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ACTIVATION OF C—H BONDS BY TRANSITION METALS

IV *. PARTIAL DEHYDROGENATION OF TRICYCLOHEXYLPHOSPHINE BY IRIDIUM(I) AND RHODIUM(I) LEADING TO THE FORMATION OF A METAL—OLEFIN COMPLEX AND A FIVE-COORDINATED METAL DIHYDRIDE, WHICH IS A HYDROGENATION CATALYST

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Summary

Reaction of tricyclohexylphosphine with $[(COT)_2MCl]_2$ (M = Rh, Ir, COT = cyclooctene) in refluxing toluene, yields the five-coordinated metal(III) complexes $H_2[P(C_6H_{11})_3]_2MCl$ and the four-coordinated metal(I) complexes $[P(C_6H_{11})_3]M[P(C_6H_9)(C_6H_{11})_2]Cl$, in which one cyclohexyl group has been dehydrogenated to a cyclohexene group, the double bond of which occupies the fourth coordination site. In refluxing toluene, triisopropylphosphine reacts with $[(COT)_2MCl]_2$ to give the five-coordinated complex $H_2[P(C_3H_7)_3]_2MCl$, which suggests a similar dehydrogenation. Reaction of the partly dehydrogenated products with CO yields $[P(C_6H_{11})_3]M[P(C_6H_9)(C_6H_{11})_2]Cl(CO)$ in which the double bond is not coordinated to the metal. Hydrogen adds oxidatively to the iridium(I) compound, but does not react with the rhodium(I) compound. The mechanism of the dehydrogenation is discussed. The complexes $H_2(PR_3)_2MCl$ are catalysts for hydrogenation of olefins at 100°C and at 1 atmosphere. 1,5-Cyclooctadiene is especially readily hydrogenated at this temperature.

Introduction

The metallation of coordinated ligands by transition metals is well studied [1,2]. As part of our studies of this type of reactions, we found that metallated products are easily formed when N- [2,3] or P- [4—6] donor ligands react with iridium(I) complexes. With N-donor ligands, aromatic and olefinic C—H bonds

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are broken, and with P-donor ligands aliphatic C—H bonds can also be metallated. A methyl group is more easily metallated than a methylene group [6]. In order to get more information about the reactivity of methylene groups, the reaction of tricyclohexylphosphine with iridium(I) and rhodium(I) was investigated. The size of this ligand prevents four-coordination of the univalent metals rhodium(I) and iridium(I), except when small molecules are used as co-ligands [7—9]. The coordinatively unsaturated complexes are of potential interest with respect to C—H bond activation, because two factors which promote reactions of C—H bonds are present viz. bulkiness of the ligands and coordinative unsaturation. The results of a study of these reactions are reported below.

Experimental

All operations were carried out under purified nitrogen.

$H_2[P(C_6H_{11})_3]_2IrCl$ *(Ia) and* $[P(C_6H_{11})_3]\overline{Ir[P(C}_6H_9)(C_6H_{11})_2]Cl$ *(IIa/IIb)*

$[(COT)_2IrCl]_2$ (0.33 mmol) was dissolved in 20 ml of toluene, $P(C_6H_{11})_3$ (1.22 mmol) was added, and the resulting orange solution was refluxed for 3 h. The red solution contained Ia and IIa/IIb. Complex Ia was more easily obtained by bubbling hydrogen through a solution of $[(COT)_2IrCl]_2$ (0.33 mmol) and $P(C_6H_{11})_3$ (1.22 mmol) in toluene at room temperature for 10 minutes. After evaporation of the solvent, the orange product was recrystallized from hexane (85% yield).

$H_2[P(C_6H_{11})_3]_2IrCl(NC_6H_7)$ *(Ib)*

After addition of 0.1 ml γ-picoline to the warm solution containing complex Ia and IIa/IIb, cooling gave white crystals of Ib in 50% yield. The filtrate was evaporated and IIa/IIb was obtained impure as a yellow solid.

$[P(C_6H_{11})_3]Ir[P(C_6H_9)(C_6H_{11})_2]Cl(CO)$ *(IIIa/IIIb)*

CO was bubbled through a solution of IIa/IIb in hexane during 10 minutes. The insoluble yellow product was filtered off and crystallized from chloroform (70% yield).

$H_2[P(C_6H_{11})_3]\overline{Ir[P(C}_6H_9)(C_6H_{11})_2]Cl$ *(IVa/IVb/IVc)*

H_2 was bubbled through a solution of IIa/IIb in hexane. The product, a light yellow solid, was obtained by evaporation of the solvent.

$H_2[P(C_3H_7)_3]_2IrCl$ *(Va)*

Compound Va was prepared in the same way as compound Ia. It is necessary to exclude γ-picoline during the reaction, otherwise the cyclometallated product is formed.

$H_2[P(C_3H_7)_3]_2IrCl(NC_6H_7)$ *(Vb)*

Upon addition of γ-picoline to a solution of Va in hexane the slightly soluble white compound was obtained. The product was crystallized from a hexane/toluene mixture. $H_2[P(C_6H_{11})_3]_2RhCl$ (VIa), $[P(C_6H_{11})_3]\overline{Rh[P(C}_6H_9)(C_6H_{11})_2]Cl$ (VII), $H_2[P(C_6H_{11})_3]_2RhCl(NC_6H_7)$ (VIb), $[P(C_6H_{11})_3\ Rh\ P(C_6H_9)(C_6H_{11})_2]Cl(CO)$ (VIII), and $H_2([P(C_3H_7)_3]_2RhCl(NC_6H_7)$ (IX) were prepared similarly as the analogous iridium products.

TABLE 1

ANALYTICAL DATA AND ASSIGNMENT OF THE COMPOUNDS

Compound	Colour	Analysis (found (calcd.) (%))		
		C	H	Cl
$H_2[P(C_6H_{11})_3]_2IrCl$ (Ia)	orange	54.28 (54.70)	8.54 (8.61)	4.53 (4.50)
$H_2[P(C_6H_{11})_3]_2IrClNC_6H_7$ (Ib)	white	57.38 (57.10)	8.28 (8.50)	4.10 (4.02)
$P(C_6H_{11})_3\overline{IrP(C_6}H_9)(C_6H_{11})_2Cl$ (IIa/IIb)	yellow			
$P(C_6H_{11})_3IrP(C_6H_9)(C_6H_{11})_2Cl(CO)$ (IIIa/IIIb)	yellow	54.12 (54.57)	7.54 (7.87)	4.62 (4.36)
$H_2P(C_6H_{11})_3\overline{IrP(C_6}H_9)(C_6H_{11})_2Cl$ (IVa/IVb/IVc)	yellow			
$H_2[P(C_3H_7)_3]_2IrCl$ (Va)	orange			
$H_2[P(C_3H_7)_3]_2IrClNC_6H_7$ (Vb)	white	44.42 (44.81)	7.85 (7.94)	5.61 (5.52)
$H_2P(C_6H_{11})_3RhCl$ (VIa)	yellow	61.32 (61.67)	9.60 (9.71)	4.92 (5.07)
$H_2P(C_6H_{11})_3RhClNC_6H_7$ (VIb)	white	64.23 (63.52)	9.28 (9.45)	3.84 (4.47)
$P(C_6H_{11})_3RhP(C_6H_9)(C_6H_{11})_2Cl$ (VII)	red-brown			
$P(C_6H_{11})_3RhP(C_6H_9)(C_6H_{11})_2Cl(CO)$ (VIII)	yellow	60.84 (61.28)	8.58 (8.83)	5.22 (4.90)
$H_2[P(C_3H_7)_3]_2RhClNC_6H_7$ (IX)	red-brown	51.88 (52.03)	9.10 (9.21)	6.32 (6.41)

The C, H and Cl analysis (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 nujoll mulls on a Beckman 4250 spectrophotometer between 4000 and 200 cm^{-1}.

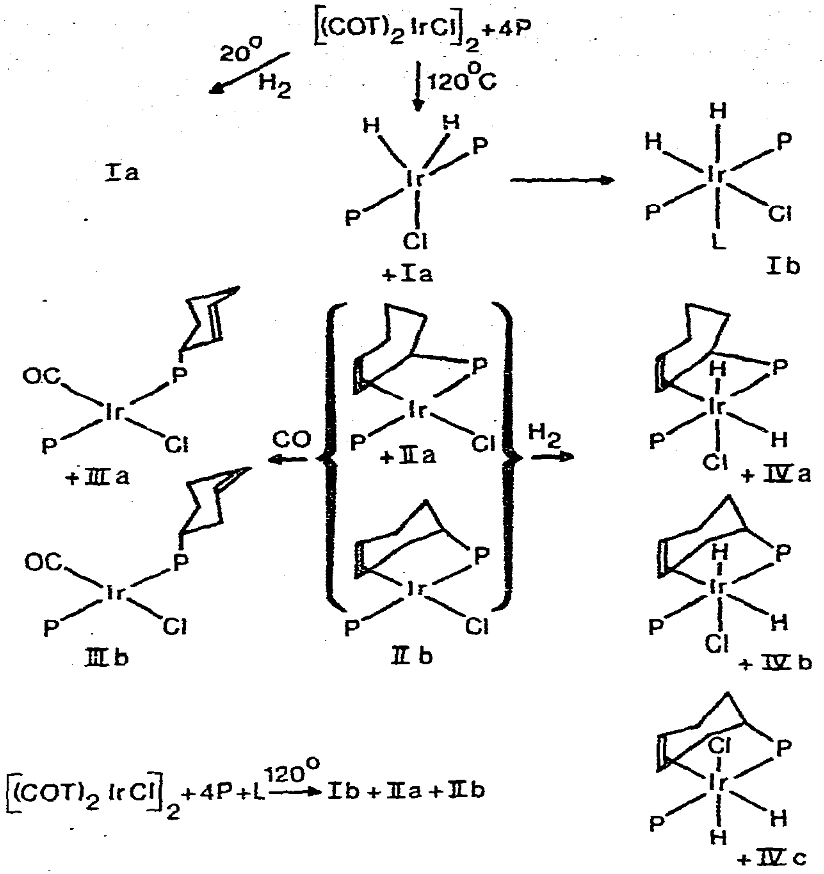
Results

The various reactions of $[(COT)_2IrCl]_2$ with $P(C_6H_{11})_3$ and some reactions of the products are shown in Scheme 1.

Upon reaction of tricyclohexylphosphine with $[(COT)_2IrCl]_2$ in refluxing toluene, two main products were formed, in about one to one ratio. One product appeared to be identical with $H_2[P(C_6H_{11})_3]_2IrCl$ (Ia) prepared via an alternative route which involved bubbling hydrogen through a solution of $[(COT)_2IrCl]_2$ and $P(C_6H_{11})_3$. During this latter reaction the cyclooctene is hydrogenated to cyclooctane. The hydrogen atoms of Ia do not originate from the solvent because, when the reaction is performed in d^8 toluene no metal-deuteride frequencies are found but only M—H stretching modes.

Reaction of Ia with γ-picoline gives $H_2[P(C_6H_{11})_3]_2IrClNC_6H_7$ (Ib). Whether γ-picoline is added before refluxing or afterwards does not affect the nature and the ratio of the products.

The other main product, $[P(C_6H_{11})_3]\overline{Ir[P(C_6}H_9)(C_6H_{11})_2]Cl$ consists of two



SCHEME 1. Products formed from the reaction of $[(COT)_2IrCl]_2$ with $P(C_6H_{11})_3$.

isomers IIa and IIb. Upon reaction with CO, $[P(C_6H_{11})_3]Ir[P(C_6H_9)(C_6H_{11})_2](CO)Cl$ (IIIa and IIIb) is quantitatively formed. In these compounds the double bond is no longer coordinated to the metal. Treatment of a mixture of IIa and IIb with H_2 yielded three isomers, the proposed structures of which are shown in Scheme 1.

$P(C_3H_7)_3$ also yielded a dihydride species $H_2[P(C_3H_7)_3]_2IrCl$ (IVa), in about 40% yield, when refluxed in toluene with $[(COT)_2IrCl]_2$, but only in the absence of γ-picoline. When γ-picoline was present, the previously reported [6] cyclometallated products were formed, *e.g.* $[P(C_3H_7)_2CH(CH_3)\overline{CH_2]Ir}HCl[P(C_3H_7)_3]NC_6H_7$. Dehydrogenated products could not be isolated.

The reactions of $[(COT)_2RhCl]_2$ with $P(C_6H_{11})_3$ or $P(C_3H_7)_3$ were almost the same as those of $[(COT)_2IrCl]_2$ with these phosphines. Thus $H_2(PR_3)_2RhCl$ and $H_2(PR_3)_2RhClNC_6H_7$ were formed, together with $[P(C_6H_{11})_3]Rh[PC_6H_9(C_6H_{11})_2]Cl$ (VIa), but only one isomer of the dehydrogenated product was found. The reaction of VIa with CO yielded a product similar to that obtained in the case of iridium, but no addition of hydrogen to VIa occurred, showing that iridium undergoes oxidative addition reactions more readily than rhodium.

The compounds $H_2(PR_3)_2MCl$ and $H_2(PR_3)MClNC_6H_7$ are hydrogenation catalysts for olefins (see discussion).

Structural characterization

$H_2(PR_3)_2MCl$ and $H_2(PR_3)_2MClNC_6H_7$ ($R = C_6H_{11}, C_3H_7; M = Rh, Ir$)

The infrared spectra of Ia (Table 2) shows, in addition to numerous ligand vibrations, one metal—hydrogen vibration at rather high frequency (2240 cm^{-1}) and a metal—chlorine frequency at 285 cm^{-1}, indicating a trigonal bipyramidal structure, with two equivalent phosphorous atoms (^{31}P NMR) and two equivalent hydrogen atoms (^1H NMR). The proposed structure (Scheme 1) is in accord with the ^1H NMR chemical shift (δ —32 ppm), which is further upfield than in comparable six-coordinated octahedral (hydridoiridium(III) compounds [19] having a ligand with a weak *trans* influence *trans* to the hydrogen atom, but is downfield from the resonance for five-coordinated pyramidal hydridoiridium(III) complexes [10,11], having an empty site *trans* to the hydrogen atom.

In the γ-picoline-containing complexes the hydrogen atoms are situated *cis* to one another because two metal hydrogen vibrations are observed in the IR at high frequencies, showing the small *trans* influence of γ-picoline and of the chlorine atom. Because complex Ib is sparingly soluble at room temperature and dissociates at higher temperatures, and because hindered rotation [12] occurs around the metal—phosphorous bond, a reliable ^1H NMR spectrum could not be obtained. However, the structurally similar complex IVb is soluble, and at —30°C a well resolved ^1H NMR spectrum was obtained. The high field part of the spectrum shows the AB part of an ABX_2 pattern, ($X = {}^{31}P$) (Fig. 1). The large chemical shift of the protons and the small value of $J(^1H—^1H)$ (8 Hz) is in accord with the proposed *cis*-structure of the hydrogen atoms.

The related rhodium complex IX shows at high field the A part of an A_2X_2Y pattern ($X = {}^{31}P$, $Y = {}^{103}Rh$) (Fig. 2) demonstrating the equivalence of both hydrogen atoms in solution, which indicates that the co-ligand, γ-picoline, is dissociated to a large extent.

$[P(C_6H_{11})_3]\overline{M[P(C}_6H_9)(C_6H_{11})_2]Cl$ ($M = Rh, Ir$)

The ^1H NMR spectrum showed only the broadened resonance arising from the cyclohexyl groups. The IR spectrum showed in addition to minor changes in the cyclohexyl frequencies, a metal—chlorine vibration at low frequency, indicating the presence of a strong *trans* influence *trans* to the chlorine atom [13].

The ^{13}C NMR spectra of these compounds revealed the presence of two non-equivalent olefinic carbon atoms bound to the metal [14]. In the case of M = Rh a $J(^{103}Rh—^{13}C)$ of 14 Hz (Table 3) was observed. The ^{31}P NMR spectrum of the iridium complex yielded two AB patterns, showing that two isomers are present.

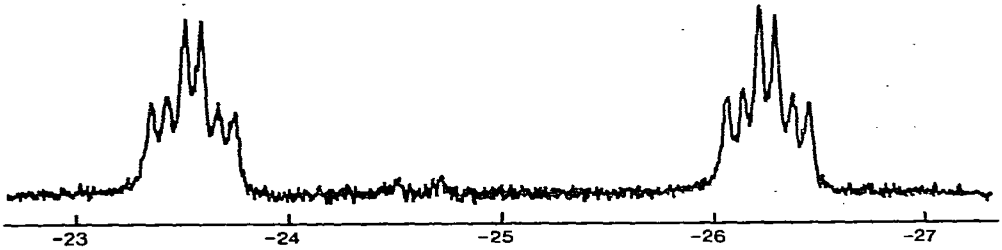


Fig. 1. High field portion of the ^1H NMR spectrum of $H_2[P(i\text{-}C_3H_7)_3]_2IrCl(NC_6H_7)$.

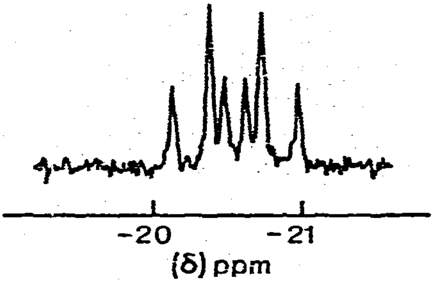


Fig. 2. High field portion of the ^1H NMR spectrum of $H_2[P(i\text{-}C_3H_7)_3]_2RhCl(NC_6H_7)$.

The chemical shifts of the phosphorous atoms of the least abundant isomer indicate the presence of a four-membered ring in this compound, while the ^{31}P chemical shifts of the other isomer show that a five-membered ring is present [15,6]. The rhodium compound shows only one AB pattern with additional ^{103}Rh coupling. The ^{31}P chemical shifts indicate that the isomer with the four-membered ring is present. All this spectroscopic evidence is consistent with structures IIa and IIb (Scheme 1).

The infrared spectra of the CO containing products show, in addition to a $\nu(C\equiv O)$ and a $\nu(M—Cl)$ at the expected frequencies (Table 2) (CO trans to Cl), a $\nu(C=C)$ at 1653 cm^{-1} (uncoordinated double bond). Furthermore the ^1H NMR shows a broad resonance at δ 5.7 ppm, the same value found for the olefinic protons in cyclohexene. The ^{13}C NMR also shows by resonances at 126.9 and at 126.6 ppm, the presence of olefinic carbon atoms (cyclohexene $\delta(^{13}C)$ (double bond) 126.75 ppm). The ^{31}P NMR spectrum shows a singlet for the iridium complex and a doublet for the rhodium complex; apparently the phosphorus atoms are approximately equivalent.

TABLE 2

RELEVANT INFRARED SPECTRAL DATA (Nujol mull, ν, cm^{-1})

Compound	$\nu(M—H)$	$\nu(M—Cl)$	other
$[P(C_6H_{11})_3]_2IrCl(CO)$		305	$\nu(C\equiv O)$ 1935
$[P(C_6H_{11})_3]Ir[P(C_6H_9)(C_6H_{11})_2]Cl(CO)$		305	$\nu(C\equiv O)$ 1935 $\nu(C=C)$ 1655
$[P(C_6H_{11})_3]\overline{Ir[P(C_6H_9}(C_6H_{11})_2]Cl$		280	
$H_2[P(C_6H_{11})_3]\overline{Ir[P(C_6H_9}(C_6H_{11})]_2Cl$	2210/2120	250	
$[P(C_6H_{11})_3]_2IrClC_2H_4$		300	
$H_2[P(C_6H_{11})_3]_2IrCl$	2240	285	
$H_2[P(C_6H_{11})_3]_2IrCl(NC_6H_7)$	2275/2215	230	
$H_2[P(C_3H_7)_3]_2IrCl$	2255	280	
$H_2[P(C_3H_7)_3]_2IrClNC_6H_7$	2240/2220	235	
$[P(C_6H_{11})_3]_2RhCl(CO)$		300	$\nu(C\equiv O)$ 1940
$[P(C_6H_{11})_3]Rh[P(C_6H_9)(C_6H_{11})_2]Cl(CO)$		300	$\nu(C\equiv O)$ 1940 $\nu(C=C)$ 1655
$[P(C_6H_{11})_3]Rh[P(C_6H_9)(C_6H_{11})_2]Cl$		275	$\nu(C=C)$ 1510
$[P(C_6H_{11})_3]_2RhClC_2H_4$		280	$\nu(C=C)$ 1510
$H_2[P(C_6H_{11})_3]_2RhCl$	2150	290	
$H_2[P(C_6H_{11})_3]_2RhCl(NC_6H_7)$	2130/2080	235	
$H_2[P(C_3H_7)_3]_2RhCl$	2160	285	
$H_2[P(C_3H_7)_3]_2RhClNC_6H_7$	2130/2090	240	

TABLE 3

^{31}P NMR DATA (δ, ppm; (δ(B) is the chemical shift of the phosphorus atom in the ring. Spectra recorded in C_7D_8 with respect to 85% H_3PO_4).

Compound	δA($J(^{31}P—^{103}Rh)$)	δB($J(^{31}P—^{103}Rh)$)	J(P—P)
$P(C_6H_{11})_3$	−46.8		
$[P(C_6H_{11})_3]_2IrCl(CO)$	−30.9		
$[P(C_6H_{11})_3]Ir[P(C_6H_9)(C_6H_{11})_2]Cl(CO)$	−30.9		
$[P(C_6H_{11})_3]\overline{Ir[P(C}_6H_9)(C_6H_{11})_2]Cl$ [a]	+3.1	+20.8	427
$[P(C_6H_{11})_3]\overline{Ir[P(C}_6H_9)(C_6H_{11})_2]Cl$ [b]	−12.9	−35.6	356
$H_2[P(C_6H_{11})_3]\overline{Ir[P(C}_6H_9)(C_6H_{11})_2]$ [a]	+2.6	+20.9	419
$H_2[P(C_6H_{11})_3]\overline{Ir[P(C}_6H_9)(C_6H_{11})_2]$ [b]	−13.6	−33.3	337
$H_2[P(C_6H_{11})_3]\overline{Ir[P(C}_6H_9)(C_6H_{11})_2]$ [b]	−14.3	−30.6	335
$[P(C_6H_{11})_3]_2IrClC_2H_4$	−8.6		
$H_2[P(C_6H_{11})_3]_2IrCl$	−41.9		
$H_2[P(C_6H_{11})_3]_2IrCl(NC_6H_7)$	−23.0 (br)		
$H_2[P(C_3H_7)_3]_2IrCl(NC_6H_7)$	−30.7		
$[P(C_6H_{11})_3]_2RhCl(CO)$	−36.8 (118.6)		
$[P(C_6H_{11})_3]Rh[P(C_6H_9)(C_6H_{11})_2]Cl(CO)$	−36.7 (118.6)		
$[P(C_6H_{11})_3]\overline{Rh[P(C}_6H_9)(C_6H_{11})_2Cl]$ [a]	−46.3 (118.1)	−21.1 (129.7)	354
$[P(C_6H_{11})_3]_2RhCl(C_2H_4)$	−47.2 (113.7)		
$H_2[P(C_3H_7)_3]_2RhCl$	−57.4 (113.0)		
$H_2[P(C_3H_7)_3]_2RhCl(NC_6H_7)$	−57.4 (113.0)		

[a] A $4\frac{1}{2}$ membered ring is present. [b] $5\frac{1}{2}$ membered ring is present.

The ^{1}H NMR chemical shifts of the metal bound protons of the mixture IVa, IVb and IVc, could not be obtained because considerable line broadening was found at all the measured temperatures (—50°C to +50°C). The ^{31}P NMR spectrum, although not very sharp, was reasonably well resolved at —20°C (Table 3).

Discussion

Numerous reports [16] have shown that organic molecules can serve as a hydrogen source for the formation of hydridometal or hydrogenated products. Most of these compounds have reactive C—H bonds for example formic acid [17], alcohols, alkoxides [18], ethers [19,20] and benzyl [21,22] or allyl [23] groups. Very few dehydrogenation reactions involve C—H bonds of purely aliphatic groups, which are generally unreactive. One report describes the hydrogenation of cyclohexane to benzene [24]. Most dehydrogenation reactions of aliphatic groups involve ligands which are bound to the metal via a hetero atom, resulting in an activation of the aliphatic group, the so-called proximity effect.

Clark [25] for example isolated {1,6-bis(diphenylphosphino)-*trans*-3-hexene}-chlorometal (metal = Rh, Ir) after treatment of 1,6-bis(diphenylphosphino)-hexane with the metal(I) complexes. The nearness of the C—H orbitals to the metal orbitals before the reaction and the chelate structure of the product are conducive to the reaction. Deeming [26] obtained dehydrogenated products from the reaction of triethylphosphine with $Os_3(CO)_{12}$. This reaction can take place because the phosphorus atom is bound to one osmium atom, so that the aliphatic group can react intramolecularly with a second one.

The partial dehydrogenation of tricyclohexylphosphine which we describe belongs to the same class of reactions. The two most likely pathways of the reac-

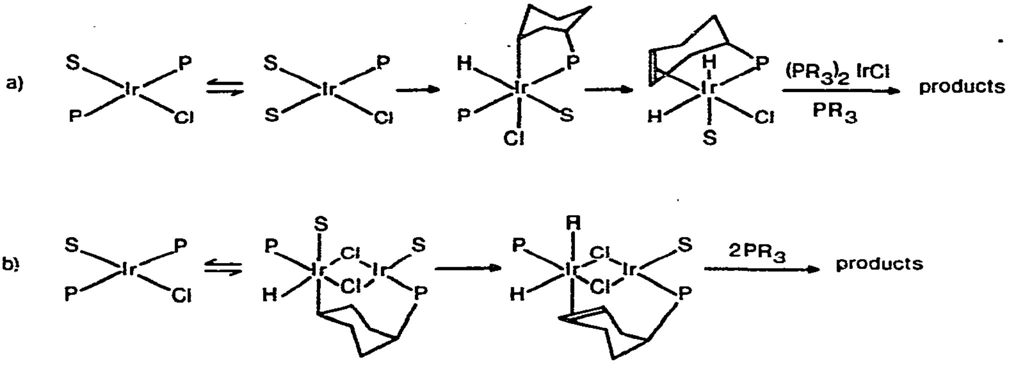
TABLE 4

^1H NMR AND ^{13}C NMR DATA (^1H chemical shifts (δ, ppm) relative to TMS, spectra in C_7D_8)

Compound	${}^{H}{>}C{=}C{<}^{H}$	M—H	$J(^{31}P-^{1}H)^a$	$J(^{103}Rh-^{1}H)$	^{13}C(double bond)	$(J(^{13}C-^{103}Rh)$
$P(C_6H_{11})_3Ir\underline{P(C}_6H_9)(C_6H_{11})_2Cl(CO)$	5.7 (br)				126.9/126.4	
$P(C_6H_{11})_3\overline{IrP(C}_6H_9)(C_6H_{11})_2Cl$					40.2/36.0	
$H_2[P(C_6H_{11})_3]_2IrCl$		−33	(12.5) t			
$H_2[P(C_3H_7)_3]_2IrCl$		−33	(12.0) t			
$H_2[P(C_3H_7)_3]_2Cl(NC_6H_7)$		−23.5/−26.2	(16.17) 2 X q	$J(^1H-^1H)$ 8		
$[P(C_6H_{11})_3]Rh\underline{[P(C}_6H_9)(C_6H_{11})_2]Cl(CO)$	5.7				126.8	
$[P(C_6H_{11})_3]\overline{Rh[P(C}_6H_9)(C_6H_{11})_2]Cl$					59.2/53.0	(13.9/14.8)
$H_2[P(C_6H_{11})_3]_2RhCl$		−22.5(14) dt		27		
$H_2[P(C_3H_7)_3]_2RhCl$		−20.5(14) dt		21		

[a] t, triplet; dt, doublet of triplets; q, quartets.

SCHEME 2. Possible routes for the dehydrogenation reaction of $(C_6H_{11})_3P$ coordinated to iridium(I).



tion will now be described (Scheme 2).

The first step of the reaction in both routes is the dissociation off of one phosphine. This is necessary because metallated products cannot be formed when two phosphine ligands are attached to the metal. Studies of a molecular model show that upon metallation the cone angle of the metallated phosphine increases to about 220°, which obstructs coordination of an unmetallated phosphine in the *trans* position. In route a, which does not involve dimerisation of the formally two-coordinate intermediate, a metallated product is formed, followed by β-hydrogen abstraction, resulting in formation of a $4\frac{1}{2}$ or $5\frac{1}{2}$ membered ring. This ring is formed by the metal atom, the phosphorus atom and the double bond system. Finally an intermolecular hydrogen transfer to a $[P(C_6H_{11})_3]_2IrCl$ molecule must occur to give the products. However, upon reaction of H_2 with IIa/IIb the products IVa/IVb/IVc were formed, and no H_2 transfer occurred upon reaction to $[P(C_6H_{11})_3]_2IrCl$. Clark [25] found that the complex [(1,6-(diphenylphosphino)-*trans*-3-hexene)chloroiridium] binds hydrogen reversibly. The lower stability of this hydrido complex may be associated with the lower basicity of the phosphine in this complex.

Therefore we prefer route b, involving an intermediate dimeric species containing one or two phosphines per metal atom. After the metallation reaction a β-hydrogen abstraction takes place, and then only a rearrangement of the double bond from one metal center to the other is necessary to give the products.

The change in the nature of the reaction of triisopropylphosphine with $[(COT)_2IrCl]_2$ when carried out in the presence or the absence of γ-picoline may have the following origins; coordination of the co-ligand to $Ir[P(C_3H_7)_3]_2Cl$ increases slightly the negative charge on the metal, and thus promotes an oxidative addition reaction. Furthermore, the cyclometallated product is stabilized because the metal becomes coordinatively saturated upon coordination of γ-picoline. In the absence of the co-ligand, higher reaction temperatures are necessary, and this leads to dihydrido products.

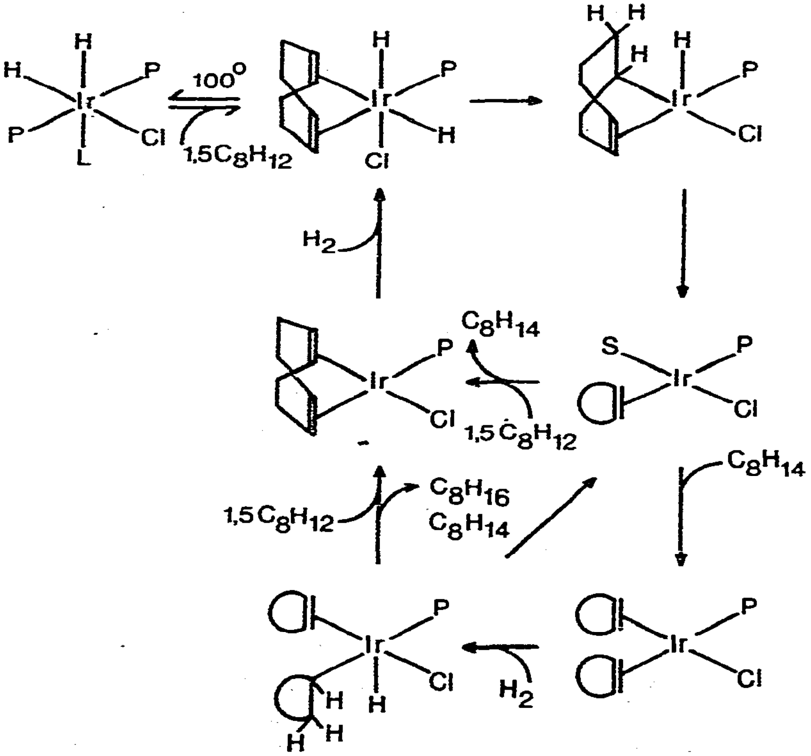
Catalytic activity of the compounds

The catalytic activity of phosphinorhodium(I) compounds in the hydrogenation of olefins is well known [27,28]. The general trend is that with the more basic phosphines the metal—hydrogen bonds in the intermediates are more stable, and hence the hydrogenation rates are lower [29]. For iridium the metal—hydrogen bond is stronger for a given phosphine than with rhodium, resulting in a lower catalytic activity [30] for the iridium complexes. However, we found that compound I hydrogenates olefins rather well at about 100°C and 1 atmosphere hydrogen pressure. A typical experiment gave complete conversion of 10 ml of 1,5-cyclooctadiene into approximately equal amounts of cyclooctene and cyclooctane during 3 hours in the presence of 200 mg catalyst.

The compound $Ir_2H_2Cl_2(1,5\text{-}C_8H_{11})(PPh_3)_2$ was reported by Gargano [31] to isomerise and hydrogenate [32] 1,5-cyclooctadiene. We tried to prepare the corresponding compound with $P(C_6H_{11})_3$ starting from $(1,5\text{-}C_8H_{12})Ir[P(C_6H_{11})_3]Cl$. Examination of the products after 10 minutes under a hydrogen atmosphere at room temperature in various solvents revealed the presence of an hydridoiridium species, probably $[H_2IrP(C_6H_{11})_3Cl]_n$ (ν(IrH) 2260/2240 cm^{-1}); upon treatment with γ-picoline this gave an insoluble white dihydrido species (ν(IrH) 2275/2215 cm^{-1}). The 1,5-cyclooctadiene was completely converted into cyclooctane. This demonstrates that $P(C_6H_{11})_3$ promotes the hydrogenation of 1,5-cyclooctadiene by the metal more effectively then PPh_3. These results suggest the following mechanism for hydrogenation with complex I (Scheme 3).

The chelating 1,5-cyclooctadiene competes more successfully for the empty coordination sites than cyclooctene. As long as this ligand is available it is hy-

SCHEME 3. Proposed mechanism for the hydrogenation of 1,5-cyclooctadiene with $H_2[P(C_6H_{11})_3]_2IrCl(NC_6H_7)$.



drogenated to cyclooctene. Only when the amount of cyclooctene becomes large does further hydrogenation occur to produce cyclooctane.

Conclusions

Dehydrogenation reactions of non-activated C—H bonds are promoted by the proximity effect, the coordinative unsaturation of the metal, and the formation of metal—olefin complexes. The influence of weakly coordinating ligands may have a pronounced effect on the reactions at the metal center.

The very different reactions of $P(C_6H_{11})_3$ compared with those of PPh_3 with transition metals appear to arise from the unusual steric requirements of this aliphatic phosphine as well as from the higher basicity.

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