Formation and Properties of Complexes of Type $IrH_3(PR_3)_2L$

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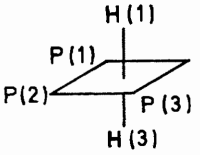
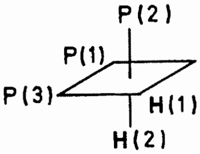
Summary $IrH_5(PEt_2Ph)_2$ reacts with a variety of ligands L to give compounds of the type $IrH_3(PEt_2Ph)_2L$ and the ^1H (hydride) n.m.r. patterns of *fac*- and *mer*-IrH_3(tertiary phosphine)$_3$ have been analysed for the first time.

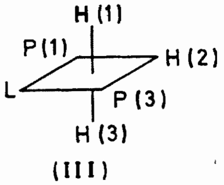
WE have reported[1] that the complex, previously formulated as a trihydride $IrH_3(PEt_2Ph)_2$,[2] is in fact a pentahydride, $IrH_5(PEt_2Ph)_2$. This complex, when treated with 1 mole proportion of PEt_2Ph in benzene evolves hydrogen and gives mainly *mer*-$IrH_3(PEt_2Ph)_3$ configuration (I) together with a few percent of *fac*-$IrH_3(PEt_2Ph)_3$ configuration (II).



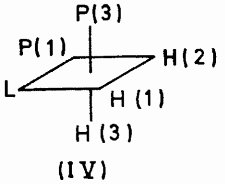
(I)



(II)



(III)



(IV)

Previously the ^1H n.m.r. (hydride) spectrum of *mer*-$IrH_3(PEt_2Ph)_3$[2] and *mer*-$IrH_3(PPh_3)_3$[3] have been reported to be 1 : 3 : 3 : 1 quartets. We now find the hydride resonance of $IrH_3(PEt_2Ph)_3$ (Table 1) to consist of a double doublet of 1 : 2 : 1 triplets due to H(1) and H(3) (I) and a double triplet of triplets due to H(2) *i.e.* it is the pattern expected for stereochemistry (I) and not that of a fluxional molecule. With the compounds $OsH_4(PMe_2Ph)_3$,[4] $ReH_5(PMe_2Ph)_3$,[5] and $WH_6(PMe_2Ph)_3$[6] the hydridic hydrogens are apparently equivalent and these hydrides are possibly fluxional.

We now find that other ligands (L) react with $IrH_5(PEt_2Ph)_2$ in benzene with hydrogen evolution to give trihydrides of type $IrH_3(PEt_2Ph)_2L$ L = PPh_3, $AsMe_2Ph$, $SbPh_3$, SMe_2, $P(OMe)_3$, $P(OMe)_2Ph$, or MeNC. The reactions are readily followed by n.m.r., which shows the yields to be high and the stereochemistry of the major ($\geqslant 90\%$) product to be (III). The other, and minor, product is *fac*-$IrH_3(PEt_2Ph)_2L$ (IV) formed in yields of from *ca.* 1% for L = $AsMe_2Ph$ to *ca.* 10% for L = SMe_2 or $SbPh_3$. N.m.r. data for the complexes of configuration (III) are given in Table 1. The complexes of configuration (III) which have so far been isolated and characterised are with L = $P(OMe)_3$, $AsMe_2Ph$, or $SbPh_3$. Thus the major reaction path stereospecifically gives a complex of stereochemistry (III). The starting complex $IrH_5(PEt_2Ph)_2$ also has its PEt_2Ph ligands in mutually *trans*-positions (from its almost zero dipole moment).[2]

When $IrH_5(PEt_2Ph)_2$ is treated with carbon monoxide some $IrH_3(CO)(PEt_2Ph)_2$ of configuration (III) is formed in solution (n.m.r. evidence, Table 1) but loss of another mole of hydrogen occurs readily giving $IrH(CO)_2(PEt_2Ph)_2$, for which the hydride resonance is a triplet at τ 21·57, J_{PH} = 24·9 Hz. Complexes of the type $IrH_3(PEt_2Ph)_2L$ (IV) with L = SMe_2 or $SbPh_3$ give spectra of the AA′MXX type. These spectra are only interpretable if $J_{P(1)H(1)}$ and $J_{P(1)H(3)}$ are opposite in sign. The data are given in Table 2. Since in *trans*-$PtHCl(PEt_3)_2$ ${}^2J_{PMH} = -14\cdot4$ Hz[7] and in *trans*-$PdI_2(PMe_3)_2$ $J_{PMP} = +572$ Hz[8] it seems likely that the upper set of signs in Table 2 is correct. Analysis of the n.m.r. pattern of *fac*-$IrH_3(PEt_2Ph)_3$ as an AA′A″XX′X″ pattern[9,10] gives the data in Table 2; the resonances are too broad to determine $J_{H(1)H(2)}$. The hydride resonances of complexes of the type *fac*-IrH_3(tertiary phosphine)$_3$ have not previously been analysed. We have also treated $IrH_5(PEt_3)_2$ with $AsMe_2Ph$ giving $IrH_3(PEt_3)_2(AsMe_2Ph)$ of configuration (III). For this complex double resonance experiments show that $J_{P(1)H(1)}$ and $J_{P(1)H(2)}$ have the same sign (probably negative).

TABLE 1

${}^1H$ *n.m.r. data for complexes of the types* $IrH_3(PEt_2Ph)_2L$ *and* $IrH_3(PEt_3)_2L$. J-*values in Hz: benzene solution*

	H *trans* to H				H *trans* to L		
L	τ_H	$J_{P(1)H(1)}$	$J_{H(1)H(2)}$	$J_{LH(1)}$	τ_H	$J_{P(1)H(2)}$	$J_{LH(2)}$
			$IrH_3(PEt_2Ph)_2L$				
PEt_2Ph	21·82	16·8	4·6	14·2	23·54	23·0	114·6
PPh_3	21·25	16·9	4·2	13·8	23·31	22·9	120·8
$AsMe_2Ph$	21·81	16·7	4·4	—	25·53	21·4	—
$SbPh_3$	21·72	16·1	3·4	—	24·95	19·7	—
SMe_2	20·89	17·2	4·8	—	28·43	20·3	—
$P(OMe)_3$	21·71	16·8	4·8	14·6	22·57	21·5	186·4
$P(OMe)_2Ph$	21·34	16·6	4·7	13·6	22·54	21·7	163·6
CO	20·79	16·5	4·8	—	21·58	20·7	—
MeNC	21·50	16·7	4·9	—	23·36	20·8	—
			$IrH_3(PEt_3)_2L$				
PEt_3	22·87	16·1	4·6	15·2	24·40	23·4	115·3
$AsMe_2Ph$	22·42	17·0	4·6	—	25·94	21·2	—

TABLE 2

${}^1H$ *n.m.r. data for complexes of types* $IrH_3(PEt_2Ph)_2L$, *configuration* (IV): *in benzene*

L	$\tau_{H(1)}$	$J_{P(1)H(1)}$	J_{HH}	$J_{P(1)H(3)}$	$\tau_{H(2)}$	$J_{P(1)H(2)}$
PEt_2Ph	21·94	±120	?	∓17	21·94	∓17
$SbPh_3$	22·83	±109·3	*ca.* 0	∓18·8	23·96	16·3
SMe_2	21·00	±131·6	4·0	∓20·4	27·44	16·4

We thank the Science Research Council and Imperial Chemical Industries Ltd. for financial support.

(*Received, May* 19*th*, 1970; *Com.* 779.)

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