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Alkyl and Aryl Compounds of Iridium and Rhodium. XXIV*. Reaction of Organoiridium Complexes Ir(R)(CO)(PPh$_3$)$_2$ with Hydrogen: Infrared Evidence for a Possible *mer, cis*-Isomer of IrH$_3$(CO)(PPh$_3$)$_2$

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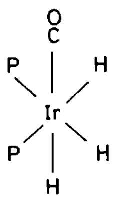
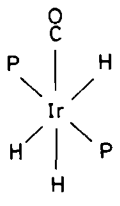
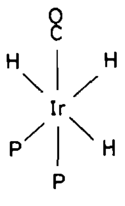
The past years have seen a renascent interest in the stereochemistry of one of the earliest complex iridium hydrides, IrH$_3$(CO)(PPh$_3$)$_2$ [2], as well as in the facile interconversion of its known isomers a-carbonyl-b,c,f-trihydridobis(triphenylphosphine)iridium(III) ('*fac*-isomer', **I**) and a-carbonyl-b,d,f-trihydridobis(triphenylphosphine)iridium(III) ('*mer, trans*-isomer', **II**) [3–6].



I



II



III

The third isomer with stereochemistry **III**, a-carbonyl-b,c,e-trihydridobis(triphenylphosphine)iridium(III) ('*mer,cis*-complex'), has been formulated by Malatesta [2] on the basis of the dipole moment of the respective material; however, the IR data given in ref. 2, ν(IrH), 2080 and 1785 cm^{-1} and ν(CO), 1965 cm^{-1}, are close to those observed by Harrod for the *mer,trans*-isomer **II**: ν(IrH), 2077, 2062, and 1780 cm^{-1} and ν(CO), 1962 cm^{-1} [5]. The δ(IrH) absorptions of **II**, the geometry of which has been established unambiguously by ^{1}H and ^{31}P NMR spectroscopy [5], occur at 845 and 809 cm^{-1} [5]. The *fac*-isomer **I**, likewise characterized by completely assigned NMR spectra [5], is reported to exhibit ν(IrH) at 2112, 2071, and 2057 cm^{-1}, the values of ν(CO) and δ(IrH) being 1953 cm^{-1} and 859, 852, 821, and 809 cm^{-1}, respectively [5].

In the course of studying the reaction of a series of organoiridium compounds of the type Ir(R)(CO)(PPh$_3$)$_2$ (R = CH$_3$, CH$_2$CMe$_3$, CH$_2$SiMe$_3$, C$_6$H$_5$, 2-MeC$_6$H$_4$, and 2,4,6-Me$_3$C$_6$H$_2$) [7] with hydrogen, we observed the facile formation of products of composition IrH$_3$(CO)(PPh$_3$)$_2$ in virtually quantitative yields:

$$\text{Ir(R)(CO)(PPh}_3)_2 + 2\text{H}_2 \longrightarrow \text{IrH}_3\text{(CO)(PPh}_3)_2 + \text{RH}$$

The complexity of the IR spectra of the materials thus produced suggested the presence of all three possible isomeric forms of the iridium hydride. In accord with earlier work [5] the relative intensities of the carbonyl and IrH absorptions originating from the different isomers were found to vary with time†.

When hexane suspensions of the alkyl or aryl precursors were stirred at room temperature with a constant stream of hydrogen passing through for less than half an hour, the infrared spectra of the products closely corresponded to that given for the *fac*-isomer (*vide supra*): ν(IrH), 2108, 2068, and 2065 cm^{-1}, ν(CO), 1950 cm^{-1}, as well as δ(IrH), 857, 849, 817, and 805 cm^{-1}. Stereochemistry **I** was therefore attributed to the materials thus obtained.

When the organoiridium complexes, again suspended in hexane, were allowed to react with hydrogen at room temperature for prolonged periods of time (1–3 h), the IR spectra of the hydride produced indicated the formation of what we believe to be a mixture of the two *mer*-isomers **II** and **III**. The presence of **II** was inferred from absorptions ocurring at 2078(br) and 1780(br) cm^{-1} [ν(IrH)], at 1960 cm^{-1} [ν(CO)], as well as at 844 and 805 cm^{-1} [δ(IrH)]. These wavenumbers are almost coincident with those found in the literature. Additional bands observed at 1986 cm^{-1} [ν(CO)] and at 840 and 827 cm^{-1} [δ(IrH)] were assigned to structure **III** (which then, similar to **II**, must be characterized by ν(IrH) values of 2078 and 1780 cm^{-1}) for the following reasons:

(1) The coincidence of the IrH stretching frequencies at 1780 cm^{-1} for the *trans*-H–Ir–H moieties of both **II** and **III** seems plausible since metal–hydrogen stretches occurring within this molecular fragment may be expected to remain essentially unaffected by an exchange of the CO and PPh$_3$ positions in the two isomers.

(2) Superposition of ν(IrH) (*trans* P) of **III** by ν(IrH) (*trans* CO) of **II** at 2078 cm^{-1} appears to be fortuitously due to resonance interaction of the IrH and CO vibrational levels of isomer **II**, which manifests itself through a shift of the ν(IrH) band to higher wavenumbers [8]. This interpretation is corroborated by deuteration experiments. A mixture of

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*For part XXIII see ref. 1.

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†Infrared spectra of KBr pellets or nujol suspensions of the complexes were recorded on a Perkin Elmer 325 spectrometer.

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$IrD_3(CO)(PPh_3)_2$ complexes prepared in the same way as the product assumed to contain isomers **II** and **III** of $IrH_3(CO)(PPh_3)_2$ showed CO stretching bands at 1986 and 1982 cm^{-1}. The 1986 cm^{-1} absorption is assigned to the deuterated analogue of isomer **III** (**III**-D_3) because ν(CO) of **III** is anticipated to be fairly insensitive to H/D exchange. Assuming that the 1982 cm^{-1} band arises from $IrD_3(CO)(PPh_3)_2$ of configuration **II** (**II**-D_3) and that the shift of 22 cm^{-1} observed on passing from **II** to **II**-D_3 represents the interaction energy of the two IrH and CO vibrational states of **II** [8], one can calculate the unperturbed wavenumber ν(IrH) of **II** according to $2078 - 22 = 2056$ cm^{-1}. This value corresponds to a ν(IrD) absorption found at 1501 cm^{-1} [ν(IrH)/ν(IrD) = 1.37] which is therefore assigned to **II**-D_3. The ν(IrD) band accompanying the 2078 cm^{-1} absorption of **III** is observed at 1510 cm^{-1} [ν(IrH)/ν(IrD) = 1.38]. The absorptions at 1780 cm^{-1} of both **II** and **III** are replaced by a band occurring at 1278 cm^{-1} in the corresponding deuterated isomers [ν(IrH)/ν(IrD) = 1.39].

(3) The variation of the relative intensities of the carbonyl and hydride absorptions from one preparation to another was found to be consistent with the assignments given above.

Isomer **III** appears to be unstable in solution, since the NMR spectra (^{31}P, ^{1}H) obtained for various samples which according to IR were conjectured to contain detectable amounts of **III** were those of the isomers **I** and **II** undergoing spontaneous isomerization, as previously described by Harrod [5].

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