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NEW ISOCYANIDE DERIVATIVES OF IRIDIUM(III) HYDRIDE

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SUMMARY

The preparation and properties of some iridium(III) isocyanide hydrides of general formula $IrH_2X(p\text{-}MeC_6H_4NC)(Ph_3As)_2$ are described, where X is Cl, Br, I, F, or N_3. The stereochemistry of these new compounds is discussed on the basis of their IR and NMR spectra.

INTRODUCTION

There is much current interest in the chemistry of transition metal compounds with isocyanide ligands and of closely related compounds[1]. In a preliminary note[2], we described a series of iridium(III) compounds in which isocyanide and hydride ligands were present simultaneously; these compounds were prepared from $IrH_3(Ph_3As)_2$ by the general reaction:

$$IrH_3(Ph_3As)_2 + CNR \rightarrow IrH_3(CNR)(Ph_3As)_2$$

(R = ethyl, C_6H_{11}, *p*-tolyl, *p*-anisyl). In this paper, we describe some derivatives of the general formula IrH_2X(*p*-tolylisocyanide)$(Ph_3As)_2$ (X = Cl, Br, I, F, N_3), which represent some of the very few isocyanide compounds of iridium so far described. Except for the fluoro-derivative, these compounds are generally soluble, and suitable for NMR measurement.

EXPERIMENTAL

Some properties of the new compounds and their spectra are reported in Table 1. Molecular weight determinations (±5%) were carried out in benzene solution (ca. 1%) on a Mechrolab Osmometer 301-A. Melting points were determined in the air on a Leitz apparatus. Infrared spectra were recorded on a Perkin–Elmer 457 spectrometer. ^1H NMR spectra were recorded on a Perkin–Elmer R-10 instrument operating at 60 MHz and 33°, using tetramethylsilane as internal standard and $CDCl_3$ as solvent. The new compounds are indefinitely stable to air, soluble in chloroform, benzene, and methylene chloride and insoluble in alcohols and acetone. All are diamagnetic, as shown by their NMR spectra.

TABLE 1

Compound	Formula	Colour	M.p. (°C)	Analysis found (calcd.) (%)				Mol. wt. found (calcd)	IR data[a] (cm^{-1})	^1H NMR		
				C	H	N	Cl or F			Hydride signals		CH_3
(I)	IrH_3(p-tolyl-NC)$(Ph_3As)_2$	White	152	57.17 (57.20)	4.38 (4.37)	1.36 (1.51)		940 (926)	2120 s 2080 m; 2060 m	22.0 t	23.3d[b]	7.75
(II)	IrH_2(p-tolyl-NC)$(Ph_3As)_2Cl$	White	173	54.96 (54.90)	4.00 (4.06)	1.47 (1.46)	3.35 (3.65)	835 (960)	2140 s 2185 m	19.5	19.6	7.77
(III)	IrH_2(p-tolyl-NC)$(Ph_3As)_2Br$	Pale-yellow	185–188 (dec.)	52.30 (52·50)	4.00 (3.90)	1.27 (1.40)		1050 (1005)	2140 s 2185 m	20.01	20.11	7.78
(IV)	IrH_2(p-tolyl-NC)$(Ph_3As)_2I$	White	187–189 (dec.)	50.94 (50.23)	3.93 (3.73)	1.38 (1.33)		1010 (1052)	2145 s 2165 m	21.1	21.2	7.75
(V)	IrH_2(p-tolyl-NC)$(Ph_3As_2)F$	Pale-yellow	143–150 (dec.)	54.26 (55.90)	3.82 (4.14)	1.42 (1.48)	1.88 (1.98)	938 (942)	2150 s	19.58	19.68	7.82
(VI)	IrH_2(p-tolyl-NC)$(Ph_3As)_2N_3$	White	172–177 (dec.)	54.90 (54.60)	4.50 (4.07)	5.44 (5.78)		878 (967)	2020 s 2135 s	19.8 d	23.5 d[c]	7.72

[a] Nujol mull. [b] $J \approx 6$ Hz. [c] $J \approx 4$ Hz.

Trihydridobis(triphenylarsine)(p-tolylisocyanide)iridium(III), (I)

This compound was prepared by the method previously described[2].

Dihydridochlorobis(triphenylarsine)(p-tolylisocyanide)iridium(III), (II)

A solution of conc. hydrochloric acid (1 ml) in ethanol (20 ml) was added dropwise to a suspension of (I) (0.46 g, 0.5 mmoles) in ethanol (40 ml). The mixture was left at 65° for 30 min. On cooling and concentrating to 30 ml under reduced pressure a white crystalline product was obtained (0.20 g) and this was recrystallized from benzene by addition of ethanol.

Dihydridochlorobis (triphenylarsine)(p-tolylisocyanide)iridium(III), (III)

This compound was prepared analogously to compound(II), from (I) (0.46 g) and a solution of conc. hydrobromic acid (1 ml) in ethanol (20 ml). Yield 0.25 g.

Dihydridoiodobis(triphenylarsine)(p-tolylisocyanide)iridium(III), (IV)

This was prepared analogously to compound(II), from (I) (0.46 g) and solution of 57% hydriodic acid (1 ml) in ethanol (7.5 ml). Yield 0.22 g.

Dihydridofluorobis(triphenylarsine)(p-tolylisocyanide)iridium(III), (V)

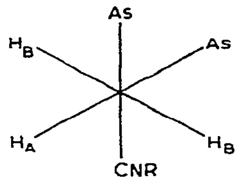
This compound was prepared analogously to compound (II), by reaction of (I) (0.46 g) in ethanol (30 ml) and ethanol solution (40 ml) of 5% HF. After 1 h at 60° with stirring, the suspension was evaporated to dryness; a crude product was obtained, which was purified by benzene elution through alumina (grade II). Compound (V) (0.18 g) was obtained by adding a large excess of hexane to the residue from the first eluates.

Dihydridoazidobis(triphenylarsine)(p-tolylisocyanide)iridium(III), (VI)

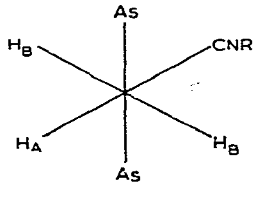
A concentrated solution of HN_3 in ether (20 ml) was added dropwise to a suspension of (I) (0.46 g) in ethanol and benzene (1/1, 40 ml). The reaction mixture was left for ca. 2 h at 80°. After cooling and concentrating, a white crystalline product was obtained by addition of benzene (2 ml) and methanol (20 ml). Yield 0.20 g.

DISCUSSION

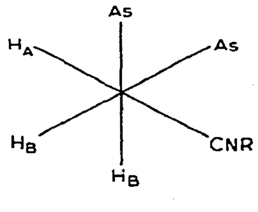
The data previously communicated[2] and reported more fully in Table 1 allow an unambiguous assignment of the structure of compound $IrH_3(Ph_3As)_2RNC$(I). The PMR spectrum, which displays a triplet at τ 22 and a doublet at τ 23.3 with $J_{AB} \approx 4$ Hz, confirms the presence of three hydride ligands; the possible structures of which are:



(A)



(B)

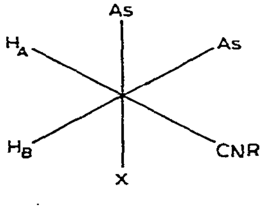


(C)

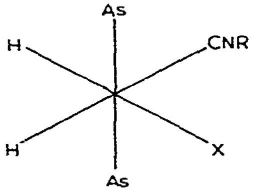
The IR spectrum, which has no band in the region 1700–1800 cm^{-1}, rules out structures (A) and (B), in which *trans* hydride ions are present.

The new halogeno-derivatives were prepared by treating (I) with the appropriate hydrogen halide or pseudohalide in ethanol. They are stable, crystalline, white or yellow solids. Elemental analyses, IR and PMR spectra are consistent with the general formula IrH_2X(*p*-tolylisocyanide)$(\text{Ph}_3\text{As})_2$.

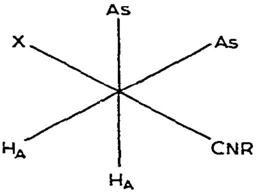
On the basis of their IR spectra (Table 1), compounds(II), (III) and (IV) have the hydrido ligands in a *cis*-octahedral configuration. Their possible structures are therefore:



(D)



(E)



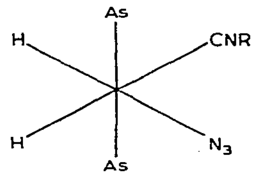
(F)

The PMR spectra of these compounds show two signals with the characteristic appearance of an AB system, with a very low coupling constant and with a low chemical shift difference ($\Delta\nu \approx 6$ Hz). This rules out the structure (F), in which the two hydrogen atoms are equivalent. Moreover, the variation of τ_H on changing the halogen ligand is very small, and much lower than that which is usually found when the halogen ligand is *trans* to the hydrogen[3,4]. This supports the view that the structure (D), in which the halogen atom is *cis* to the hydrogen atoms, is the most probable (see also the PMR data of Atkins *et al.*[5] interpreted according to Buckingham and Stephen's theory[6]). The small variations of τ_H in the spectra of the present compounds can be attributed to the inductive effect of the halogen atom. The replacement of hydrogen in compound (I) [structure (C)] by halogen of increasing electronegativity has the same effect as lowering the electron density of the metal; consequently the electron density on the hydride hydrogens must be lowered, and their PMR absorptions shifted to a lower field. The chemical shifts of the hydrides in the halogeno-derivatives are all smaller than those of compound (I), and they diminish in a fairly regular way with increasing electronegativity of the halogen, as predicted. Moreover, replacement of one hydride by one halide ligand of increasing electronegativity must cause a diminution of the back donation from the metal *d*-orbitals to the π^*-orbitals of arsine and isonitrile ligands. The consequent decrease of the Ir–C bond order would be expected to cause a rise in the wave number of the ν(CN) stretching vibration. The 2200–2000 cm^{-1} region contains both ν(CN) and ν(Ir–H) bands: the highest vibration observed is likely to be that for ν(CN), which is only slightly displaced from the value in the free ligand, and it rises in the predicted way. It must be added that, although some di-halogen-substituted derivatives of the type $\text{IrHX}_2(\text{Ph}_3\text{P})_2$ are known, in the present case it was possible to replace only one hydride hydrogen.

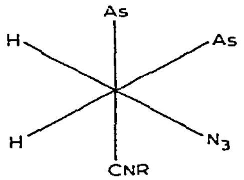
The PMR spectrum of IrH_2F(*p*-tolylisocyanide)$(\text{Ph}_3\text{As})_2$ (V) is poorly resolved in the hydride region: moreover, the ^{19}F NMR spectrum does not display a sufficiently high signal because of the low solubility of the compound. Nevertheless, the broad signal at $\tau \approx 20$ in the PMR spectrum is proof of the coupling of the hydride ligands with ^{19}F ($I = 1/2$). In addition, elemental analyses (including the determination of the fluorine, Table 1) and the PMR spectrum, which is similar to those of the other halogeno- derivatives, support the view that the formula and the structure of compound (V) are analogous to those of the others.

In the infrared spectrum of compound (V) only one strong band is present at 2150 cm^{-1}. Since the presence of the isocyanide and of hydride ligands have been demonstrated by the PMR spectrum (see also the nitrogen analysis, Table 1), this band may be attributed to the superposition of ν(Ir–H) and ν(CN).

The compound IrH_2N_3(*p*-tolylisocyanide)$(Ph_3As)_2$ (VI) shows two strong absorption bands in the infrared spectrum in the region 2000–2150 cm^{-1}; the higher absorption can be attributed to the isonitrile ligand and the lower to $\nu(N_3)$. The ν(Ir–H) absorption is probably obscured by the absorption at the higher frequency. The PMR spectrum, in addition to a signal at τ 7.7 caused by the CH_3 of the isonitrile ligand, shows a pair of doublets in the τ 20–24 region. This indicates that configuration of this compound is different from those of the compounds discussed above. The following structures can be suggested:



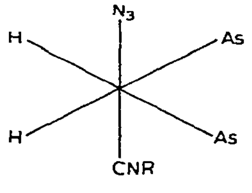
(G) [=(E)]



(H)

Structure (G) is the most probable if the high steric hindrance between the two bulky arsine ligands in structure (H) is taken into account. The separation of the hydride signals ($\Delta\tau \approx 4$) can be ascribed to the influence of the $-N_3$ ligand which is *trans* to one H^- and *cis* to the other.

We note finally that in some cases the compounds obtained from the reaction of IrH_3(*p*-tolylisocyanide)$(Ph_3As)_2$ with HN_3 showed only one strong band in the IR spectrum, at 2080 cm^{-1} with a shoulder, and only one hydride absorption at $\tau \approx 24$ (apart from the usual signal of the isonitrile CH_3). This may be taken as evidence for the formation, not easily reproducible, of an unstable isomer, probably:



(J) [=(F)]

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