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Carborane Reductive-Elimination Reaction from a Six-Coordinate Hydridocarboranyliridium(III) Complex: Kinetic and Mechanistic Study

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A kinetic and mechanistic study of the reductive-elimination reaction of the carborane 1-H-7-C$_6$H$_5$-1,7-C$_2$B$_{10}$H$_{10}$ (H-carb) from the six-coordinate iridium(III) complex Ir(H)(Cl)(σ-carb)(CO)(PPh$_3$)$_2$ has been carried out in 1,2-dichloroethane by IR spectroscopy between 20 and 50 °C. The mechanism of the carborane-elimination reaction implies a preliminary PPh$_3$ dissociation to give the five-coordinate Ir(H)(Cl)(σ-carb)(CO)(PPh$_3$) complex. This intermediate then undergoes a reductive elimination of the carborane molecule through two pathways: (i) direct elimination to give the three-coordinate iridium(I) complex, IrCl(CO)(PPh$_3$); (ii) a phosphine-induced elimination via trans → cis isomerization of the H and carb ligands. The kinetic and thermodynamic parameters are also reported and discussed.
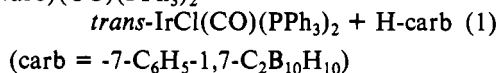
Introduction

In a previous paper we reported[1] a study on the stereochemistry of oxidative-addition reactions of diatomic molecules, such as HX (X = Cl, Br, I) and Cl$_2$ and Br$_2$, to the square-planar carboranyliridium(I) complexes Ir(σ-carb)(CO)L$_2$, in which carb = -2-R-1, 2- and -7-R-1,7-C$_2$B$_{10}$H$_{10}$ (R = H, CH$_3$, C$_6$H$_5$) and L = PPh$_3$, PMePh$_2$. A number of octahedral iridium(III) complexes have been obtained and characterized by IR and ^{1}H NMR spectroscopy.

Unlike the adducts of the type Ir(X)$_2$(σ-carb)(CO)L$_2$, the hydrogen halide adducts Ir(H)(X)(σ-carb)(CO)L$_2$ exhibit reductive elimination of the carborane molecule, H-carb, which occurs at measurable rate.

The reductive-elimination reaction is a very important step in homogeneous catalysis as well as in any application of transition-metal reagents to organic synthesis, either catalytic or stoichiometric. However, the reductive-elimination reactions have been much less studied than oxidative-addition ones and, at least for group 8 metals, only the β-hydrogen elimination has been well investigated so far.[2] While large numbers of dialkyls and dihydrides of transition metals are known, stable and isolable alkyl hydrides are rare, and this, of course, has prevented any systematic kinetic and mechanistic study of the R–H reductive-elimination processes.

We wish to report here a kinetic study of the carborane reductive-elimination reaction (eq 1) carried out in 1,2-di-

$$Ir(H)(Cl)(\sigma\text{-carb})(CO)(PPh_3)_2 \rightarrow$$
$$\textit{trans-}IrCl(CO)(PPh_3)_2 + H\text{-carb} \quad (1)$$
$$(carb = \text{-7-C}_6H_5\text{-1,7-C}_2B_{10}H_{10})$$

chloroethane between 20 and 50 °C by IR monitoring of the reaction mixture in the range 2300–1650 cm^{-1}.

Experimental Section

The complex Ir(H)(Cl)(σ-carb)(CO)(PPh$_3$)$_2$ (1), where carb = -7-C$_6$H$_5$-1,7-C$_2$B$_{10}$H$_{10}$, was prepared and characterized as previously reported[1] by adding to a benzene solution of Ir(σ-carb)(CO)(PPh$_3$)$_2$ a solution of anhydrous hydrogen chloride in benzene at room temperature. White crystals of the HCl adduct 1 were then precipitated by addition of *n*-hexane. The reaction product *trans*-Ir(Cl)(CO)-(PPh$_3$)$_2$ (2) was compared with an authentic sample prepared according to literature methods.[3]

The complex Ir(H)(Cl)(σ-carb)(CO)$_2$(PPh$_3$) (3) was obtained in 1,2-dichloroethane (DCE) solution upon treating the complex 1 with a CO atmosphere at room temperature. The ^{1}H NMR spectrum of 3 exhibits a doublet at τ 18.48 (J_{PH} = 14.6 Hz) due to the hydride proton trans to a CO ligand. The IR spectrum in 1,2-dichloroethane shows a weak band at 2183 cm^{-1} due to ν(Ir–H) and two strong ν(CO) absorptions at 2103 and 2067 cm^{-1}.

The Rh(acac)(C$_2$H$_4$)$_2$ was prepared according to literature methods.[4]

The triphenylphosphine (EGA product) was recrystallized from CH$_2$Cl$_2$/CH$_3$OH. The reagent grade solvents were purified by standard methods. Argon and carbon monoxide were high purity SIO products. Certified Ar/CO mixtures were provided by SIAD, relative errors in their analyzed contents being always less than 0.5%.

The carborane elimination reaction was investigated by monitoring by IR spectroscopy 1,2-dichloroethane solutions prepared by transferring under Ar (or under CO) the carefully deoxygenated phosphine solutions or the pure solvents to a Schlenk tube containing a weighted quantiy of 1. The reactions were followed by sampling, through a steel capillary system, aliquot portions of the reacting solution. Samples were injected directly into IR cells and spectra recorded immediately in the CO stretching region on a Perkin-Elmer 457 spectrophotometer, with reference cells being filled with matching PPh$_3$ when appropriate. A similar procedure was followed for the reaction in the presence of PPh$_3$ sponge. In this case the solution of 1 was rapidly transferred into a Schlenk tube containing a weighted quantity of Rh(acac)(C$_2$H$_4$)$_2$ under Ar.

Results

Reductive-Elimination Reaction. Reaction 1 proceeds in 1,2-dichloroethane solution under Ar, both in the presence and/or absence of added PPh$_3$, to give quantitative conversion of 1 to 2. Analyses of the changes in the absorbance of the ν(CO) bands at 2040 and 1960 cm^{-1} due to the complexes 1 and 2, respectively, indicate that the rate of disappearance of 1 is equal to the rate of formation of 2, thus excluding appreciable accumulation of intermediates. The reaction rates were generally determined from the slope of the plots of log $(A_t - A_\infty)$ vs. time, where A_t and A_∞ are the absorbances of the peak at 2040 cm^{-1}. In all cases these plots were linear over three half-lives, indicating that the reaction rate is first order in complex concentration. The observed rate constant, k_{obsd}, markedly decreases with increasing PPh$_3$ concentration to reach a low limiting value which is independent of PPh$_3$ content and initial complex concentration. On the contrary, at low or zero concentration of added PPh$_3$, the rate constant k_{obsd} is significantly higher for lower initial complex concentration (Figure 1). Furthermore, no effect due to added H-carb was observed.

Reaction of 1 with Rh(acac)(C$_2$H$_4$)$_2$. The reaction has been studied by IR and ^{1}H NMR spectroscopy. Complex 1 quantitatively converts into a mixture of hydridoiridium(III) complexes containing only one PPh$_3$ ligand. In fact the ^{1}H NMR spectrum of a solution of 1 (8.6 × 10^{-2} mol dm^{-3} in

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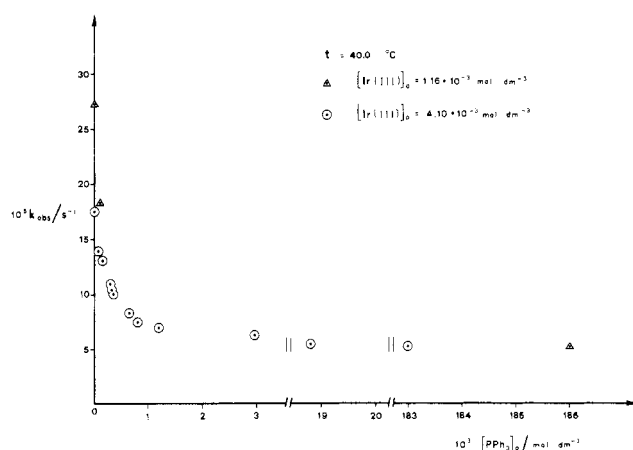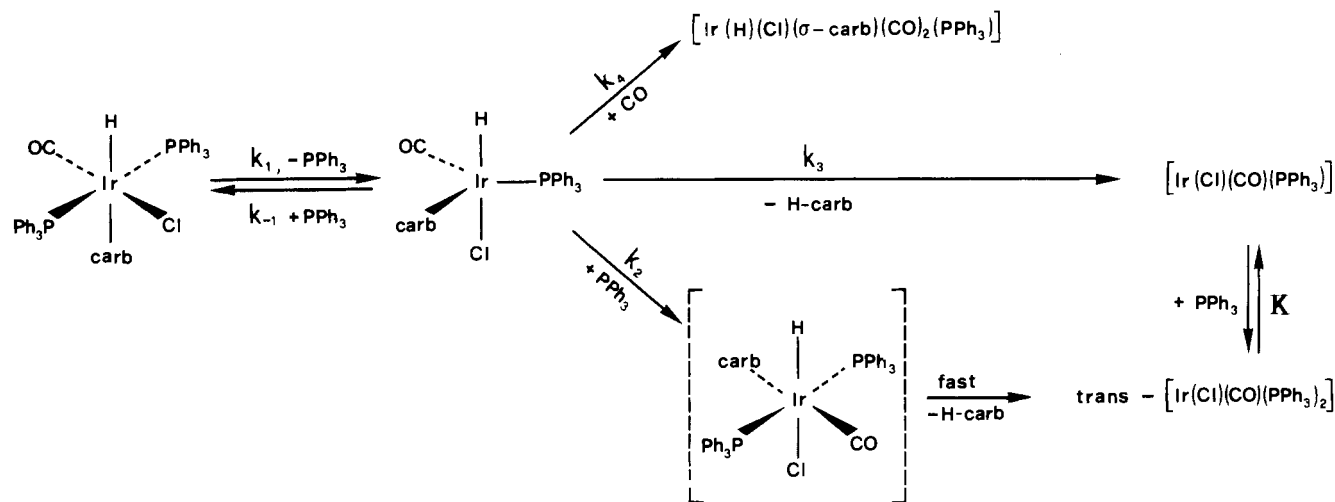(4) Cramer, R. *Inorg. Synth.* **1974**, *15*, 14.

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Scheme I

Figure 1. Dependence of k_{obsd} on the initial concentration of PPh$_3$ and complex 1.

CDCl$_3$) and Rh(acac)(C$_2$H$_4$)$_2$ in a 1:1 molar ratio shows the progressive disappearance of the hydride resonance of 1 (triplet at τ 21.1, J_{PH} = 17.4 Hz) and the concomitant appearance of a series of doublets at τ 29.4 (J_{PH} = 13.7 Hz, intensity 10), 28.5 (J_{PH} = 11.0 Hz, intensity 5), 28.3 (J_{PH} = 11.9 Hz, intensity 3), and 28.8 (J_{PH} = 11.3 Hz, intensity 1). Furthermore, the IR spectrum of the mixture ([1] = [Rh^I] = 4.1 × 10^{-3} mol dm^{-3}) in DCE shows a smooth decrease of the hydride absorption ν(Ir–H) at 2175 cm^{-1}. This band does not completely disappear in that the final products show two broad bands centered at 2175 and 2215 cm^{-1} with approximately the same intensity.

This reaction can be simply seen as the conversion of the bis(phosphino)iridium(III) complex into monophosphino complexes whose nature was not investigated.

The reaction rate of this process has been determined in one case by ^{1}H NMR techniques ($t_{1/2}$ ca. 45 min. at ca. 28 °C in CDCl$_3$). However a more convenient determination of the reaction rate has been obtained by plotting log ($A_t - A_\infty$) vs time, where A_t is the absorbance at various times and A_∞ is the absorbance of the final solution at 2175 cm^{-1}. These semilogarithmic plots are linear over two half-lives, giving k_{obsd} values 10 times higher than those observed for the reductive-elimination reaction and independent of the phosphine sponge concentration.

Reaction of 1 with CO. Reaction of 1 with CO leads to the substitution of a PPh$_3$ ligand by CO (eq 2) and formation of

Ir(H)(Cl)(σ-carb)(CO)(PPh$_3$)$_2$ + CO →

Ir(H)(Cl)(σ-carb)(CO)$_2$(PPh$_3$) + PPh$_3$ (2)

the iridium(III) dicarbonyl derivative, 3, which is fairly stable under CO toward reductive elimination. During this substitution complex 1 rearranges, the ligands H and carb moving to a cis position. The carbonylation rate at constant CO pressure is pseudo first order in complex concentration. The k_{obsd} values determined from the usual semilogarithmic plots are at least 10 times higher than those observed in the case of the reductive-elimination reaction. Furthermore they are independent of CO pressure in the absence of added PPh$_3$, but are lowered by large PPh$_3$ concentrations ([PPh$_3$] = 0.382 mol dm^{-3}; y_{CO} = 0.251). All rate data are collected in Table I.

Discussion

The observed kinetic behavior is consistent with the reaction mechanism shown in Scheme I.

According to this scheme the carborane reductive-elimination reaction occurs through a preliminary PPh$_3$ dissociation (k_1) to give the five-coordinate complex Ir(H)(Cl)(σ-carb)-(CO)(PPh$_3$). This intermediate species in turn can react in the following ways: (i) with PPh$_3$ to restore the iridium(III) starting complex (k_{-1}); (ii) with PPh$_3$ to give carborane reductive elimination via trans → cis isomerization of the H and carb ligands (k_2); (iii) by direct elimination (k_3) to form the three-coordinate iridium(I) species, Ir(Cl)(CO)(PPh$_3$); (iv) with CO (k_4) to give the bis(carbonyl) derivative, Ir(H)-(Cl)(σ-carb)(CO)$_2$(PPh$_3$) (3), in which the H and carb ligands are mutually cis.

In the following treatment we have assumed that the five-coordinate complex Ir(H)(Cl)(σ-carb)(CO)(PPh$_3$) is a very reactive intermediate to which the steady-state treatment can be applied, so that the observed reaction rate for the disappearance of 1 takes the form of eq 3. This rate equation is

$$k_{obsd} = \frac{k_1 k_2 [PPh_3] + k_1 k_3 + k_1 k_4 [CO]}{k_{-1}[PPh_3] + k_2[PPh_3] + k_3 + k_4[CO]} \quad (3)$$

seen to be consistent with the experimental kinetic data as follows.

Equation 3 under Ar, i.e., when [CO] = 0 mol dm^{-3}, takes a reduced form, which can be rearranged as

$$k_{obsd} = \frac{k_1 k_2}{k_{-1} + k_2 + k_3/[PPh_3]} + \frac{k_1 k_3}{(k_{-1} + k_2)[PPh_3] + k_3} \quad (4)$$

The first term of the right side of eq 4 becomes independent of [PPh$_3$] for sufficiently high phosphine concentration so that (k_3/[PPh$_3$]) << (k_{-1} + k_2), and it represents the recognized reaction pathway whose rate constant k_{obsd} = $k_1 k_2/(k_{-1} + k_2)$

Table I. Kinetics of Disappearance of
$1-[Ir(H)(Cl)(CO)(PPh_3)_2]-7-C_6H_5-(\sigma-B_{10}C_2H_{10})$ at Various PPh_3 Concentrations, under Ar or under CO, in 1,2-Dichloroethane

θ_c, °C	$[Ir^{III}]_0$, mol dm^{-3}	$[PPh_3]_0$, mol dm^{-3}	$y_{CO}{}^a$	k_{obsd}, s^{-1}
20.0	4.20×10^{-3}	0.00	0.251	8.38×10^{-5}
		0.00	1.00	8.37×10^{-5}
		0.00^b	0.00	8.24×10^{-5}
30.0	4.10×10^{-3}	0.00	0.498	3.85×10^{-4}
		0.00	1.00	3.73×10^{-4}
		0.00^b	0.00	3.85×10^{-4}
		0.00^c	0.00	3.69×10^{-4}
		3.82×10^{-1}	0.251	ca.2×10^{-4} ^{d}
40.0	1.16×10^{-3}	0.00	0.00	2.72×10^{-4}
	4.10×10^{-3}	0.00	0.00	1.75×10^{-4}
		0.00^e	0.00	1.70×10^{-4}
		0.00	0.251	2.20×10^{-3}
		0.00	1.00	2.22×10^{-3}
		7.10×10^{-5}	0.00	1.39×10^{-4}
	1.16×10^{-3}	9.79×10^{-5}	0.00	1.83×10^{-4}
	4.10×10^{-3}	1.49×10^{-4}	0.00	1.30×10^{-4}
		2.97×10^{-4}	0.00	1.09×10^{-4}
		3.26×10^{-4}	0.00	1.04×10^{-4}
		3.67×10^{-4}	0.00	1.00×10^{-4}
		6.26×10^{-4}	0.00	8.25×10^{-5}
		8.92×10^{-4}	0.00	7.45×10^{-5}
		1.19×10^{-3}	0.00	6.95×10^{-5}
		2.97×10^{-3}	0.00	6.24×10^{-5}
		1.88×10^{-2}	0.00	5.45×10^{-5}
		1.83×10^{-1}	0.00	5.25×10^{-5}
	1.16×10^{-3}	1.86×10^{-1}	0.00	5.14×10^{-5}
50.0	4.00×10^{-3}	0.00	0.00	1.28×10^{-3}
	3.00×10^{-3}	1.41×10^{-4}	0.00	1.00×10^{-3}
		2.82×10^{-4}	0.00	8.25×10^{-4}
		4.24×10^{-4}	0.00	7.00×10^{-4}
		5.65×10^{-4}	0.00	6.08×10^{-4}
	4.00×10^{-3}	7.72×10^{-4}	0.00	4.87×10^{-4}
		1.29×10^{-3}	0.00	3.85×10^{-4}
	3.00×10^{-3}	1.41×10^{-3}	0.00	3.85×10^{-4}
	4.00×10^{-3}	1.87×10^{-1}	0.00	2.04×10^{-4}

^{a} CO molar ratio in the cylinder; P_{tot} (including solvent vapor pressure) = 1.1 atm. ^{b} $[Rh(acac)(C_2H_4)_2]_0 = [Ir^{III}]_0$. ^{c} $[Rh(acac)(C_2H_4)_2] = 2 \times [Ir^{III}]_0$. ^{d} Initial rate (see text). ^{e} [H-carb] = 0.266 mol dm^{-3}.

is independent of $[PPh_3]$. In these conditions eq 4 can be rearranged as

$$\frac{1}{k_{obsd} - k_1 k_2/(k_{-1} + k_2)} = \frac{1}{k_1} + \frac{(k_{-1} + k_2)[PPh_3]}{k_1 k_3} \quad (5)$$

This means that a linear relationship is expected by plotting the reciprocal of the difference between k_{obsd} and the experimental low limiting rate value vs. phosphine concentration. Figure 2 shows as an example the data at 40 °C of Figure 1 rearranged according to eq 5. The linearity obtained is not obeyed at low or zero concentration of added PPh_3 as a consequence of reaction rates lower than expected on the basis of $[PPh_3]$ added. Clearly, the phosphine concentration in the rate equation is the total concentration, so it seems reasonable to assume that the dissocitive equilibrium in step 1 is fast if compared with the elimination process and produces an additional "finite and constant" PPh_3 concentration in solution. With an iterative method we have calculated a $K_d(k_1/k_{-1})$ value (see Scheme I), for which phosphine concentrations are estimated to give the best linear fit. Figure 2 reports the very good linearity obtained by correcting the PPh_3 concentrations according to $K_d = 6.5 \times 10^{-6}$ mol dm^{-3}.

It is worth noting in this context that two runs carried out under different initial concentrations ($[1]_0 = 1.16 \times 10^{-3}$ mol dm^{-3} and $[PPh_3]_0 = 9.79 \times 10^{-5}$ mol dm^{-3}; $[1]_0 = 4.10 \times 10^{-3}$ mol dm^{-3} and $[PPh_3]_0 = 0$ mol dm^{-3}) show a very similar reaction rate ($k_{obsd} = 1.83 \times 10^{-4}$ s^{-1} and 1.75×10^{-4} s^{-1}, respectively), as expected when we consider that the same free
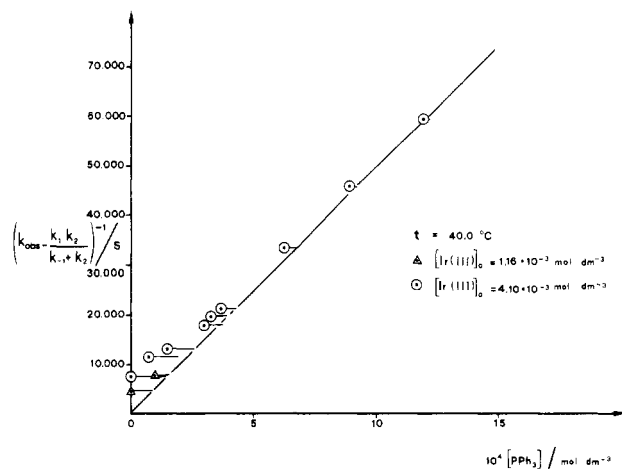

Figure 2. Data of Figure 1 rearranged according to eq 5 (see text). The horizontal lines represent the additional concentration of PPh_3 derived from dissociation of complex 1.

phosphine concentration should be realized in both cases.

The observed good linearity of the semilogarithmic plots even in the absence of added PPh_3 should indicate that the phosphine concentration is constant during the run. This requires that the dissociation constant (K) of the product *trans*-$Ir(Cl)(CO)(PPh_3)_2$ is very close to the dissociation constant of the reagent 1 (K_d) and that the rate of formation of $Ir(Cl)(CO)(PPh_3)$ is much lower than the rate of its recombination with PPh_3. The similarity between the values of the two dissociation constants has been already assumed by Puddephatt[5] in the study of the ethane reductive elimination from *fac*-$PtI(CH_3)_3L_2$ (L = PR_3, ArR_3) complexes. Furthermore, a value of 3.9 mol^{-1} dm^3 s^{-1} at 25 °C has been reported for the recombination rate constant of PPh_3 to give *trans*-$Ir(Cl)(CO)(PPh_3)_2$ complex in dimethylacetamide.[6] Finally, the K_d value found is in agreement with those reported for the phosphine dissociation constants shown by *trans*-$Ir(Cl)(CO)(PPh_3)_2$ in dimethylacetamide (10^{-6} mol dm^{-3} at 80 °C)[6] and in toluene (10^{-5} mol dm^{-3}, temperature not stated).[7]

Turning to a consideration of the linear relationship obtained by the above procedure (eq 5), we can determine with accuracy the slope $(k_{-1} + k_2)/k_1 k_3$ whereas only an approximate value of k_1 can be estimated (Figure 2). When one considers that k_1 represents the rate constant of PPh_3 dissociation, its value corresponds to the observed rate constant in the reaction of 1 occurring in the presence of the phosphine sponge.

Further convincing evidence for the proposed mechanism is offered by the carbonylation reaction (eq 2). The inhibiting PPh_3 effect on the reaction rate also suggests in this case a PPh_3 dissociative mechanism involving the same five-coordinate $Ir(H)(Cl)(\sigma-carb)(CO)(PPh_3)$ complex (Scheme I). As consequence the limiting carbonylation rate, reached in the absence of added PPh_3 for $y_{CO} = 0.251$ and $y_{CO} = 1$, represents in the proposed mechanism k_1 the specific rate of PPh_3 dissociation, which is the initial step for all considered processes. As expected, k_1 determined from the kinetic dat for the reductive-elimination reaction has been shown to be equal to the limiting rate of the carbonylation reaction. Because of the better accuracy of the kinetic data for the carbonylation reaction, this independent determination of k_1 has been inserted in all the kinetic data for the reductive-elimination reaction at 40 and 50 °C.

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Table II. Kinetic Parameters[a] of the Reactions (in 1,2-Dichloroethane): $Ir(H)(Cl)(\sigma\text{-carb})(CO)(PPh_3)_2 \rightarrow$ $trans\text{-}IrCl(CO)(PPh_3)_2 + H\text{-carb}$ (Eq 1) and $Ir(H)(Cl)(\sigma\text{-carb})(CO)(PPh_3)_2 + CO \rightarrow$ $Ir(H)(Cl)(\sigma\text{-carb})(CO)_2(PPh_3) + PPh_3$ (Eq 2)

ϑ_c, °C	$k_1 k_2/(k_{-1} + k_2)$, s^{-1}	k_1,[b] s^{-1}	$(k_{-1} + k_2)/k_1 k_3$, s mol^{-1} dm^3	K_d, mol dm^3
20.0		8.38×10^{-5}		
30.0		3.79×10^{-4}		
40.0	$5.27\ (0.20) \times 10^{-5}$ [c]	2.21×10^{-3}	$4.69\ (0.25) \times 10^{7}$ [f]	6.5×10^{-6} [f]
50.0	$2.04\ (0.13) \times 10^{-4}$ [d]		$3.96\ (0.06) \times 10^{6}$ [g]	1.2×10^{-5} [f]

$$\Delta H_1^*\,[e] = 122\ (6)\ \text{kJ mol}^{-1}$$
$$\Delta S_1^*\,[e] = 94\ (19)\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$\Delta H° = 52\ \text{kJ mol}^{-1}$$
$$\Delta S° = 65\ \text{J K}^{-1}\ \text{mol}^{-1}$$

[a] Derived parameters: $k_{-1}(40.0\,°C) = 340\ \text{s}^{-1}\ \text{mol}^{-1}\ \text{dm}^3$; $k_{-1}(50.0\,°C) = 770\ \text{s}^{-1}\ \text{mol}^{-1}\ \text{dm}^3$; $\Delta H_{-1}^* = 66\ \text{kJ mol}^{-1}$; $\Delta S_{-1}^* = 13\ \text{J K}^{-1}\ \text{mol}^{-1}$; $k_2(40.0\,°C) = 8.3\ \text{s}^{-1}\ \text{mol}^{-1}\ \text{dm}^3$; $k_2(50.0\,°C) = 17.4\ \text{s}^{-1}\ \text{mol}^{-1}\ \text{dm}^3$; $\Delta H_2^* = 60\ \text{kJ mol}^{-1}$; $\Delta S_2^* = -37\ \text{J K}^{-1}\ \text{mol}^{-1}$; $k_3(40.0\,°C) = 3.36 \times 10^{-3}\ \text{s}^{-1}$; $k_3(50.0\,°C) = 2.15 \times 10^{-2}\ \text{s}^{-1}$; $\Delta H_3^* = 154\ \text{kJ mol}^{-1}$; $\Delta S_3^* = 198\ \text{J K}^{-1}\ \text{mol}^{-1}$; $k_4(30.0\,°C) =$ ca. $3 \times 10^4\ \text{s}^{-1}\ \text{mol}^{-1}\ \text{dm}^3$. Values in parentheses are standard deviations (95% confidence limit) only for k_1; in all other cases they are approximate evaluations of the precision of the data. [b] From reaction 2; all other kinetic data from reaction 1. [c] $\sigma_{k_{obsd}}(40.0\,°C) = 6.5\%$. [d] Assuming $\sigma_{k_{obsd}}(50.0\,°C) = \sigma_{k_{obsd}}(40\,°C)$. [e] $\sigma_{k_{obsd}}(CO) = 16.0\%$; $\sigma_{k_1}(40.0\,°C) = 0.25 \times 10^{-3}\ \text{s}^{-1}$. [f] Value obtained according to the equation $1/[k_{obsd} - [k_1 k_2/(k_{-1} + k_2)]] - 1/k_1 = [(k_{-1} + k_2)/(k_1 k_3)][PPh_3]$. Each $1/[k_{obsd} - [k_1 k_2/(k_{-1} + k_2)]] - 1/k_1$ value has been weighted according to the estimated deviations of the k's; $[PPh_3]$ represent the total concentrations of phosphine which minimize the relative deviation on $(k_{-1} + k_2)/(k_1 k_3)$; these best values have been found by stepwise changing of the K_d value. No independent value of K is available (see text). [g] Using for k_1 the extrapolated value $9.2 \times 10^{-3}\ \text{s}^{-1}$ (rough estimated deviation $1.8 \times 10^{-3}\ \text{s}^{-1}$).

A first series of constants are collected in Table II. The rate parameters determined directly are often a complex function of rate constants, so preventing a detailed evaluation of the relative importance of the various steps.

We may observe however that the PPh_3-dissociative process, represented by k_1, is favored by a high positive activation entropy. The activation parameters $\Delta H_1^* = 122\ \text{kJ mol}^{-1}$ and $\Delta S_1^* = 94\ \text{J K}^{-1}$ are in line with other reported PPh_3-dissociative processes, as, for example, in $Cr(CO)_5(PPh_3)$ ($\Delta H^* = 152\ \text{kJ mol}^{-1}$ and $\Delta S^* = 52\ \text{J K}^{-1}\ \text{mol}^{-1}$)[8] and $(Ph_3P)(CO)_2Fe(\mu\text{-SPh})_2Fe(CO)_2(PPh_3)$ ($\Delta H^* = 142\ \text{kJ mol}^{-1}$ and $\Delta S^* = 68\ \text{J K}^{-1}\ \text{mol}^{-1}$).[9]

The value of the dissociation constant K_d is rather low as a consequence of the standard endothermic enthalpy not being compensated by a positive $\Delta S°$. This means that in all our experimental conditions the concentration of the reactive species $Ir(H)(Cl)(\sigma\text{-carb})(CO)(PPh_3)$ is small.

A more clear and comprehensive discussion of the results can be done if we use the K_d values, which are of course affected by some uncertainty, to derive a few other approximate rate parameters (Table II). This makes very tentative the discussion of the activation parameters for the various steps.

The rate constants clearly show that the five-coordinate complex $Ir(H)(Cl)(\sigma\text{-carb})(CO)(PPh_3)$ largely discriminates between the various entering ligands. In fact we may compare values of k_{-1} up to $3.4 \times 10^2\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$ for PPh_3 attack at 40 °C and an approximate value of 3×10^4 (at 30 °C) for CO attack (k_4). This is probably attributable to a greater

steric hindrance of PPh_3, which makes more difficult its approach to the crowded intermediate. The importance of steric effects in the rate of addition reactions on coordinatively unsaturated complexes has been already reconized, for example, in dinuclear intermediates of the type $(OC)_4M(\mu\text{-PEt}_2)_2M(CO)_3$ (M = Cr, Mo, W, and Mn).[10]

Furthermore, the site of PPh_3 attack is important, as shown by the different values of k_{-1} and k_2. It is not clear if k_2 represents the rate of formation of an isomer, which in turn gives the reductive elimination, or the rate of a phosphine-induced reductive elimination. Anyway it surely implies a phosphine attack that forces the carboranyl ligand close to H to favor the elimination of H-carb. So the two paths for k_{-1} and k_2 have different steric requirements. The activation entropy values support this statement; in fact the positive value of $13\ \text{J K}^{-1}\ \text{mol}^{-1}$ for k_{-1} indicates a process entropically slightly favored, whereas the value of $-37\ \text{J K}^{-1}\ \text{mol}^{-1}$ for k_2 indicates a rather crowded activated complex.

A further comment is required by the fairly high activation enthalpies ($\Delta H_{-1}^* = 66\ \text{kJ mol}^{-1}$ and $\Delta H_2^* = 60\ \text{kJ mol}^{-1}$), which indicate for the 16-electron Ir^{III} intermediate a behavior very similar to that exhibited by coordinatively saturated complexes.

The reaction pathway zero order in PPh_3 could represent in principle a simple intramolecular reductive-elimination process. This seems less likely compared to a mechanism based on a phosphine exchange isomerization. In agreement with the latter suggestion we have also observed the facile trans → cis migration of the H and carb ligands occurring via CO attack on the same Ir^{III} intermediate. Furthermore, a mechanism in which a ligand rearrangement takes place through five-coordinate intermediates formed by phosphine dissociation has been also reported for the isomerization of the neutral six-coordinate $Ir(Cl)_2(COEt)(CO)(PR_3)_2$ complexes.[11]

Also our assumption that $k_3/[PPh_3] \ll (k_{-1} + k_2)$ is verified a posteriori for $[PPh_3] \gg 10^{-4}\ \text{mol dm}^{-3}$.

Furthermore, the approximate values obtained for k_{-1} and k_2 indicate that the latter term is negligible compared with k_{-1} in the rate function $k_1 k_2/(k_{-1} + k_2)$. As a consequence the values of the experimental activation parameters $\Delta H^* = 111\ (6)\ \text{kJ mol}^{-1}$ and $\Delta S^* = 28\ (19)\ \text{J K}^{-1}\ \text{mol}^{-1}$ approximately correspond to $\Delta H_1^* + \Delta H_2^* - \Delta H_{-1}^*$ and $\Delta S_1^* + \Delta S_2^* - \Delta S_{-1}^*$, respectively. As expected for an isomerization process, which in the total number of moles does not change, an experimental activation entropy not very far from zero is obtained.

A final comment can be made for k_3, that is, the specific rate constant of the intramolecular reductive-elimination reaction of H-carb from the five-coordinate intermediate. Its low value, $3.36 \times 10^{-3}\ \text{s}^{-1}$ at 40 °C, compared with the value $3.4 \times 10^2\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$ for PPh_3 recombination (k_{-1}), justifies the overall high phosphine inhibiting effect on the reductive-elimination process.

A different behavior was found in the reductive elimination of N-acetylphenylalanine methyl ester from the corresponding hydroidoalkylbis(phosphine)rhodium(III) complex.[12] In this case the reaction rate is much higher ($5.9 \times 10^{-3}\ \text{s}^{-1}$ at -43.4 °C) owing to a very low activation enthalpy ($\Delta H^* = 71\ \text{kJ mol}^{-1}$) and the small positive activation entropy ($\Delta S^* = 25\ \text{J K}^{-1}\text{mol}^{-1}$). A high reactivity was also found in the CH_4 reductive elimination from cis-$PtH(CH_3)(PPh_3)_2$ ($k = 4.5 \times 10^{-4}\ \text{s}^{-1}$ at -25 °C).

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In our case the activation parameters ($\Delta H^* = 154$ kJ mol^{-1}, $\Delta S^* = 198$ J K^{-1} mol^{-1}) indicate that the driving force of the elimination step is the favorable entropic variation related to the removal of the large carboranyl ligand rather than the incipient formation of a H–C bond in the transition state.

The reductive elimination of H-carb from the complex **1** shows another example of a reductive-elimination process going through a preliminary ligand dissociation mechanism and can be compared with the similar behavior found in the reductive elimination of ethane from *fac*-PtI(CH$_3$)$_3$L$_2$ (L = PR$_3$, AsR$_3$),[5] Au(CH$_3$)$_3$L (L = PR$_3$),[14] and *cis*-Pd(CH$_3$)$_2$L$_2$ (L = PMePh$_2$, PPh$_3$).[15]

The major novelty of this study consists (i) in the quantitative determination of all the kinetic and thermodynamic

parameters and (ii) in the clear identification of an Ir^I three-coordinate complex as the primary reaction product (at least at low [PPh$_3$], where pathway 3 is predominant). For the principle of microscopic reversibility the reverse reaction of oxidative addition should also proceed via attack on the same coordinatively unsaturated intermediate, whereas direct attack on the squre Ir^I complex is generally reported.[16]

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Novel Fluorosulfate Derivatives of Germanium(IV) and Tin(IV)

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The synthesis of fluorosulfate derivatives of germanium, GeF$_2$(SO$_3$F)$_2$, (ClO$_2$)$_2$[Ge(SO$_3$F)$_6$], and Cs$_2$[Ge(SO$_3$F)$_6$], by metal oxidation in a HSO$_3$F/S$_2$O$_6$F$_2$ mixture is described. In the tin system a new fluorosulfate of the composition M[Sn(SO$_3$F)$_5$] (M = K$^+$ or Cs$^+$) is obtained. A polynuclear anionic structure is suggested with hexacoordination around tin. Structural characterizations are based on Raman, infrared, and ^{119}Sn Mössbauer spectra. Solutions in HSO$_3$F are studied by conductometry and NMR (^{19}F and ^{119}Sn). K[Sn(SO$_3$F)$_5$] is found to be very soluble in HSO$_3$F and to behave as a weak acid.

Introduction

A number of simple tin(IV) fluorosulfates have been known for some time; however, the corresponding germanium compounds seem to be unknown. The tin(IV) fluorosulfates include tetrakis(fluorosulfato)tin(IV), Sn(SO$_3$F)$_4$,[1] difluorobis(fluorosulfato)tin(IV), SnF$_2$(SO$_3$F)$_2$,[2] and the hexakis-(fluorosulfato)stannate(IV) ion [Sn(SO$_3$F)$_6$]$^{2-}$.[3] The principal preparative routes to these compounds have been the reactions of bis(fluorosulfuryl) peroxide, S$_2$O$_6$F$_2$,[4] with chloro derivatives of tin(IV). These routes are rather time consuming even though the initial reaction is rather vigorous and occasionally will proceed explosively.

Structural proposals for these compounds are based on ^{119}Sn Mössbauer and vibrational spectra, with hexacoordination for tin, common to all three, achieved by bidentate bridging fluorosulfate groups for Sn(SO$_3$F)$_4$ and SnF$_2$(SO$_3$F)$_2$. These proposals are supported by the known crystal structure of (CH$_3$)$_2$Sn(SO$_3$F)$_2$[5] and trends in the isomer shifts and quadrupole splitting data for these and other tin(IV) fluorosulfato derivatives.[6]

Our renewed interest in these compounds centers around four aspects: (i) Metal oxidation by S$_2$O$_6$F$_2$ with HSO$_3$F as solvent is a simple and fast route to metal fluorosulfates and fluorosulfato anions.[7] This method should afford the known compounds more efficiently and safely and may be extendable to the synthesis of germanium compounds as well. (ii) In situ generation of dissolved Sn(SO$_3$F)$_4$ and hopefully Ge(SO$_3$F)$_4$ may give HSO$_3$F-based superacid systems in analogy to Au-(SO$_3$F)$_3$/HSO$_3$F systems studied by us previously.[7] (iii)

Synthesis of salts containing the [Ge(SO$_3$F)$_6$]$^{2-}$ anion is both a necessary prerequisite for meaningful superacidity studies on this system and a preparative challenge in view of the rather small covalent radius of germanium. (iv) We have recently synthesized a number of complexes with the previously unknown [M(SO$_3$F)$_5$]$^-$ ion, where M = Ru and Pt.[8,9] A tin(IV) analogue should be obtained and would provide a better insight into the structure through the use of ^{119}Sn Mössbauer and NMR spectroscopy.

Experimental Section

Chemicals. Commercially available chemicals of analytical or reagent grades were generally used without purification. Technical grade HSO$_3$F (Baker and Adamson) was purified by double distillation at atmospheric pressure as described previously. Germanium powder (325 mesh, 99.97% pure) was obtained from Ventron Corp. Tin powder (20 mesh, 99.97% pure) was supplied by BDH.

The following compounds were synthesized according to published methods: bis(fluorosulfuryl) peroxide, S$_2$O$_6$F$_2$,[10] chlorine dioxide, ClO$_2$,[11] chloryl fluorosulfate, ClO$_2$SO$_3$F,[12] and potassium fluorosulfate, KSO$_3$F.[13]

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