

## KINETICS OF PROTONATION OF HEXAFLUORO-2-BUTYNE COMPLEXES OF PALLADIUM(0) WITH HALOACETIC ACIDS

J. BURGESS, R. D. W. KEMMITT and G. W. LITTLECOTT

Department of Chemistry, The University, Leicester LE1 7RH (Great Britain)

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### SUMMARY

The palladium(0) complexes,  $\text{Pd}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{PPh}_3)_2$  and  $\text{Pd}(\text{CF}_3\text{C}\equiv\text{C}-\text{CF}_3)(\text{PPh}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$  react with trifluoroacetic acid to give the alkenyl complexes, *trans*- $\text{Pd}(\text{OCOFCF}_3)(\text{CCF}_3=\text{CHCF}_3)(\text{PPh}_3)_2$  and *cis*- $\text{Pd}(\text{OCOFCF}_3)(\text{CCF}_3=\text{CHCF}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$  respectively.  $\text{Pd}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{PPh}_3)_2$  similarly reacts with trichloroacetic acid to give *trans*- $\text{Pd}(\text{OCOCl}_3)(\text{CCF}_3=\text{CHCF}_3)(\text{PPh}_3)_2$ . The reactions of  $\text{Pd}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$  with trifluoroacetic, difluoroacetic, and trichloroacetic acids, in chloroform solution, follow a second-order rate law; the activation parameters for the reaction with trifluoroacetic acid are  $\Delta H^\ddagger = 11.2 \text{ kcal}\cdot\text{mol}^{-1}$  and  $\Delta S^\ddagger = -35 \text{ cal}\cdot\text{deg}^{-1}\cdot\text{mol}^{-1}$ . A more complicated kinetic pattern has been observed for analogous reactions of  $\text{Pd}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{PPh}_3)_2$  and can be attributed to reversible loss of triphenylphosphine previous to reaction with the haloacetic acid.

### INTRODUCTION

We have shown<sup>1</sup> that the hexafluoro-2-butyneplatinum(0) complexes  $\text{Pt}(\text{CF}_3\text{C}\equiv\text{CCF}_3)\text{L}_2$  ( $\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{PMePh}_2, \text{PMe}_2\text{Ph}$ ;  $\text{L}_2 = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) react with trifluoroacetic acid to give alkenyl complexes of formula *cis*- $\text{Pt}(\text{OCOFCF}_3)(\text{CCF}_3=\text{CHCF}_3)\text{L}_2$ . Similar reactions have now been observed for the palladium(0) complexes  $\text{Pd}(\text{CF}_3\text{C}\equiv\text{CCF}_3)\text{L}'_2$  ( $\text{L}' = \text{PPh}_3$ ;  $\text{L}'_2 = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) and the kinetics of some of these reactions, particularly that of  $\text{Pd}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$  with several haloacetic acids, in chloroform solution have been investigated.

### EXPERIMENTAL

IR spectra were recorded using a Perkin-Elmer model 225 spectrophotometer. <sup>19</sup>F NMR spectra were measured relative to benzotrifluoride as internal standard using a Varian Associates DA60 spectrometer operating at 56.4 MHz. The complexes  $\text{Pd}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$ <sup>2</sup> and  $\text{Pd}(\text{fumaronitrile})(\text{PPh}_3)_2$ <sup>3</sup> were prepared as described in the literature. Baddley<sup>3</sup> has shown that fumaronitrile may be displaced from complexes of palladium(0) by dicyanoacetylene and we have found this to be a convenient method for preparing the hexafluoro-2-butyne complexes.

*Preparation of Pd(trans-CHCN=CHCN)(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)*

Fumaronitrile (1.5 g) and Pd(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub> (1.5 g) in benzene (80 ml) were stirred at room temperature for 30 min when a clear yellow solution was obtained. Benzene (ca. 15 ml) was removed under reduced pressure and addition of ethanol (20 ml) gave white crystals of fumaronitrile[1,2-bis(diphenylphosphino)ethane]-palladium(0) (1.8 g, 80%). M.p. 155–160°,  $\nu(\text{CN})$  2220  $\text{cm}^{-1}$ . (Found: C, 61.9; H, 4.4; N, 4.75. C<sub>30</sub>H<sub>26</sub>N<sub>2</sub>P<sub>2</sub>Pd calcd.: C, 62.0; H, 4.50; N, 4.82%.)

*Preparation of Pd(CF<sub>3</sub>C≡CCF<sub>3</sub>)(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)*

An excess of hexafluoro-2-butyne was condensed onto a solution of Pd(*trans*-CHCN=CHCN)(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) (1.8 g) in benzene (20 ml) contained in a Carius tube cooled in liquid nitrogen. The tube was sealed and after 1 day at room temperature the tube was opened and the solution was filtered and evaporated to dryness under reduced pressure. Recrystallisation of the residue from methylene chloride/hexane gave white crystals of the product; (1.8 g, 77%) m.p. 160–163°. (Found: C, 53.9; H, 3.5. C<sub>30</sub>H<sub>24</sub>F<sub>6</sub>P<sub>2</sub>Pd calcd.: C, 54.0; H, 3.6%)  $\nu(\text{C}=\text{C})$  1832  $\text{m cm}^{-1}$ . The <sup>19</sup>F NMR spectrum (CH<sub>2</sub>Cl<sub>2</sub>) showed a doublet at –10.4 ppm [ $J(\text{P}-\text{F})$  13.8 Hz].

*Preparation of Pd(CF<sub>3</sub>C≡CCF<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>*

As above Pd(*trans*-CHCN=CHCN)(PPh<sub>3</sub>)<sub>2</sub> (3 g) and excess hexafluoro-2-butyne gave white crystals of Pd(CF<sub>3</sub>C≡CCF<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub> (2.5 g, 74%). M.p. 192–194° (lit. 194–195°)<sup>4</sup>.  $\nu(\text{C}=\text{C})$  1838  $\text{m}$  and 1811  $\text{m cm}^{-1}$ .

*Reaction of trifluoroacetic acid with Pd(CF<sub>3</sub>C≡CCF<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>*

Pd(CF<sub>3</sub>C≡CCF<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub> (0.2 g) and trifluoroacetic acid (0.1 ml) in chloroform (10 ml) were shaken together for 30 min. Petroleum spirit (b.p. 100–120°) was added and the solvent was removed under reduced pressure to give a pale yellow solid. The solid was recrystallised from methylene chloride/hexane at –78° to give pale yellow crystals of *trans*-Pd(OCOCF<sub>3</sub>)(CCF<sub>3</sub>=CHCF<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub> (0.2 g, 91%). M.p. 165–169°. (Found: C, 55.8; H, 3.6; F, 19.3. C<sub>42</sub>H<sub>31</sub>F<sub>9</sub>O<sub>2</sub>P<sub>2</sub>Pd calcd.: C, 55.6; H, 3.4; F, 18.9%)  $\nu(\text{C}=\text{C})$ , 1620  $\text{cm}^{-1}$ . The <sup>19</sup>F NMR spectrum (CH<sub>2</sub>Cl<sub>2</sub>) showed resonances at –11.3 [3F, q,  $J(\text{F}-\text{F})$  12 Hz,  $\alpha$ -CF<sub>3</sub>] and –4.7 ppm (3F, quin,  $J(\text{F}-\text{F})=J(\text{H}-\text{F})$  12 Hz,  $\beta$ -CF<sub>3</sub>).

Using a similar procedure the following complexes were also prepared: *trans*-Pd(OCOCl<sub>3</sub>)(CCF<sub>3</sub>=CHCF<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub> as yellow crystals (54%). M.p. 105–108° (Found: C, 52.5; H, 3.3; F, 11.7. C<sub>42</sub>H<sub>31</sub>Cl<sub>3</sub>F<sub>6</sub>O<sub>2</sub>P<sub>2</sub>Pd calcd.: C, 52.7; H, 3.3; F, 11.9%)  $\nu(\text{C}=\text{C})$  1600  $\text{cm}^{-1}$ . The <sup>19</sup>F NMR spectrum (CH<sub>2</sub>Cl<sub>2</sub>) showed resonances at –10.6 (3F, q,  $J(\text{F}-\text{F})$  11 Hz,  $\alpha$ -CF<sub>3</sub>) and –4.2 ppm (3F, quin,  $J(\text{F}-\text{F})=J(\text{H}-\text{F})$  11 Hz,  $\beta$ -CF<sub>3</sub>). Pd(OCOCF<sub>3</sub>)(CCF<sub>3</sub>=CHCF<sub>3</sub>)(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) as white crystals (89%). M.p. 212–214°. (Found: C, 49.0; H, 3.2; F, 21.8. C<sub>32</sub>H<sub>25</sub>F<sub>9</sub>O<sub>2</sub>P<sub>2</sub>Pd calcd.: C, 49.2; H, 3.2; F, 21.9%)  $\nu(\text{C}=\text{C})$  1622  $\text{cm}^{-1}$ . The <sup>19</sup>F NMR spectrum (CH<sub>2</sub>Cl<sub>2</sub>) showed resonances at –10.7 (3F, quin,  $J(\text{F}-\text{F})$  11.6,  $J(\text{P}-\text{F})$  11.6 Hz,  $\alpha$ -CF<sub>3</sub>), –3.4 (3F, quin,  $J(\text{F}-\text{F})$  11.6,  $J(\text{H}-\text{F})$  11.6 Hz,  $\beta$ -CF<sub>3</sub>), and +11.9 ppm (3F, s, O<sub>2</sub>CCF<sub>3</sub>).

*General*

Trifluoroacetic acid (Koch–Light Laboratories Limited), trichloroacetic acid (Fisons Scientific Apparatus Limited), and difluoroacetic acid (Mann Research

Laboratories Inc., New York) were used without further purification; dried AnalaR solvents were used throughout.

Solutions for the kinetic experiments were freshly prepared for each set of runs, as chloroform solutions of these palladium complexes are stable only for a matter of hours at ambient temperatures. Kinetic runs were conducted in 1 cm cells in the thermostatted cell compartment of a Unicam SP800A recording spectrophotometer. Reagent concentrations are detailed in the Table captions. The runs were monitored at 290 or 295 nm for the palladium complexes, 310 nm for the platinum complex. Rate constants were derived from the variation of absorbance values with time, and activation parameters from the variation of rate constants with temperature, using a standard least-mean-squares programme (Elliott 803 computer).

## RESULTS AND DISCUSSION

Trifluoroacetic acid readily reacts with the hexafluoro-2-butyne complexes  $\text{Pd}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{L})_2$ , ( $\text{L} = \text{PPh}_3$ ;  $\text{L}_2 = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) to give the air-stable alkenyl complexes,  $\text{Pd}(\text{OCOCF}_3)(\text{CCF}_3=\text{CHCF}_3)\text{L}_2$ . The  $^{19}\text{F}$  NMR spectrum of both complexes exhibits two resonances which may be assigned to  $\alpha$ - and  $\beta$ - $\text{CF}_3$  groups in the alkenyl system  $\text{Pd}[\text{C}(\text{C}^\alpha\text{F}_3)=\text{CH}(\text{C}^\beta\text{F}_3)]$ . The magnitude of  $^{19}\text{F}$ - $^{19}\text{F}$  coupling between the inequivalent  $\text{CF}_3$  groups implies a *cis*-configuration of  $\text{CF}_3$  groups in the coordinated alkenyl ligand<sup>5</sup>. As in the analogous platinum systems<sup>1</sup>, these protonation reactions occur with retention of configuration about the carbon-carbon bonds of the alkyne. The absence of  $^{31}\text{P}$ - $^{19}\text{F}$  coupling with the  $\alpha$ - $\text{CF}_3$  group in the complex  $\text{Pd}(\text{OCOCF}_3)(\text{CCF}_3=\text{CHCF}_3)(\text{PPh}_3)_2$  indicates a *trans*-arrangement of phosphine ligands as is observed in the corresponding *trans*- $\text{Pt}(\text{OCOCF}_3)(\text{CCF}_3=\text{CHCF}_3)(\text{PPh}_3)_2$ <sup>1</sup>. In the complex *cis*- $\text{Pd}(\text{OCOCF}_3)(\text{CCF}_3=\text{CHCF}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$  the  $\alpha$ - $\text{CF}_3$  resonance of the alkenyl system is coupled to both fluorine and phosphorus. The protonation of  $\text{Pd}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{PPh}_3)_2$  presumably gives an intermediate *cis*-complex, *cis*- $\text{Pd}(\text{OCOCF}_3)(\text{CCF}_3=\text{CHCF}_3)(\text{PPh}_3)_2$  as is observed in the corresponding platinum complexes. Our inability to detect the formation of a *cis*-complex is presumably a consequence of the known lability of *cis*-tertiary phosphine complexes of palladium(II)<sup>6</sup>.

TABLE I

OBSERVED FIRST-ORDER RATE CONSTANTS ( $k_{\text{obs}}$ ) FOR THE REACTION OF  $\text{Pd}(\text{C}_4\text{F}_6)$ -  
(Diphos) WITH TRIFLUOROACETIC ACID IN CHLOROFORM AT 35.0°

$10^4 \times [\text{CF}_3\text{CO}_2\text{H}]$ (M)	$10^4 \times k_{\text{obs}}$ (s <sup>-1</sup> )
5.0	5.8
8.3	6.2
17.0	11.0
25.0	19.8
50.0	31
58.0	35
83.0	56
100.0	75

TABLE 2

OBSERVED FIRST-ORDER RATE CONSTANTS ( $k_{obs}$ ) FOR THE REACTION OF  $Pd(C_4F_6)$ -  
(Diphos) WITH TRICHLOROACETIC ACID IN CHLOROFORM AT 35.0°

$10^4 \times [CCl_3CO_2H]$ (M)	$10^4 \times k_{obs}$ (s <sup>-1</sup> )
21	18
48	43
76	63
103	88

TABLE 3

OBSERVED FIRST-ORDER RATE CONSTANTS ( $k_{obs}$ ) FOR THE REACTION OF  $Pd(C_4F_6)$ -  
(Diphos) WITH DIFLUOROACETIC ACID IN CHLOROFORM AT 35.0°

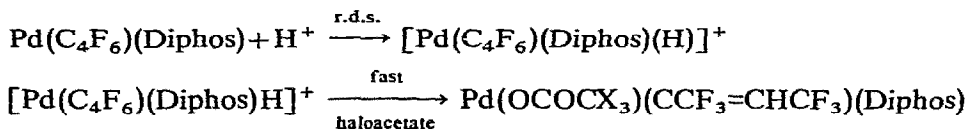
$10^4 \times [CF_2HCO_2H]$ (M)	$10^4 \times k_{obs}$ (s <sup>-1</sup> )
25	2.4
58	4.9
92	7.8
125	10.2

*Pd(CF<sub>3</sub>C≡CCF<sub>3</sub>)(Diphos)*

The kinetics of the reaction of this complex with an excess of trifluoroacetic acid, trichloroacetic acid, or difluoroacetic acid, in chloroform were first-order with respect to the palladium complex. Observed first-order rate constants are reported in Tables 1 to 3. Plots of these rate constants against acid concentration are linear, with a zero intercept. Thus the rate law for these reactions is:

$$-d[Pd(C_4F_6)(Diphos)]/dt = k_2[Pd(C_4F_6)(Diphos)] \cdot [acid]$$

Values of  $k_2$  for several acids are collected in Table 4, which shows a qualitative correlation between acid strength and rate; the lack of p*K* values for these acids in chloroform precludes any quantitative correlation. The most likely sequence for the reaction is:



If the bonding in these hexafluoro-2-butyne complexes is envisaged as a three-membered metallocyclopropene ring then protonation of the ring could initially involve attack at the palladium, at the carbon-carbon double bond, at a palladium-carbon bond or at the fluorine atoms of the trifluoromethyl groups. The last possibility seems unlikely; if a proton hydrogen-bonded to fluorine was needed to activate the molecule to proton attack elsewhere then a second-order dependence on acid concen-

TABLE 4

SECOND-ORDER RATE CONSTANTS ( $k_2$ ) FOR THE REACTION OF Pd(C<sub>4</sub>F<sub>6</sub>)(Diphos) WITH HALOACETIC ACIDS IN CHLOROFORM AT 35.0°

Acid	$k_2$ ( $l \cdot mol^{-1} \cdot s^{-1}$ )
CCl <sub>3</sub> CO <sub>2</sub> H	0.85
CF <sub>3</sub> CO <sub>2</sub> H	0.70
CF <sub>2</sub> HCO <sub>2</sub> H	0.08
CH <sub>3</sub> CO <sub>2</sub> H	very slow

tration would be expected. The other three mechanisms all seem possible, and indeed it is not possible to choose between them on the evidence available. Thus although perfluoroalkynes, unlike alkynes, are difficult to protonate, coordination of hexafluoro-2-butyne to palladium(0) will enhance electrophilic attack at the alkyne. Such direct protonation of the alkyne would result in the proton being advantageously sited for transition state formation and for carbon-hydrogen bond formation to give the observed product. On the other hand there is kinetic evidence for direct proton attack at metal centres, for example at nickel(0) in Ni[P(OEt<sub>3</sub>)<sub>4</sub>]<sup>7</sup>, and at ruthenium(II) in the [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> cation<sup>8</sup>. Rapid and facile interconversion of a hydride-alkyne complex to the observed products would seem a likely process in the present system. Examples of compounds containing an alkene and a hydride coordinated to the same metal atom include [Pt(H)(SnCl<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(COD)<sup>9</sup> and the intermediates recently demonstrated in proton exchange reactions of 1,3-cyclohexadiene complexes of rhodium(I) and iridium(I)<sup>10</sup>. Features of the preceding mechanisms can be combined in a mechanism of proton attack at one of the platinum-carbon bonds.

The variation of the rate of the reaction with trifluoroacetic acid with temperature is shown in Table 5. From these results an activation enthalpy of 11.2 (±0.3) kcal·mol<sup>-1</sup> and an activation entropy of -35 cal·deg<sup>-1</sup>·mol<sup>-1</sup> can be derived. It is interesting, though probably not significant, that this activation enthalpy is similar to that (13 kcal·mol<sup>-1</sup>) reported for protonation of tetrakis(triethyl phosphite)nickel(0)<sup>7</sup>.

TABLE 5

FIRST-ORDER RATE CONSTANTS ( $k_{obs}$ ) FOR THE REACTION OF Pd(C<sub>4</sub>F<sub>6</sub>)(Diphos) WITH TRIFLUOROACETIC ACID ( $5.0 \times 10^{-3}$  M) IN CHLOROFORM

Temp. (°C)	$10^4 \times k_{obs}$ (s <sup>-1</sup> )
25.0	14.6
29.6	19.2
32.3	23.6
34.9	29.6
37.8	33.5
41.1	39.5

$$\text{Pd}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{PPh}_3)_2$$

Again reactions of this complex with an excess of haloacetic acid follow first-order kinetics, to at least 65% of complete reaction, so the rate law contains a term in the first power of the complex, but for this complex the dependence of observed first-order rate constant on (excess) acid concentration is not simply linear as for the Diphos analogue. Both in trifluoroacetic acid and in trichloroacetic acid plots of observed first-order rate constants against acid concentration are curved; values are reported in Table 6, and the curved dependence is illustrated in Fig. 1. Graphs of observed first-order rate constants against logarithms of acid concentrations are linear, with a slope of about 0.2; the difficulty of constructing a reaction mechanism which is consistent with a rate law with a term in  $[\text{H}^+]^{0.2}$  suggests that this approach is not meaningful. A more likely reason for the observed dependence of rate on acid concentration is partial dissociation, and subsequent protonation, of a phosphine ligand<sup>11</sup>:

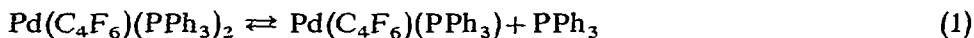


TABLE 6

FIRST-ORDER RATE CONSTANTS ( $k_{\text{obs}}$ ) FOR THE REACTION OF  $\text{Pd}(\text{C}_4\text{F}_6)(\text{PPh}_3)_2$  WITH TRICHLOROACETIC ACID AND WITH TRIFLUOROACETIC ACID IN CHLOROFORM AT 35.0°

$10^4 \times [\text{CCl}_3\text{CO}_2\text{H}]$ (M)	$10^4 \times k_{\text{obs}}$ (s <sup>-1</sup> )	$10^4 \times [\text{CF}_3\text{CO}_2\text{H}]$ (M)	$10^4 \times k_{\text{obs}}$ (s <sup>-1</sup> )
10	3.0	10	3.1
13	3.2	25	3.8
25	3.7	50	4.8
50	4.2	100	6.1
100	5.0		

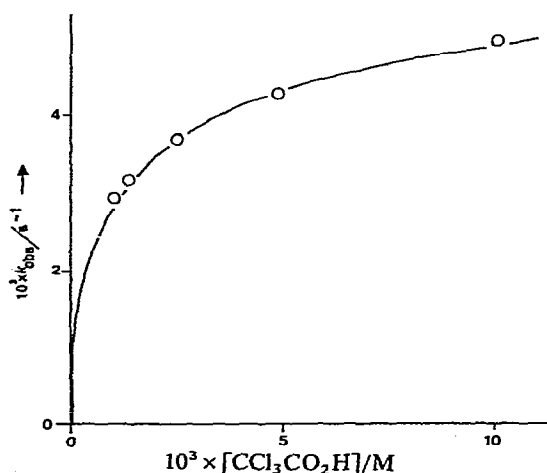
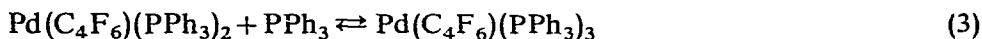


Fig. 1. The dependence of observed first-order rate constants ( $k_{\text{obs}}$ ) on acid concentration for the reaction of  $\text{Pd}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{Diphos})$  with trichloroacetic acid in chloroform solution.

Addition of triphenylphosphine to reaction mixtures has a marked effect on reaction rates. Thus in reaction mixtures containing a ten-fold excess of acid the addition of one mole of triphenylphosphine per mole of palladium complex resulted in a thirty-fold decrease in rate; in a fifty-fold excess of acid only a small reduction in rate was observed. These observations are consistent with equilibria (1) and (2) above, with a lower reactivity of  $\text{Pd}(\text{C}_4\text{F}_6)(\text{PPh}_3)_2$  than of  $\text{Pd}(\text{C}_4\text{F}_6)(\text{PPh}_3)$ . They are also consistent with the production of a less reactive tris(triphenylphosphine) complex in the presence of added triphenylphosphine.



This latter seems a less likely explanation, for the addition of triphenylphosphine to reaction mixtures containing  $\text{Pd}(\text{C}_4\text{F}_6)(\text{Diphos})$  and haloacetic acids has only a very small effect on rates.

Rates of reaction of  $\text{Pd}(\text{C}_4\text{F}_6)(\text{PPh}_3)_2$  with trichloroacetic acid over a range of temperatures are reported in Table 7. From these values the activation enthalpy for the reaction is  $19.5 \text{ kcal} \cdot \text{mol}^{-1}$  and the activation entropy  $-12 \text{ cal} \cdot \text{deg}^{-1} \cdot \text{mol}^{-1}$ .

TABLE 7

FIRST-ORDER RATE CONSTANTS ( $k_{\text{obs}}$ ) FOR THE REACTION OF  $\text{Pd}(\text{C}_4\text{F}_6)(\text{PPh}_3)_2$  WITH TRICHLOROACETIC ACID ( $10^{-2} \text{ M}$ ) IN CHLOROFORM

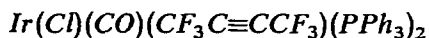
Temp. (°C)	$10^4 \times k_{\text{obs}}$ ( $\text{s}^{-1}$ )
27.5	2.4
30.0	2.8
35.5	5.0
39.9	9.2
43.3	11.2

These activation parameters are very different from those for the analogous Diphos complex. This fact provides evidence in favour of a marked difference in mechanism between the two complexes. If equilibrium (1) plays an important role in the reaction of the bis(triphenylphosphine) complex, then the experimental activation parameters ( $\Delta X_{\text{obs}}^\ddagger$ ) will be composite quantities, containing  $\Delta X^0$  for equilibrium (1) as well as  $\Delta X^\ddagger$  for the actual reaction with the acid. The higher value of  $\Delta H^\ddagger$  for the bis(triphenylphosphine) complex than for the Diphos complex could be associated with the enthalpy of dissociation of the phosphine ligand in eqn. (1).

The rates of reactions of  $\text{Pd}(\text{C}_4\text{F}_6)(\text{PPh}_3)_2$  with acids vary surprisingly little with the nature of the solvent. Thus the observed first-order rate constants in  $5 \times 10^{-3} \text{ M}$  trichloroacetic acid are  $9.0 \times 10^{-4} \text{ s}^{-1}$  in benzene,  $4.2 \times 10^{-4} \text{ s}^{-1}$  in chloroform, and  $1.8 \times 10^{-4} \text{ s}^{-1}$  in ethanol, at  $35.0^\circ$ . Solvation of the species  $\text{Pd}(\text{C}_4\text{F}_6)(\text{PPh}_3)_2$ ,  $\text{Pd}(\text{C}_4\text{F}_6)(\text{PPh}_3)$ , and  $\text{PPh}_3$  will be important in determining reactivities via equilibrium (1), while solvation of protons from the acid will also have an important bearing on the concentration of protons and thence on rates. The very small rate variation observed presumably arises from an almost complete cancellation of opposite effects from the factors mentioned.



A preliminary study of the kinetics of reactions of this complex with haloacetic acids indicated a more complicated kinetic pattern. However it proved possible to estimate that the half-life for these reactions is a week or more, so the rate constants are very much less than for the analogous palladium complexes discussed above. This difference in reactivities can probably be ascribed to the greater strength of platinum-alkyne bonding, for whatever mechanism operates is likely to involve some platinum-carbon bond stretching.



This iridium complex and the vinyl product resulting from its reaction with trifluoroacetic acid<sup>1</sup> had ultraviolet spectra which differed insufficiently for the precise estimation of rate constants. Qualitatively, the reaction is much slower for this iridium(0) complex than for the palladium(0) complexes discussed above.

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#### REFERENCES

- 1 D. M. Barlex, R. D. W. Kemmitt and G. W. Littlecott, *Chem. Commun.*, (1969) 613; G. W. Littlecott, B. Y. Kimura and R. D. W. Kemmitt, *J. Chem. Soc. Dalton Trans.*, in press.
- 2 B. Clarke, M. Green, R. B. L. Osborn and F. G. A. Stone, *J. Chem. Soc. A*, (1968) 167.
- 3 G. L. McClure and W. H. Baddley, *J. Organometal. Chem.*, 27 (1971) 155.
- 4 E. O. Greaves, C. J. L. Lock and P. M. Maitlis, *Can. J. Chem.*, 46 (1968) 3879.
- 5 H. C. Clark and W. S. Tsang, *J. Amer. Chem. Soc.*, 89 (1967) 529, 533.
- 6 L. L. Martin and R. A. Jacobson, *Inorg. Chem.*, 10 (1971) 1795.
- 7 C. A. Tolman, *J. Amer. Chem. Soc.*, 92 (1970) 4217.
- 8 P. C. Ford, J. R. Kuempel and H. Taube, *Inorg. Chem.*, 7 (1968) 1976.
- 9 See, for example, A. J. Deeming, B. F. G. Johnson and J. Lewis, *Chem. Commun.*, (1970) 598; H. A. Tayim and J. C. Bailar, *J. Amer. Chem. Soc.*, 89 (1967) 3420, 4330.
- 10 B. F. G. Johnson, J. Lewis and D. J. Yarrow, *J. Chem. Soc. Dalton Trans.*, (1972) 2084.
- 11 See, for example, M. L. Tobe, *Inorganic Reaction Mechanisms*, Nelson, London, 1972, p. 154.