice of the phosphines was based upon the possibility of forming a five-membered ring, and the bulky cyclohexyl and *t*-butyl groups were chosen because these groups promote metallation reactions [14]. The steric hindrance between the metallated and the unmetallated phosphine is large in five-membered ring compounds, as demonstrated earlier [15]. This is especially so when a secondary rather than a primary carbon atom is metallated, as is the case for benzylphosphines (Fig. 5).

For the metallated palladium and rhodium compounds this hindrance is so large that not even an unmetallated phosphine is present. In the metallated *ortho*-F compounds even more steric hindrance occurs, as shown by the spectral data. Therefore, the large amount of *ortho*-F product in the cases of iridi-

um and rhodium shows that this site is much more reactive. Even in the case of four-membered ring systems, for which less steric hindrance between the metallated and the unmetallated phosphine is expected, always a primary C atom is metallated in favor of a secondary one, when there is a choice\*.

The low reactivity of  $Pt^{II}$  towards metallation of  $(C_6H_5CH_2)P(C_6H_{11})_2$  is in contrast with the easy metallation of  $(t\text{-butyl})_3P$  [22] or  $(\text{neopentyl})PR_2$  [23] with this metal. It should be noted that in the latter two cases a primary carbon atom is metallated.

## Conclusions

(1) The sequence of metallation of  $(C_6H_5CH_2)PR_2$  with  $d^8$  metals is  $Ir^I > Rh^I \gg Pd^{II} \sim Pt^{II}$ .

(2) The reaction mechanism is probably nucleophilic for  $Rh^I$  and  $Ir^I$ , electrophilic for  $Pd^{II}$ , and borderline for  $Pt^{II}$ .

(3) Primary carbon atoms are more easily metallated than secondary carbon atoms.

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\* Cheney and coworkers [11] could not decide whether a four- or five-membered ring was formed after reaction of  $[(t\text{-Bu})(n\text{-Pr})_2P]_2PtBr_2$ . However, as Garrou [16] has pointed out, a five-membered ring must be formed. Dehand and Pfeffer stated in their review article that a four-membered ring was formed [1].