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THE RELATIVE STABILITIES OF TETRAFLUOROETHYLENE AND HEXAFLUORO-2-BUTYNE ADDUCTS OF FLUORO- OR CHLOROBIS-(TRIPHENYLPHOSPHINE)CARBONYLIRIDIUM

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SUMMARY

Tetracyanoethylene, tetrafluoroethylene and hexafluoro-2-butyne form 1/1 adducts with *trans*-$IrF(CO)(PPh_3)_2$. Enthalpies of dissociation for the reactions:

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

($X = F$ or Cl; $L = C_2F_4$ or C_4F_6) have been measured. More stable adducts are formed when $X = F$.

Although many electrophilic olefins and acetylenes form adducts with the square-planar complexes, *trans*-$IrX(CO)(PPh_3)_2$ ($X = Cl$, Br or I)[1-3], there are no published data on adducts of the corresponding fluoro complex.

We have found that tetrafluoroethylene, tetracyanoethylene, and hexafluoro-2-butyne readily combine with $IrF(CO)(PPh_3)_2$ (I)[4] to form the 1/1 adducts $IrF(CO)(PPh_3)_2(L)$ [$L = C_2F_4$, $C_2(CN)_4$, and $C_2(CF_3)_2$, respectively]. In contrast with $IrCl(CO)(PPh_3)_2(C_2F_4)$, which readily loses C_2F_4 on attempted recrystallisation[1], the corresponding fluoride is more stable, and can be obtained as well-formed crystals from acetone.

TABLE 1

CARBONYL STRETCHING FREQUENCIES (cm^{-1})

	X=F[a]	*X=Cl*	*Ref.*
$IrX(CO)(PPh_3)_2[C_2(CN)_4]$	2034	2075[b]	9
		2025[c]	10
$IrX(CO)(PPh_3)_2(C_2F_4)$	2028	2040[c]	1
$IrX(CO)(PPh_3)_2(C_4F_6)$	2005	2025[a]	1

[a] In Nujol mulls, [b] In CH_2Cl_2 solution. [c] KBr disc.

In these complexes, the $\nu(CO)$ frequency (Table 1) increases, compared to that in (I), and this increase is similar to that found in many analogous complexes. This feature has been taken as evidence that the formal oxidation state of the metal has increased during the oxidative addition reaction[5]. In the IR spectra of (I), bands occur at 451 [$\nu(IrF)$] and 420 cm^{-1} [?$\nu(IrC)$], whereas with the tetrafluoroethylene adduct, bands occur at 456, 453, 441 and 417 cm^{-1} in this region.

Enthalpies of the following dissociation reactions

$$IrX(CO)(PPh_3)_2(L)\,(cryst.) \rightarrow IrX(CO)(PPh_3)_2\,(cryst.) + L(g) \qquad (1)$$

have been measured, and are shown in Table 2. Also listed are the temperatures, T, to which these values refer, together with the observed and calculated weight losses.

TABLE 2

DISSOCIATION ENTHALPIES (ΔH) FOR $IrX(CO)(PPh_3)_2(L)$, eqn. (1)

X	*L*	$\Delta H/kJ \cdot mol^{-1}$	*T/K*	*Weight loss (%)*	
				Obs.	*Calcd.*
F	C_4F_6	99.2±0.3	480	17.5±0.1	17.50
Cl	C_4F_6	95.7±1.7	430	18.1±0.7	17.19
F	C_2F_4	79.4±1.9	480	11.8±0.2	11.58
Cl	C_2F_4	67.2±1.9	460	10.9±0.6	11.36

Extrapolation of trends in stabilities for the adducts with dioxygen[5,6,7] where stabilities decrease in the order I > Cl, suggest that adducts of (I) might be expected to be even less stable than those of the chloride. However our results indicate that these trends are reversed, at least for the adducts reported herein. Indeed, it is possible to draw a parallel between the behaviour of C_2F_4, and that of dioxygen; in both instances, the adducts formed with (I) are more stable than those formed with $IrCl(CO)(PPh_3)_2$. Possible reasons for this increased stability may involve relative π-bonding effects of the halide ligands, or simply a closer approach of the unsaturated molecule to the metal atom, resulting from the smaller size of the fluorine atom. Either or both of these features can account for improved back-donation from iridium to the coordinated unsaturated molecule, and for the ready substitution of fluoride by other ligands.

EXPERIMENTAL

Tetrafluoroethylene (4 mmol) was condensed into a Carius tube containing a suspension of *trans*-$IrF(CO)(PPh_3)_2$ (460 mg) in dry benzene (20 ml) at −196°. The tube was sealed *in vacuo*, and kept at 60°. After 8 days, the tube was opened, and white prisms of $IrF(CO)(PPh_3)_2(C_2F_4)$ (330 mg, 63%), m.p. 147° (dec.), were filtered off. (Found: C, 54.35; H, 3.35; F, 10.8; Ir, 22.2; P, 7.1%; mol. wt. in $CHCl_3$, 872. $C_{39}H_{30}F_5IrOP_2$ calcd.: C, 54.25; H, 3.5; F, 11.0; Ir, 22.25; P, 7.15% mol. wt., 864.) The ^{19}F NMR spectrum contained two complex resonances centred on 119.75 and 138.5 ppm.

Similarly hexafluorobutyne-2 gave white prisms of $IrF(CO)(PPh_3)_2(C_4F_6)$ (76%), m.p. 137° (dec.). (Found: C, 52.85; H, 3.3; F, 14.1. $C_{41}H_{30}F_7IrOP_2$ calcd.:

C, 53.19; H, 3.3; F, 14.3%.) The ^{19}F NMR spectrum contained two singlets centred at 76.09 and 73.37 ppm (relative to $CFCl_3$).

Tetracyanoethylene and (I) in benzene gave white crystals of $IrF(CO)(PPh_3)_2[C_2(CN)_4]$ (72%), m.p. >300°. (Found: C, 57.89; H, 3.4; F, 2.2; N, 6.1. $C_{43}H_{30}FIrN_4OP_2$ calcd.: C, 57.91; H, 3.4; F, 2.1; N, 6.2%.)

The enthalpies of the dissociation reactions were measured using a Perkin-Elmer DSC-1 scanning calorimeter[8].

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