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ACTIVATION OF C—H BONDS BY TRANSITION METALS

III *. METALLATION OF ALKYLPHOSPHINES COORDINATED TO IRIDIUM(I)

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Summary

Six-coordinated cyclometallated compounds are easily obtained by the reaction of the tertiary aliphatic phosphines, di(t-butyl)n-propyl-, di(t-butyl)n-butyl-, tri-t-butyl- or tri-isopropyl-phosphine with $[(COT)_2IrCl]_2$ (COT = cyclo-octene) in the presence of γ-picoline or acetonitrile. Both four and five membered rings are formed, but no six membered ring, as was deduced from the ^{31}P NMR spectra. The steric effects of the phosphine and of the co-ligand determine the composition and the stereochemistry of the products. Some exchange reactions with CO, and $P(OPh)_3$ were studied to give more structural information.

Introduction

It has previously been shown [1—7], that both aromatic and olefinic C—H bonds of N— or P—donor ligands are easily cleaved by transition metal complexes, especially when the ligand has the appropriate steric and electronic properties and when the metal is in a suitable oxidation state. Cyclometallation reactions involving aliphatic C—H bonds breaking, except for benzylic C—H bonds, have rarely been observed [8,9]. The results of a study of this type of cyclometallation are presented here.

Experimental

All operations were carried out under purified nitrogen.

Preparation of the complexes

$[\{i\text{-}C_3H_7)_2PCH(CH_3)\overline{CH_2\}Ir}HCl\{(i\text{-}C_3H_7)_3P\}NC_6H_7]$ *(Ia)*. $[(COT)_2IrCl]_2$ (0.33

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* For part II see ref. 7.

TABLE 1

ANALYTICAL DATA AND ASSIGNMENT OF THE COMPOUNDS

Compound		Colour	Analysis found (calcd.) (%)		
			C	H	Cl
$[\{(i\text{-}C_3H_7)_2PCH(CH_3)CH_2\}IrHCl\{(i\text{-}C_3H_7)_3P\}NC_6H_7]$	Ia [a]	off-white	44,70(44,94)	7,63(7,65)	5,55(5,53)
$[\{(i\text{-}C_3H_7)_2PCH(CH_3)CH_2\}IrHCl\{(i\text{-}C_3H_7)_3P\}CO]$	Ib [a]	oil			
$[\{(i\text{-}C_3H_7)_2PCH(CH_3)CH_2\}IrHCl\{(i\text{-}C_3H_7)_3P\}P(OPh)_3]$	Ic [a]	oil			
$[\{(t\text{-}C_4H_9)_2PCH_2CH_2CH_2\}IrHCl\{(t\text{-}C_4H_9)_2P(n\text{-}C_3H_7)\}NC_6H_7]$	IIa	off-white	47,36(48,24)	7,94(8,18)	5,11(5,10)
$[\{(t\text{-}C_4H_9)(n\text{-}C_3H_7)PC(CH_3)_2CH_2\}IrHCl\{(t\text{-}C_4H_9)_2P(n\text{-}C_3H_7\}NC_6H_7]$	IIb	off-white	48,42(48,24)	8,36(8,18)	5,02(5,10)
$[\{(t\text{-}C_4H_9)_2PCH_2CH_2CH_2\}IrHCl\}(t\text{-}C_4H_9)_2P(n\text{-}C_3H_7\}CO]$	IIc	oil			
$[\{(t\text{-}C_4H_9)(n\text{-}C_3H_7)PC(CH_3)_2CH_2\}IrHCl\{(t\text{-}C_4H_9)_2P(n\text{-}C_3H_7)\}CO]$	IId	oil			
$[\{(t\text{-}C_4H_9)_2PCH_2CH_2CH_2\}IrHCl\{P(OPh)_3\}_2]$	IIe [b]	white			
$[\{(t\text{-}C_4H_9)(n\text{-}C_3H_7)PC(CH_3)_2CH_2\}IrHCl\{P(OPh)_3\}_2]$	IIf [b]	white			
$[\{(t\text{-}C_4H_9)_2PCH_2CH_2CHCH_3\}IrHCl(NC_6H_7)_2]$	IIIa [a]	yellow oil			
$[\{(t\text{-}C_4H_9)(n\text{-}C_4H_9)PC(CH_3)_2CH_2\}IrHCl(t\text{-}C_4H_9)_2P(n\text{-}C_4H_9)NC_6H_7]$	IIIb	off-white	49,83(49,68)	8,36(8,42)	4,76(4,89)
$[\{(t\text{-}C_4H_9)_2PCH_2CH_2CHCH_3\}IrHCl\{(t\text{-}C_4H_9)_2P(n\text{-}C_4H_9)\}CO]$	IIIc [a]	oil			
$[\{(t\text{-}C_4H_9)(n\text{-}C_4H_9)PC(CH_3)_2CH_2\}IrHCl\{(t\text{-}C_4H_9)_2P(n\text{-}C_4H_9)\}CO]$	IIId	oil			
$[\{(t\text{-}C_4H_9)(n\text{-}C_4H_9)PC(CH_3)_2CH_2\}IrHCl\{P(OPh)_3\}_2]$	IIIf	white	55,16(54,88)	5,54(5,43)	3,19(3,38)
$[\{(t\text{-}C_4H_9)_2PC(CH_3)_2CH_2\}IrHCl(NC_6H_7)_2]$	IVa	yellow oil			
$[\{(t\text{-}C_4H_9)_2PC(CH_3)_2CH_2\}IrHCl\{P(POPh)_3\}_2]$	IVb	white	55,28(54,88)	5,52(5,43)	3,25(3,88)

[a] Two isomers were found. [b] These isomers could not be completely separated.

mmol) was suspended in 15 ml hexane and 0.1 ml γ-picoline was added. After addition of $(i\text{-}C_3H_7)_3P$ (1.22 mmol) a clear yellow solution was slowly formed. After being warmed for 15 min at 50°C the solution was filtered and cooled to −30°C. The white crystals thus obtained were washed with cold hexane and dried under vacuum (yield 80%),

$[\{(t\text{-}C_4H_9)_2PCH_2CH_2\overline{CH_2\}Ir}HCl\{(t\text{-}C_4H_9)_2P(n\text{-}C_3H_7)\}NC_6H_7]$ *(IIa)*. The complex was obtained in the same way (yield 55%). After concentrating the mother liquid, the very soluble complex $[\{(t\text{-}C_4H_9)(n\text{-}C_3H_7)PC(CH_3)_2\overline{CH_2\}Ir}HCl\{(t\text{-}C_4H_9)_2P\text{-}(n\text{-}C_3H_7)\}NC_6H_7]$ (IIb) was obtained (yield 20%).

$[\{(t\text{-}C_4H_9)(n\text{-}C_4H_9)PC(CH_3)_2\overline{CH_2\}Ir}HCl\{(t\text{-}C_4H_9)_2P(n\text{-}C_4H_9)\}NC_6H_7]$ *(IIIb)*. Refluxing a mixture of $[(COT)_2IrCl]_2$ (0.33 mmol), 0.1 ml γ-picoline and $(t\text{-}C_4H_9)_2P(n\text{-}C_4H_9)$ (1.22 mmol) in hexane for 1 h, followed by filtration, concentration and cooling of the solution gave the very soluble product (50% yield). Trace amounts of $[\{(t\text{-}C_4H_9)_2PCH_2CH_2\overline{CHCH_3\}Ir}HCl(NC_6H_7)_2]$ (IIIa) were found. The yield of IIIa could be somewhat increased by using acetonitrile as the co-ligand. After the metallation was complete, γ-picoline was added and about 20% of IIIa could be isolated.

$[\{(t\text{-}C_4H_9)_2PC(CH_3)_2\overline{CH_2\}Ir}HClNC_6H_7]$ *(IVa)*. After refluxing $(t\text{-}C_4H_9)_3P$ (0.66 mmol) with 0.2 ml γ-picoline and $[(COT)_2IrCl]_2$ (0.33 mmol) for 3 h in hexane the non crystallizable product was obtained in low yield (20%). Under the same conditions tri-n-butylphosphine did not yield metallated products. The following CO containing products were obtained by bubbling carbon monoxide through a solution of Ia, IIa, IIb and IIIb respectively, in hexane. All these products were oils, and were thus only investigated spectroscopically: $[\{(i\text{-}C_3H_7)_2\text{-}PCH(CH_3)\overline{CH_2\}Ir}HCl\{(i\text{-}C_3H_7)_3P\}CO]$, (Ib), $[\{(t\text{-}C_4H_9)_2PCH_2CH_2\overline{CH_2\}Ir}HCl\text{-}\{(t\text{-}C_4H_9)_2P(n\text{-}C_3H_7)\}CO]$ (IIc); $[\{(t\text{-}C_4H_9)(n\text{-}C_3H_7)PC(CH_3)_2\overline{CH_2\}Ir}HCl\{(t\text{-}C_4H_9)_2\text{-}P(n\text{-}C_3H_7)\}CO]$ (IId); $[\{(t\text{-}C_4H_9)_2PCH_2CH_2\overline{CHCH_3\}Ir}HCl\{(t\text{-}C_4H_9)_2P(n\text{-}C_4H_9)\}\text{-}CO]$, (IIIc); $[\{(t\text{-}C_4H_9)(n\text{-}C_4H_9)PC(CH_3)_2\overline{CH_2\}Ir}HCl\{(t\text{-}C_4H_9)_2P(n\text{-}C_4H_9)\}CO]$, (IIId). The $P(OPh)_3$-containing products were obtained by adding the calculated amount of triphenylphosphite to solutions of the γ-picoline compound. The following products were obtained: $[\{(i\text{-}C_3H_7)_2PCH(CH_3)\overline{CH_2\}Ir}HCl\{(i\text{-}C_3H_7)_3\text{-}P\}P(OPh)_3]$, (Ic), oil; $[\{(t\text{-}(C_4H_9)_2PCH_2CH_2\overline{CH_2\}Ir}HCl\{P(OPh)_3\}_2]$, (IIe); $[\{(t\text{-}C_4H_9)(n\text{-}C_3H_7)PC(CH_3)_2\overline{CH_2\}Ir}HCl\{P(OPh)_3\}_2]$, (IIf); $[\{(t\text{-}C_4H_9)(n\text{-}C_4H_9)\text{-}PC(CH_3)_2\overline{CH_2\}Ir}HCl\,\{P(OPh)_3\}\ _2]$, (IIIf); $[\{(t\text{-}C_4H_9)_2PC(CH_3)_2CH_2\}IrHCl\text{-}\{P(OPh)_3\}_2]$, (IVb). The oily nature of some compounds prevented a reliable elemental analysis. This lack of crystalline structure probably arises from the presence of different enantiomers and the large asymmetry of the molecules. Some products appeared to be mixtures of isomers which could not be separated. The C, H, and Cl analyses (Table 1) were carried out by the Elemental Analysis section of the Institute of Organic Chemistry TNO, Utrecht.

Spectroscopic measurements

The ^1H 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 the IR spectra as nujol mulls on a Beckmann 4250 spectrophotometer. (4000—200 cm^{-1}).

TABLE 2

RELEVANT INFRARED SPECTRA OF THE COMPLEXES (in cm^{-1})

Compound	ν(Ir—H)	ν(Ir—Cl)	ν(CO)
Ia	2220	230	
Ib	2220	250	1980
Ic	2260	230	
IIa	2345	225	
IIb	2225	230	
IIc	2115	230	1990
IId	2090	225	1990
IIe	2255	235	
IIf	2240	230	
IIIa	2220	235	
IIIb	2275	210	
IIIc	2110	225	1990
IIId	2125	225	1990
IIIf	2210	240	
IVa	2255	220	
IVb	2250	240	

Results

The metallated compounds were characterized by C, H and Cl analyses and by their infrared, ^{1}H and ^{31}P NMR spectra.

Infrared spectra (Table 2)

The relevant bands in the spectra of the complexes resemble those of other cyclometallated iridium compounds [4,6,7]. The hydrido ligand is shown to be present by a band in the region 2100—2350 cm^{-1}. The high frequency of the band in the γ-picoline complexes shows that the weak *trans*-directing ligand γ-picoline is situated *trans* to the hydrogen atom, which agrees with the ^{1}H NMR data. In the carbonyl compounds the CO ligand is also found in a *trans* position with respect to hydrogen, as indicated by the low value of ν(Ir—H) (2120 cm^{-1}). Only compound Ib is an exception, with the CO group *cis* to the hydrogen atom and ν(Ir—H) at 2220 cm^{-1}. In the $P(OPh)_3$ compounds, the high value of ν(Ir—H) (2250 cm^{-1}) indicates that the hydrogen atom is *cis* to all three phosphorus atoms. A rearrangement around the metal has thus accured upon reactions with $P(OPh)_3$ (Fig. 1). The large frequency difference between

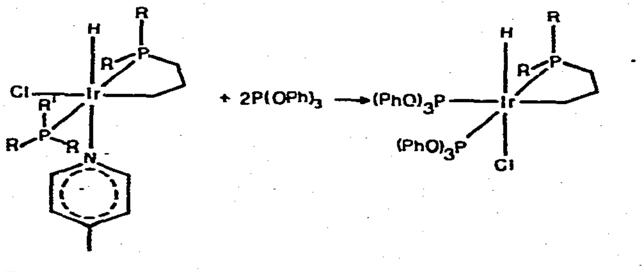

Fig. 1. Reaction of IIa with $P(OPh)_3$.

the metal—hydrogen vibrations in the complexes IIa and IIb may be caused by a weakening of the metal—hydrogen bond in the latter complex as a result of a distortion of the angles around the iridium atom by the four membered ring [10].

^{1}H NMR spectra (Table 3)

In most of the compounds the aliphatic part of the spectrum is very complex and the resonances are broad. The large line-width results partly from unresolved couplings and partly from hindered rotation of the unmetallated phosphine around the iridium—phosphorus bond [6]. Furthermore, some compounds existed as a mixture of inseparable isomers, giving complex spectra which could not easily be interpreted. The compounds were therefore allowed to react with P(OPh)$_3$ giving, in most cases, compounds with two P(OPh)$_3$ ligands and one metallated phosphine (Fig. 1). The aliphatic part of the spectrum was then much simpler and could be interpreted. It was found that a primary carbon atom is more easily metallated than a secondary one. Thus for di-t-butyl-n-butylphosphine nearly exclusive t-butyl group metallation occurred and a four membered ring was obtained, while for di-t-butyl-n-propylphosphine about 80% of the n-propyl group was metallated and a five membered ring was formed. For compound IIa no resonance for the metal bound proton was found up to 65 ppm upfield from TMS. This is ascribed to an exchange and partly dissociation of γ-picoline, which causes line broadening of the metal—hydrogen resonance. When the γ-picoline is exchanged for CO the metal—hydrogen resonance is found in the region —6 to —9 ppm which is indicative of the *trans* position of CO with respect to hydrogen [11]. The only exception is compound Ic, which has a resonance at —18.6 ppm, showing the *cis* position of the hydrogen atom with respect to CO.

TABLE 3

RELEVANT ^{1}H NMR DATA FOR THE COMPLEXES

Compound	Chemical shift δ (ppm) relative to TMS	$^2J(^1H—^{31}P)$ (Hz) [a]	Number of t-butyl groups
Ia	—22	2 × t 16	
Ib	—18.6	2 × t 14	
Ic	—24.0	m	
IIa	not observed		4
IIb	—22.5	t 16	3
IIc	—7.8	t 17	4
IId	—6.1	t 16	3
IIe	—20.3	q 15	2
IIf	—18.0	q 16	1
IIIa	—25.0/—24.8	2 × d 22	2
IIIb	—22.3	t 14	3
IIIc	—7.0	t 16	3
IIId	—9.0	t 16	3
IIIf	—17.8	q 16	1
IVa	—23.7	d 19	2
IVb	—19.3	q 14	2

[a] t = triplet; m = multiplet; q = quartet; d = doublet.

The shape of the resonance signal of the metal-bound proton in all the complexes with two non-equivalent phosphorus atoms is the same as reported earlier [6]. In the $P(OPh)_3$ compounds the resonance of the metal-bound proton appeared as a broadened quartet, showing that the coupling constants of all three phosphorus atoms with this proton do not differ substantially. Thus the hydrogen atom is located *cis* to all three phosphorus atoms.

^{31}P NMR spectra (Table 4)

Recently, Garrou and co-workers [12] reported that the ^{31}P chemical shift in phosphorus containing ring compounds can be used to decide whether the phosphorus atom is part of a four, five or six membered ring. Compared with a coordinated but unmetallated phosphine, a downfield shift for a five membered ring was found and an upfield shift for both a four and a six membered ring. Other groups of workers have mentioned this empirical rule [13,14]. These rules make it possible to assign the phosphorus resonances in the previously published [6] compounds $[(R_2PCH_2CH{=}\overline{CH)Ir}HCl(R_2PCH_2CH{=}CH_2)L]$ which show a chemical shift for the metallated phosphines between −55.5 and −70.9 ppm and a chemical shift between −14.8 and −27.9 ppm for the unmetallated phosphine (thus giving a ring contribution (ΔR) of about −40—50 ppm). This value of the ring contribution is in accord with the proposed five membered rings.

TABLE 4

^{31}P NMR DATA FOR THE METALLATED COMPLEXES

Compound	P_1 (metallated)	$J(P_1P_3)$ (*cis*)	P_2 (unmetallated)	$J(P_1P_2)$ (*trans*)	P_3	$J(P_2P_3)$ (*cis*)	ΔR	Ring size
Ia	+31.20		−10.53	369.3			+41.55	4
Ia′	+25.00		−14.18	367.5			+38.18	4
Ib	+30.15		−18.25	308.3			+48.40	4
Ib′	+36.84		−18.20	311.0			+55.09	4
Ic	+42.83	~5	−8.58	315.7	−85.54	15	+51.41	4
Ic′	+41.14	~5	−6.33	315.0	−81.79	15	+47.47	4
IIa [c]	−76.2		−39.6	360			−36.6	5
IIb	+19.93		−20.43	367.3			+40.36	4
IIc [a]	−67.83		−24.87	300.8			−42.96	5
IId	+13.98		−33.24	302.5			+47.22	4
IIe	−63.42	24.1	−77.37 [d]	533.9	−90.60	27.7	[b]	5
IIf	+22.55	~5	−86.11 [d]	559.2	−94.77	21.9	[b]	4
IIIa/IIIa′	−51.68/−51.29						[b]	5
IIIb	+22.28		−14.28	366.2			+36.55	4
IIIc [a]	−62.51		−26.26	301.2			−36.25	5
IIId	+18.75		−28.50	302.5			+47.25	4
IIIf	+7.51	~5	−79.30 [d]	562.5	−88.03	20.5	[b]	4
IVa	+7.58						[b]	4
IVb	+27.47	~5	−82.49 [d]	560.0	−91.36	21.5	[b]	4

δ di-t-butyl-n-butylphosphine = −32.46

δ di-t-butyl-n-propylphosphine = −31.36

δ tri-t-butylphosphine = −62.53

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[a] At −30°C, two conformations are present. [b] Since the chemical shift of the unmetallated phosphine is unknown, ΔR could not be obtained. [c] The spectrum was recorded at −50°C. [d] P_2 is $P(OPh)_3$.

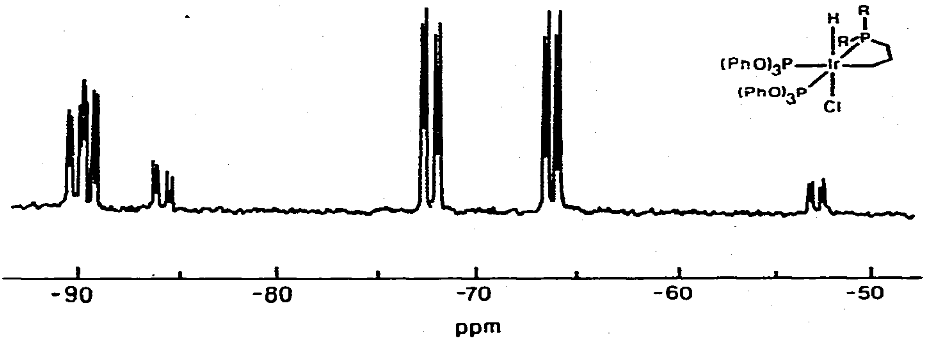

Fig. 2. ^{31}P NMR spectrum of IIe.

The compounds Ia, Ib and Ic, that can only have four membered rings, show a ring contribution (ΔR) between +38.18 to +51.41. These values are in good agreement with the empirical rules of Garrou [12] for four-membered rings. The compounds IVa and IVb must also have four membered rings, but because there is no unmetallated phosphine ligand in the molecule, ΔR could not be determined exactly. Since for the compounds IIb, IId, IIf, IIIb, IIId and IIIf a positive ΔR is also found, a four membered ring must be present. This agrees with the ^{1}H NMR spectra, which showed that a t-butyl group was metallated in these complexes and consequently a four membered ring must be formed. A downfield shift of the resonance of the metallated phosphine with respect to the unmetallated phosphine ($\Delta R \approx -40$ ppm) was found for the compounds IIa, IIc and IIIc, showing the presence of a five membered ring. The compounds IIe and IIIa also show a negative ring contribution, but again ΔR could not be obtained exactly because of the absence of an unmetallated phosphine.

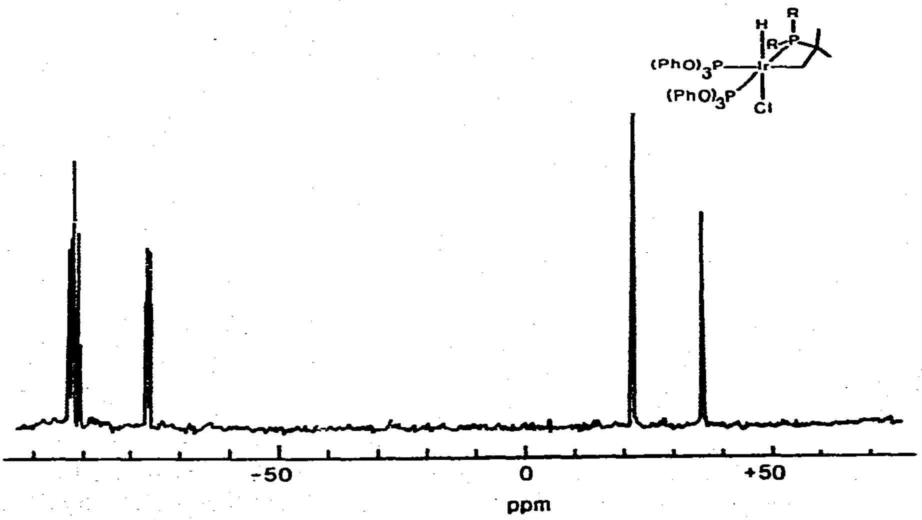

Fig. 3. ^{31}P NMR spectrum of IVb.

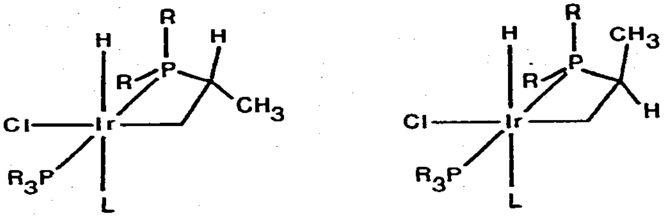

Fig. 4. Diastereoisomers of Ia.

Compound IIa showed a broadened AB spectrum at room temperature, and on cooling still more broadening occurred. Only at −50°C did the signals sharpen to show two AB patterns, revealing the presence of two conformations. This behaviour is consistent with partial dissociation of γ-picoline at room temperature. On cooling two mechanisms occur; one is the slowing down of the reversible dissociation of γ-picoline and the other is the decrease of the hindered rotation around the iridium—phosphorus bond. For the P(OPh)$_3$-containing complexes the spin system is second order, showing an ABC spectrum (Fig. 2,3). For the complexes with a four membered ring (IIb, Ib, IIIe, IVb) a small *cis*-coupling of P(OPh)$_3$ with the metallated phosphine was found (~5 Hz), while in the five membered rings this coupling is 20—25 Hz. This difference is probably due to an angle distortion around the metal by the four membered ring.

Another difference between the four and the five-membered ring complexes is the greater steric hindrance in the latter. In the products with two phosphine ligands the freezing out of the conformations occurs in the five membered ring compounds between room temperature and −40°C. The AB spectrum of the four membered ring compounds starts broadening at −30°C, so clearly there is a less hindered rotation of the unmetallated phosphine around the Ir—P bond.

For the metallated products of tri-isopropylphosphine two isomers were found. These originate from the two asymmetric centres in the molecule providing two diastereo isomers. For the same reason two isomers were found for compound IIIb (Fig. 4). For all compounds with a proton chemical shift of more than 15 ppm upfield from TMS, the coupling of this proton with the phosphorus nuclei was observed in the ^{31}P NMR spectra, because the broad band decoupler was not powerful enough to completely decouple this proton [7].

Discussion

In this study it has been found that the reactivity of aliphatic C—H bonds towards the used Ir^{I} system used does not differ much from the reactivity of allylic and aromatic C—H bonds with the same system. Since the bond energies of all three types of C—H bonds are in the same region, we suggest that when the steric conditions are well chosen the bond energy of the C—H bond determines the reactivity towards metallation reactions. Pre-coordination of an unsaturated group to Ir^{I} does not enhance the reactivity towards metallation but rather prevents it, as illustrated by the remarkable difference between allyl phosphines and 3-butenylphosphines in the reaction with Ir^{I}. When the phosphorus atom is bound to the metal the allyl group cannot be brought near enough to the metal to give a strain-free bond between Ir^I and the double bond, Model studies show that the vinylic hydrogen atom at C_3 can point directly towards the metal and thus a metallated product is easily formed [6,7]. However, the butenyl group, which has one methylene group more, can easily be arranged in such a way that the double bond overlaps perfectly with the d_{z^2} and p_z orbitals of the metal giving a stable 5,5 membered chelate ring [15,16]. For metallation to occur this chelate ring has to be broken; apparently this is unfavorable and no metallated products are obtained. The importance of the steric factors is illustrated by this investigation and others [17—20]. The reactivity towards metallation is tri-isopropylphosphine ≈ di(t-butyl)n-propylphosphine > di(t-butyl)n-butylphosphine > tri-t-butylphosphine. Tri-n-butylphosphine yielded no metallated products. Obviously the cone angle of the phosphine determines the reactivity; when this angle is small no metallated products are obtained and when the angle is extreme large, the yield is rather low. Only when the bulkiness is moderate are good yields of metallated products obtained. The influence of even one methyl group in the course of the reaction is rather large. Di(t-butyl)-n-propylphosphine upon reaction with Ir^I yields predominantly a cyclometallated product with a five membered ring, showing that the n-propyl group is metallated. The crowding around the metal is such that the co-ligand, γ-picoline, is only just small enough to fit into the vacant coordination site. The by-product with the strained four membered ring has less crowding around the metal and the coligand now fits easily into the sixth coordination place. The release of crowding is also illustrated by the less hindered rotation around the iridium—phosphorus bond.

A four membered ring is formed almost exclusively upon reaction of di(t-butyl)n-butylphosphine, because a five or six membered ring would increase the crowding around the metal, since the ethyl or methyl group on the ring adds to the steric hindrance near the metal. When a smaller co-ligand, acetonitrile, is used, however, the crowding is slightly less and now some five membered ring product is formed. Addition of γ-picoline to this product illustrates the increase in crowding; the unmetallated phosphine being replaced and product IIIa formed.

A further study of electronic effects on metallation reactions with phosphines is under way.

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