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RELATIVE DIOXYGENATION RATES OF SOME *trans*-$Ir(CO)X(PR_3)_2$ COMPLEXES: THE EFFECT OF PHOSPHINE AND HALOGEN CHANGES

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Summary

Relative rates of dioxygen uptake by the complexes *trans*-$Ir(CO)X(PPh_2R)_2$ (R = Ph, Me, Et; X = F, Cl, Br, I) have been measured in dichloromethane and found to follow the order R = Ph < Et < Me and X = F < Cl < Br < I. The basicity of these *trans*-$Ir(CO)X(L)_2$ complexes, as measured by their affinity for dioxygen, is not reflected in the energy of the ν(CO) absorption in the parent compounds; a previous report that complex basicity $\propto 1/\nu(CO)$ does not hold for the complexes reported here.

Introduction

Studies on synthetic model compounds have, to a certain extent, provided a foundation for the formulation of criteria necessary for dioxygen uptake. In particular, a great deal of work has been performed on *trans*-chlorocarbonylbis(triphenylphosphine)iridium(I) and related compounds. Considering dioxygen addition (eqn. 1) as an acid-base reaction, where the metal complex acts as a

$$\text{Metal complex} + O_2 \rightleftharpoons O_2\text{-metal complex} \qquad (1)$$

Lewis base [1], then factors which increase electron density at the metal centre should, in the absence of unfavourable steric effects, enhance dioxygen addition. Vaska and Chen [2] have related the basicity of ligands in *trans*-$IrCl(CO)(L)_2$ species to the carbonyl stretching frequency in the complex: basicity $\propto 1/\nu(CO)$. Since the basicity of the complex determines the degree of oxygen binding, then dioxygen complex formation is also inversely related to ν(CO) in the parent complex. In this [2] and related studies [3—5] steric factors were found to be complicating. The basicity of the halide also affects dioxygen coordination. Thus, in *trans*-$Ir(CO)(O_2)(PPh_3)_2Cl$, which is a reversible dioxygenating system, the

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O—O distance is 130 ± 3 pm [6], whereas *trans*-$Ir(CO)I(PPh_3)_2$ irreversibly adds dioxygen and the resulting dioxygen has O—O = 147 ± 2 pm [7].

In the present study we report on the dioxygen affinity of the complexes *trans*-$Ir(CO)X(PPh_2R)_2$ (X = F, Cl, Br, I; R = Ph, Me, Et) in an attempt to examine more closely the combined effects of both phosphine and halide basicity. This is part of a larger investigation we are making on the dioxygen transporting abilities of iridium(I) complexes [8, 9].

Results and discussion

Table 1 lists the complexes, *trans*-$Ir(CO)X(PPh_2R)_2$, prepared, together with the analytical data and infrared absorptions ν(CO) and ν(Ir—X). In general the ν(CO) frequency shifts very little (± 3 cm^{-1}) when the complexes are dissolved in dichloromethane. The rate of dioxygenation was measured on a standard complex concentration in dichloromethane at a standard rate of dioxygenation. Dioxygenation was accompanied by the gradual disappearance of the original carbonyl peak and the growth of a new absorption peak ≈ 35 cm^{-1} higher in energy. The relative rates of dioxygenation of the complexes were determined from the intensities of the carbonyl peaks. By measuring their areas the ratio oxy/deoxy was calculated. A plot of time vs. oxy/deoxy allows an estimate of the time for half of the complex to be oxygenated ($t_{\frac{1}{2}}$, oxy/deoxy = 1), see Fig. 1.

Table 1 shows, not unexpectedly, that as the basicity of the phosphine increases and the electronegativity of the halogen decreases the rate of oxygenation also increases. With the phosphine constant, variation of the halide enhances the rate in the order $F < Cl < Br < I$. This is more clearly shown in the plot of halide vs. $t_{\frac{1}{2}}$ (Fig. 1). In all cases where X = F the rate is substantially slower than for the other three halides, especially in the *trans*-$Ir(CO)X(PPh_3)_2$ complexes, where

TABLE 1

ANALYTICAL, INFRARED AND KINETIC DATA FOR THE MONODENTATE PHOSPHINE COMPLEXES

Complex	Analysis (%)[a] C	Analysis (%)[a] H	ν(CO) (cm^{-1})[b]	ν(Ir—X) (cm^{-1})[b]	$t_{\frac{1}{2}}$ (min)
$IrF(CO)(PMePh_2)_2$	50.1 (50.7)	4.3 (4.06)	1944		32.0
$IrCl(CO)(PMePh_2)_2$	49.5 (49.4)	4.1 (3.96)	1959	310	13.5
$IrBr(CO)(PMePh_2)_2$	45.5 (46.2)	4.0 (3.71)	1966	357	11.5
$IrI(CO)(PMePh_2)_2$	42.7 (43.3)	4.1 (3.48)	1951		2.5
$IrF(CO)(PPh_3)_2$	57.9 (58.2)	3.7 (3.93)	1943	453	360.0
$IrCl(CO)(PPh_3)_2$	57.0 (57.0)	4.1 (3.85)	1946	313	75.0
$IrBr(CO)(PPh_3)_2$	53.6 (53.8)	3.8 (3.64)	1951		40.0
$IrI(CO)(PPh_3)_2$	49.2 (49.2)	4.0 (3.3)[c]	1953		25.0
$IrF(CO)(PEtPh_2)_2$	51.7 (52.2)	4.1 (4.5)	1937	420	37.0
$IrCl(CO)(PEtPh_2)_2$	51.3 (50.8)	4.4 (4.38)	1936	305	27.5
$IrBr(CO)(PEtPh_2)_2$	48.1 (47.7)	4.4 (4.12)	1942	352	21.0
$IrI(CO)(PEtPh_2)_2$	44.6 (44.9)	3.9 (3.86)	1946		6.75

[a] Calculated values in parentheses. [b] Nujol. [c] Analytical values given for oxygen adduct.

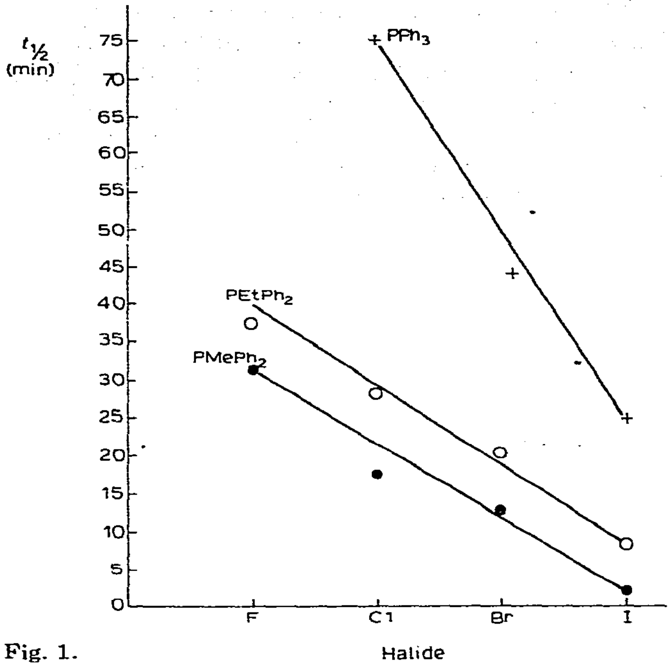

Fig. 1.

$t_{\frac{1}{2}}$ for $Ir(CO)F(PPh_3)_2$ is completely off the graph. Construction of a horizontal line from one plot to another intersects the plots at points where complexes show identical rates of oxygen uptake. This can result in imaginary complexes. For example, the graph shows that similar $t_{\frac{1}{2}}$ values exist for *trans*-$Ir(CO)F(PPh_2Et)_2$ and *trans*-$Ir(CO)Br_{0.5}I_{0.5}(PPh_3)_2$. However, a more reasonable use of the graph indicates that *trans*-$Ir(CO)F(PPh_2Me)_2$, *trans*-$Ir(CO)Cl(PPh_2Et)_2$ and *trans*-$Ir(CO)I(PPh_3)_2$ have similar $t_{\frac{1}{2}}$ values and, thus, similar rates of oxygenation. Other comparisons can be made on the graph, and the utility of such a graph is obvious.

The observations of Vaska and Chen [2] that the carbonyl stretching frequency of a complex, *trans*-$Ir(CO)XL_2$, is inversely related to the basicity of ligands L, do not seem to be valid for the extended series of phosphines (or halides) used in this study. As can be seen from Table 1 the $\nu(CO)$ frequencies do not follow any regular pattern whatsoever, either for change of phosphine or change of halide. There is always some risk in speculating about the significance of back-bonding in complexes which have not been proved to be isostructural, and it may well be that earlier trends [2] may have been coincidences rather than a true measure of electron density on the metal.

Experimental

All reactions were performed under nitrogen and solvents deaerated by refluxing under nitrogen. Elemental analyses were performed by the Microanalytical Service of this Department. Infrared spectra were recorded on a Perkin—Elmer 625 spectrophotometer.

The ligands were prepared using standard Grignard methods. The complexes of type *trans*-Ir(CO)XL$_2$ (L = PPh$_2$Me, PPh$_2$Et) were synthesised by ligand exchange from the corresponding *trans*-Ir(CO)X(AsPh$_3$)$_2$ complexes [10]. Complexes of type *trans*-Ir(CO)X(PPh$_3$)$_2$ were prepared by standard methods [11].

Dioxygenation was measured at room temperature by monitoring the ν(CO) absorption at $\approx$ 2000 cm^{-1}. A 1.43×10^{-4} *M* solution in dichloromethane was contained in a 5 cm^3 volumetric flask fitted with a rubber seal, through which passed three syringe needles allowing for entry of dioxygen, and access for sampling. Samples were taken at regular intervals.

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