Inorganica Chimica Acta, 63 (1982) 209–211 209

The Reactions of Phosphorus- and Arsenic-containing Multidentate Ligands with some Iridium Complexes.
Part V. The Formation of Octahedral Complexes [$IrHX_2T$]

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Received April 13, 1982

The new series of iridium compounds of the type $IrHX_2T$, *where* X = *Cl, Br and* $T = (\text{o-}Ph_2LC_6H_4)_2L'$ *as TP (L = L' = P); PDAS (L = As, L' = P); ASDP (L = P, L' = As); TAS (L = L' = As) have been prepared and characterized (only in the X = Br, T = TAS case was the complex* $IrBr_3TAS$ *obtained instead). The nature of these products has been investigated by i.r. spectroscopy and their stereochemistry has been assigned on the basis of* ^1H *and* ^{31}P *nmr spectral analysis. Evidence is given that the isomer having the meridional structure is always preferred, probably on steric grounds, due to the crowding of the phenyl groups.*

Other iridium hydrides, probably ionic, have been observed in the same preparation but not identified because of their instability.

An earlier publication described the reaction of [$IrHX_2(Ph_3P)_3$] where X = Cl or Br, with quadridentate ligands Q such as $(o\text{-}Ph_2LC_6H_4)_3L'$ where L and L' = P or As, obtaining complexes of the type [$Ir(PPh_3)Q$] [BPh_4], [IrHXQ] [BPh_4], [IrXQ] [1].

We report here on the reaction of [$IrHCl_2(Ph_3P)_3$] (ν(Ir–H) = 2199 cm^{-1}), and [$IrHBr_2(Ph_3P)_3$] (ν(Ir–H) = 2224 cm^{-1}) with the potentially tridentate ligands $T = (o\text{-}Ph_2LC_6H_4)_2L'Ph$ as TP (L = L' = P) [2]; PDAS (L = As, L' = P); ASDP (L = P, L' = As); TAS (L = L' = As) [3, 4], which give complexes of the type [$IrHX_2T$].

Experimental

The ligands PDAS and ASDP were prepared from $o\text{-}Ph_2AsC_6H_4Br$, BuLi, $PhPCl_2$, and $o\text{-}Ph_2PC_6H_4Br$, BuLi, $PhAsI_2$ respectively as described for TP and TAS in references [2–4].

In a typical reaction equimolecular amounts of [$IrHX_2(Ph_3)_3$] and of T were allowed to react in chlorobenzene, refluxing for three hours under nitrogen. The crude product, obtained by rotary evaporation of the solvent, was washed with petroleum ether to remove Ph_3P and then obtained as a white, microcrystalline, non-electrolyte solid after recrystallization from CH_2Cl_2/EtOH. Some physical and analytical data are reported in Table I and are consistent with an [$IrHX_2T$] formulation. C, H analyses were performed by classical semimicro methods, halogen with the standard Carius method, phosphorus spectrophotometrically with the molybenum blue technique, iridium and arsenic by atomic absorption using a Perkin Elmer mod. 603 spectrophotometer.

The infrared spectra were recorded as nujol mulls using a Perkin Elmer mod. 325 instrument.

The nmr spectra were run on a Brücker mod. HX 90 E spectrophotometer by the Eidgenossische Technische Hochschule, Zürich, Switzerland, with the details reported in Table II.

TABLE I. Analytical Data and Some Physical Properties.

Compound	Yield	Dec. point °C	C% found (req.)	H%	X%	Ir%	P%	As%	ν(Ir–H) cm^{-1} nujol
$IrHCl_2TP$	78%	245–50°	56.30(56.38)	3.15(3.83)	7.79(7.93)	21.73(21.48)	10.39(10.39)		2210
$IrHBr_2TP$	74%	275–80°	50.75(51.28)	3.22(3.48)	15.20(16.25)	19.67(19.54)	9.41(9.45)		2212
$IrHCl_2PDAS$	65%	245–50°	51.12(51.34)	3.98(3.49)	7.36(7.22)	19.30(19.56)		15.83(15.25)	2193 and 2097
$IrHBr_2PDAS$	63%	250–55°	47.35(47.08)	3.81(3.20)	14.77(14.92)	17.45(17.94)		15.52(13.98)	2193 and 2109
$IrHCl_2ASDP$	73%	255–60°	53.12(53.74)	3.74(3.65)	7.30(7.55)	20.29(20.47)		8.22(7.98)	2191 and 2121
$IrHBr_2ASDP$	71%	275–80°	48.84(49.09)	3.43(3.34)	15.10(15.55)	18.44(18.70)		7.92(7.29)	2195 and 2130
$IrHCl_2TAS$	32%	260–65°	49.03(49.14)	3.65(3.34)	6.76(6.91)	18.38(18.72)		20.90(21.89)	2174
$IrBr_3TAS$	5%		41.86(42.24)	3.17(2.78)	19.02(20.07)	15.92(16.09)		20.00(18.82)	–

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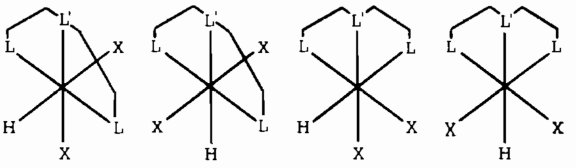
TABLE II. Nmr Parameters^a of Complexes [$IrHX_2T$].

Compound	$\delta\,^{31}P^b_{apical}$	$\delta\,^{31}P^b_{equat.}$	$\delta\,^1H^c$	$^2J(P,P)^d$	$^2J(P,H)^d$
[$IrHCl_2TP$]	56.2	24.1	−19.55	*ca.* 2.5	12.5
[$IrHBr_2TP$]	57.1	20.3	−19.11	3.0	11.8
[$IrHCl_2ASDP$]	–	27.1^e	−21.47	–	12.0
[$IrHBr_2ASDP$]	–	23.5	−20.51	–	11.8
[$IrHCl_2PDAS$]^f	62.7	–	−20.56	–	15.1
[$IrHBr_2PDAS$]^g	65.8	–	−19.54	–	13.5
[$IrCl_3TP$]	35.5	14.6	–	*ca.* 3	–

^{a}Measured as $CDCl_3$ solutions. ^{b}Relative to external H_3PO_4; in ppm (±0.1). ^{c}Relative to TMS, in ppm. ^{d}In Hz (±0.8). ^{e}A second ^{31}P signal, of low intensity, at 35.4 ppm is also observed. Selective decoupling experiments indicate that this species is a hydrido complex, *e.g.*, isomer (2) or (4). ^{f}A second ^{31}P signal, of low intensity, is observed at 34.3 ppm. Selective decoupling experiments indicate that this species is not a hydrido complex. Its position suggests that this signal may be due to [$IrCl_3$-PDAS]. ^{g}A second ^{31}P signal, of low intensity, is observed at 34.2 ppm. Also this species is not a hydrido complex and is due to the presence of a species such as [$IrClBr_2PDAS$].

Results and Discussion

For these complexes [$IrHX_2T$] a maximum number of four isomers, as shown below, could exist:



(1) (2) (3) (4)

The products obtained using TP as ligand, [$IrHX_2TP$], (X = Cl and Br) show only one ν(Ir–H) band at 2210 and 2212 cm^{-1} respectively. The ir spectra of the freshly prepared solution of the corresponding PDAS species show one ν(Ir–H) band at 2193 cm^{-1} (X = Cl and Br). However, on standing in solution, the products slowly isomerize reaching equilibrium where the above species are present with small amounts of another compound with ν(Ir–H) at 2097 and 2109 cm^{-1} respectively. Also the complexes with ASDP show the existence of two isomeric forms in solution (see Table I).

Structural assignments for the TP complexes and for the major products with PDAS and ASDP can be made on the basis of the ^1H and ^{31}P nmr data. The isomeric form of the [$IrHCl_2(TP)$] obtained is unambiguously deduced from its ^{31}P and ^1H nmr spectra (see Table II). The ^{31}P resonances of P_{apical} and $P_{equat.}$ are easily assigned on the basis of their relative intensities and of the multiplicities of the signals. The values of the $^2J(P,H)$ coupling constants, *ca.* 12 Hz, to *both* types of phosphorus atoms, are typical for *cis*-mutual positions of the two coupled atoms [5]. This all *cis* P–H arrangement is only compatible with structure (1).

The nmr data for [$IrHX_2(ASDP)$] (X = Cl and Br) are consistent with structures (1), (2) and (4) while the data for [$IrHX_2(PDAS)$] are consistent with structures (1) and (3) only. As it is found [6] that the ^1H nmr chemical shifts of iridium hydrides of the type [$IrHX_2L_3$] (X = Cl and Br; L = R_3P or R_3-As) with H-atoms in *trans*-position to phosphorus or arsenic atoms (*i.e.*, with structures equivalent to those of types (2), (3) and (4)) resonate between −12 and −15 ppm and that H-atoms in *trans*-positions to halogen atoms resonate above −20 ppm, we propose that the complexes [$IrHX_2T$] (T = PDAS and ASDP) also have structure (1). Thus it appears likely that the isomer having the meridional structure (1) is always preferred, probably on steric grounds due to the crowding of the phenyl groups.

The reaction of [$IrHBr_2(Ph_3P)_3$] with TAS did not give [$IrHBr_2TAS$] and only [$IrBr_3TAS$] could be characterized. This compound was described elsewhere [7]. In the mother liquor an amorphous white yellow solid was obtained. It reacts with sodium tetraphenylborate to give amorphous intractable products that show a large band in the ν(Ir–H) region. Similar amorphous solids, but in very low amounts, were obtained in all the other reactions (except in the TP case).

All attempts made to obtain satisfactory samples of these amorphous solids for analysis did not give consistent results, because of instability.

Acknowledgements

The authors are indebted to Prof. L. M. Venanzi for the nmr spectra of the compounds and for helpful suggestions.

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