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STRENGTH OF IRIDIUM—OLEFIN AND IRIDIUM—ACETYLENE BONDS

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Summary

Enthalpies of the dissociation reactions:

$IrX(CO)(PPh_3)_2(L)(cryst.) \rightarrow IrX(CO)(PPh_3)_2(cryst.) + L(g)$

($X = F, Cl, Br$, or I; $L = C_2F_4$ or C_4F_6) have been measured. These enthalpies decrease to a minimum value at $X = Br$, indicating an order of stability of $F > Cl > Br < I$.

Introduction

Previously [1] we reported enthalpies of the following dissociation reactions,

$IrX(CO)(PPh_3)_2(L)(cryst.) \rightarrow trans\text{-}IrX(CO)(PPh_3)_2(cryst.) + L(g)$

where L is tetrafluoroethylene, C_2F_4, or hexafluoro-2-butyne, C_4F_6, and X is F or Cl. Our findings showed a decrease in the enthalpies of dissociation along the series $F > Cl$. This is the reverse of the trend found by Vaska, Chen and Senoff [2] for the enthalpies of dissociation of the dioxygen adducts (L is O_2) in chlorobenzene solution, i.e. F 42.3, Cl 71.0, Br 85.4, and I 97.0 kJ · mol^{-1}, i.e. $F < Cl < Br < I$. Moreover, this latter also appears to be the trend for the ethylene complexes in that there is no measurable uptake of ethylene by $IrCl(CO)(PPh_3)_2$ in chlorobenzene solution at 298 K, whereas the iodo compound does absorb ethylene with an enthalpy change [3] of ΔH −49.3 kJ · mol^{-1}. Evidence for the tetracyanoethylene complexes is less clear, although the fluoro complex is stable [1], whereas the iodo complex is less so [4], implying an order $F > Cl > Br > I$, as indicated by the trend in their melting points, at which decomposition occurs [1,4].

Results

We now report measurement of enthalpies of dissociation of the C_2F_4 and C_4F_6 adducts of *trans*-$IrX(CO)(PPh_3)_2$, where X is Br or I. For the C_2F_4 and C_4F_6 adducts the enthalpies of dissociation are in the order $F > Cl > Br < I$, showing a minimum value at Br. An attempt has been made to determine the enthalpies of dissociation of the acrylonitrile adducts. This was only partially successful, because of the difficulty of obtaining pure samples. However, the temperatures at which decomposition begins indicate an order of stability $F > Cl > Br > I$.

Experimental

$IrX(CO)(PPh_3)_2(L)$

The compounds $IrX(CO)(PPh_3)_2(L)$, where X is Br or I and L is C_2F_4 or C_4F_6, were prepared by the methods described [1] for the corresponding fluoro compounds. They had the following characteristics.

$IrBr(CO)(PPh_3)_2(C_2F_4)$. (Found: C, 51.1; H, 3.4. Calcd.: C, 50.6; H, 3.3%.) ν(CO) (Nujol) 2033 cm^{-1}; after loss of C_2F_4 ν(CO) (Nujol) 1951 cm^{-1}, lit. [5] 1955 cm^{-1}.

$IrI(CO)(PPh_3)_2(C_2F_4)$. (Found: C, 48.2; H, 3.2. Calcd.: 48.2; H, 3.1%.) ν(CO) (Nujol) 2040 cm^{-1}; after loss of C_2F_4 ν(CO) (Nujol) 1955 cm^{-1}, lit. [5] ($CHCl_3$) 1967 cm^{-1}.

$IrBr(CO)(PPh_3)_2(C_4F_6)$. (Found: C, 48.3; H, 3.0. Calcd.: C, 49.9; H, 3.1%.) ν(CO) (Nujol) 1995 cm^{-1}, ν(CC) (Nujol) 1763; after loss of C_4F_6 ν(CO) (Nujol) 1953 cm^{-1}. The crystalline compound contained 5.36% by weight of solvent (CH_2Cl_2 or C_6H_6) which was lost on heating to 355—390 K.

$IrI(CO)(PPh_3)_2(C_4F_6)$. (Found: C, 47.2; H, 2.8. Calcd.: C, 47.6; H, 2.9%.) ν(CO) (Nujol) 1994, 1984 cm^{-1}, ν(CC) (Nujol) 1778 cm^{-1}; after loss of 0.2 mol C_4F_6 ν(CO) (Nujol) 1997, 1983 cm^{-1}, ν(CC) (Nujol) 1775 cm^{-1}; after complete loss of C_4F_6 ν(CO) (Nujol) 1953 cm^{-1}.

$IrX(CO)(PPh_3)_2(C_2H_3CN)$

The compounds $IrX(CO)(PPh_3)_2(C_2H_3CN)$ were prepared according to Baddley's [4] method for the chloro compound by addition of acrylonitrile to $IrX(CO)(PPh_3)_2$, except for the fluoro compound, where benzene was used as solvent. Only the fluoro compound was sufficiently stable for a satisfactory C, H, N analysis to be obtained. The high carbon and hydrogen analyses were assumed to be due to retention of benzene. For the chloro and bromo compounds the analyses are based on the weight loss observed on heating.

$IrF(CO)(PPh_3)_2(C_2H_3CN)_{0.7}(C_6H_6)_{0.4}$. (Found: C, 59.2; H, 4.27; N, 1.2. $C_{41.5}H_{34.5}FN_{0.7}IrOP_2$ calcd.: C, 59.77; H, 4.17; N, 1.18%.) ν(CO) (Nujol) 2010, 1947 cm^{-1}, the value 1947 cm^{-1} indicating the presence of a trace of the parent compound, lit. [6] $IrF(CO)(PPh_3)_2(C_2H_3CN)$ ν(CO) (Nujol) 2008 cm^{-1}; after loss of C_2H_3CN ν(CO) (Nujol) 1947 cm^{-1}, lit. [6] ($CHCl_3$) 1957 cm^{-1}.

$IrCl(CO)(PPh_3)_2(C_2H_3CN)_{0.74}$. ν(CO) (Nujol) 2020 cm^{-1} lit. [4] (Nujol) 2017 cm^{-1}; after loss of C_2H_3CN ν(CO) (Nujol) 1952 cm^{-1}, lit. [4] (benzene) 1955 (chloroform) 1954 cm^{-1}.

$IrBr(CO)(PPh_3)_2(C_2H_3CN)_{1.5}$. ν(CO) (Nujol) 2019 cm^{-1}, after loss of C_2H_3CN ν(CO) (Nujol) 1954 cm^{-1}, lit. [5] 1955 cm^{-1}.

Enthalpies of the dissociation reactions

The Perkin—Elmer differential scanning calorimeter (DSC-1) was used [7] to measure the enthalpies of thermal decompositions in a nitrogen atmosphere. The scan rate was 16° $K \cdot min^{-1}$ and the sensitivity was either 2,4, or 8 millical · (full scale deflection)$^{-1}$ · sec^{-1}. The instrument was calibrated by use of the enthalpy of fusion of indium and checked by measuring the enthalpies of *(i)* dehydration of $CuSO_4 \cdot 5H_2O$, *(ii)* fusion of Pb metal, and *(iii)* decomposition of $CoCl_2$(pyridine)$_2$ as described previously [8].

Enthalpies of the decomposition reactions are shown in Table 1, where the symbols T_i, T_p, and T_f refer to the initial, peak (where the rate of ΔH change was greatest), and final temperatures of the dissociation reaction, respectively. In all cases, the ΔH values, which refer to T_p, are the mean of at least five experiments and the associated uncertainties are standard deviations of mean values.

For the acrylonitrile adducts the observed dissociation enthalpies were as follows: $IrF(CO)(PPh_3)_2(C_2H_3CN)_{0.4}$ 39.1 ± 2, $IrCl(CO)(PPh_3)_2(C_2H_3CN)_{0.74}$ 35.0 ± 2, and $IrBr(CO)(PPh_3)_2(C_2H_3CN)_{1.5}$ 87.3 ± 2 kJ · (formula weight)$^{-1}$. Further analysis of these data was not possible because of the disparate stoichiometry of this series of compounds.

Discussion

For an interpretation of the enthalpies of dissociation of the tetrafluoroethylene and hexafluoro-2-butyne adducts, it would be preferable to refer the data to gas-phase reactions and also to a common temperature. It has not been possible to measure either the specific heats or the enthalpies of sublimation of

TABLE 1

ENTHALPIES OF THE DISSOCIATION REACTIONS

$IrX(CO)(PPh_3)_2(L)(cryst.) \rightarrow IrX(CO)(PPh_3)_2(cryst.) + L(g)$

L	X	ΔH ($kJ \cdot mol^{-1}$)	T_i (K)	T_p (K)	T_f (K)	Wt. loss (%)	
						Obs.	Calc.
C_4F_6	F	99.2 ± 0.3	410	450	500	17.5 ± 0.1	17.50
	Cl	95.7 ± 1.7	355	430	450	18.1 ± 0.7	17.19
	Br	78.6 ± 0.5	405	450	470	16.0 ± 0.2[a]	16.42[a]
	I	82.4 ± 3.2	(405 (440	430 480	440[b]) 490)	16.3 ± 0.2	15.67
C_2F_4	F	79.4 ± 1.9	420	480	495	11.8 ± 0.2	11.58
	Cl	67.2 ± 1.9	385	445,475	490	10.9 ± 0.6	11.36
	Br	41.0 ± 0.7	410	435,470	480	11.3 ± 0.1	10.81
	I	57.2 ± 2.0	420	455,470	480	10.9 ± 0.1	10.29
C_2H_3CN	F		350	385	410	≈ 7	6.50
	Cl		310	335	345	4.8 ± 0.1	6.37
	Br		305	330	340	8.6 ± 0.7	6.05

[a] Based on a sample from which solvent benzene had been removed by heating to 390 K. [b] First peak corresponds to a loss of 0.2 mole C_4F_6 and ΔH 13.8 kJ.

the complexes, and we make the assumption, which may not be justified, that the trends in the observed enthalpies of dissociation are the same as those in the gas phase.

Although these trends are interpreted in terms of variations in σ- and π-bond strengths, they may be caused by conformational changes in structure. NMR data [9] suggest that for the analogous $IrCl(CO)(PMePh_2)_2(C_4F_6)$, the $PMePh_2$ molecules are *trans* to each other, and in $IrCl(CO)(PMePh_2)_2(C_2F_4)$, the $PMePh_2$ molecules are *cis* to each other and *trans* to C_2F_4. It is likely [10] that in $IrCl(CO)(PPh_3)_2(C_2F_4)$ the PPh_3 molecules are also *cis* to each other. The possibility remains that this conformation may alter on changing the halogen.

Metal—olefin bonding is explained, in terms of the Chatt—Dewar [11] model, in terms of combined σ(olefin→metal) and π(metal→olefin) bonding so that the bond strength will depend on the importance of these two components of the bond.

For a particular olefin complex, it seems reasonable to suppose that, if changes in the π-bonding component are the more important, substitution of the halogen, X, in the complex $IrX(CO)(PPh_3)_2$(olefin) would lead to an increasing stability along the series $F < Cl < Br < I$. This order is observed for the dioxygen complexes and is probably the case for the ethylene complexes. On the other hand, if changes in the σ-bonding component were more significant, then the order will be reversed, $F > Cl > Br > I$. Clearly, there is a fine balance between the two components which is sensitive to both the halogen bonded to the metal and also to the substituents attached to olefin or acetylene. The tetrafluoroethylene and hexafluoro-2-butyne adducts are intermediate between these two extremes in showing an order of stability $F > Cl > Br < I$.

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