

Preliminary communication

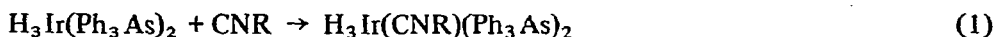
Isocyanide derivatives of iridium(III) hydride

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Apart from the mention of a few $[\text{Ir}(\text{CNC}_6\text{H}_4\text{-}p\text{-CH}_3)_4]^+$ derivatives¹, no compounds of iridium containing isocyanide ligands are known². We now describe the preparation of iridium(III) derivatives in which both isocyanide and hydride ligands are present simultaneously. These were obtained by reaction (1) which was carried out at room



temperature by stirring a benzene suspension of the starting material³ with the required quantity of CNR until a solution was obtained (ca. 2 days). The compounds and some of their properties are listed in Table 1.

The NMR data suggest a *cis*-configuration for the hydrido groups. Correspondingly, no band is present in the IR spectrum between 1700 and 1800 cm^{-1} , region typical of the *trans* H—Ir—H system. The 2200–2000 cm^{-1} region contains both $\nu(\text{CN})$ and $\nu(\text{IrH})$. Although a definitive assignment requires additional evidence, e.g.

TABLE 1

R in (1)	Analyses: found (calcd.) (%)				IR data ^b	Hydride signals ^c (τ units)	Purified from
	C	H	N	mol. wt. ^a			
ethyl	54.18 (54.5)	4.53 (4.43)	1.45 (1.62)	836 (864)	2130s; 2090m; 2075m	21.6 t, 22.6 d	PhH/MeOH
C ₆ H ₁₁	56.63 (56.35)	4.98 (4.80)	1.84 (1.93)		2128s; 2120m,sh; 2080m	21.73 t, 22.62 d	PhH/hexane
<i>p</i> -tolyl	57.17 (57.2)	4.38 (4.37)	1.36 (1.51)	940 (926)	2120s; 2080m; 2060m	20.88 t, 22.14 d	PhH/EtOH
<i>p</i> -anisyl	56.08 (55.9)	4.26 (4.28)	1.29 (1.49)	924 (941)	2120s; 2075m; 2060m	20.98 t, 22.21 d	PhH/hexane

^aOsmometry, 37°, ca. 1% benzene solution. ^bUpper line: $\nu(\text{CN})$; lower line: $\nu(\text{IrH})$ (nujol mull). ^cC₆D₆ solution at 33°; *J* was always ca. 3 Hz (Perkin-Elmer R-10 instrument, 60 Mc).

deuteration, the strongest and the highest vibration observed, at $2120\text{--}2130\text{ cm}^{-1}$, is likely to be $\nu(\text{CN})$, only slightly displaced from the value in the free ligand. Although the known isocyanide derivatives in which the metal has a formal oxidation state of +2 or of +3 generally show² higher $\nu(\text{CN})$ values than those in the free ligand (*i.e.* there is little or no π -back donation to the isocyanide ligand), the presence of a strongly σ -bonded hydrido group causes accumulation of electron density on the metal atom and makes π -back donation necessary. For comparison, the pair of compounds $\text{Cl}_3\text{Ir}(\text{CO})(\text{PhPEt}_2)_2$ and $\text{Cl}_2\text{HIr}(\text{CO})(\text{PhPEt}_2)_2$ may be considered: substitution of a Cl by a H atom makes π -back donation significant and lowers⁴ $\nu(\text{CO})$ from 2105 to 2033 cm^{-1} . In agreement with an observation by Adams⁵, two $\nu(\text{Ir-H})$ frequencies are observed, as required by the presence of two H-Ir-ligand systems.

The isolation of *cis*-hydrides by reactions of $\text{H}_3\text{Ir}(\text{Ph}_3\text{E})_2$ (E = P, As) with isocyanide and with other ligands⁶ suggests that the hydrido group has a trans labilizing influence.

ACKNOWLEDGEMENTS

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