Reactivity and Mechanism in the Oxidative Addition of Iodoalkanes and Di-iodoalkanes to a Dimethylplatinum(II) Complex

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The complex [PtMe$_2$(phen)], (**1**) (phen = 1,10-phenanthroline), reacts with primary alkyl iodides by the S_N2 mechanism. Cyclopropylmethyl bromide adds to (**1**) without any ring opening of the cyclopropyl group. The reactivity ratio towards (**1**) for MeI : EtI : PrI : BuI = 1 000 : 1 : 0.5 : 0.6 and the much greater reactivity of MeI is due to the bulky nature of the nucleophile (**1**). Di-iodoalkanes I(CH$_2$)$_n$I also react by the S_N2 mechanism to give first [PtIMe$_2${(CH$_2$)$_n$I}(phen)] and then, with excess of complex (**1**), [{PtIMe$_2$(phen)}$_2$(μ-CH$_2$)$_n$], when n = 3—5. The neighbouring platinum atom in the Pt(CH$_2$)$_3$I group is found to activate the C–I bond by a factor of 5.6, compared to PrI, in oxidative addition to (**1**). The di-iodoalkanes CH$_2$I$_2$ and C$_2$H$_4$I$_2$ react with complex (**1**), at least in part, by a free-radical mechanism and the reasons for the change in mechanism are discussed.

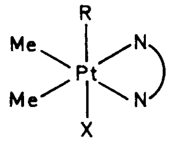
Oxidative addition of alkyl halides to transition-metal complexes is a key step in several homogeneously catalysed organic reactions, and is one of the most studied organometallic reactions.[1] This reaction has often been used for the synthesis of alkylplatinum(IV) complexes, most commonly by oxidation of platinum(II) complexes containing phosphine or arsine ligands.[2–7] Platinum(II) complexes with di-imine ligands such as 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) are particularly reactive to oxidative addition, and a much wider variety of alkyl halides can therefore be studied.[8–16] This paper reports on the mechanism of reaction of the complex [PtMe$_2$(phen)], (**1**) with primary alkyl halides and with α,ω-di-iodoalkanes. A preliminary account of parts of this work [17] and details of the synthesis and characterization of many of the products [12] have been published elsewhere.

Results and Discussion

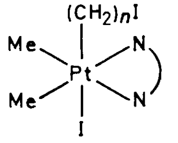
Complex (**1**) is particularly useful for studies of the mechanisms of oxidative addition since it is stable to air, and therefore easily handled, it is bright red in colour, thus allowing its reactions to be monitored easily by u.v.–visible spectroscopy,[15,17–20] and it reacts cleanly with a wide variety of alkyl halides.[10–18] Most other platinum(II) complexes undergo clean oxidative addition only with methyl halides, benzyl halides, allyl halides, or fluoroalkyl halides.[1–8]

Primary Alkyl Halides.—Kinetic studies of the reactions of complex (**1**) with primary alkyl halides to give the products (**2**) were carried out in acetone solution, using a large excess of the alkyl halide. Under these conditions the reactions followed good first-order kinetics for at least four half-lives in all cases (Figure 1). Plots of the observed first-order rate constants *versus* the concentration of alkyl halide also gave good linear plots passing through the origin, showing a first-order dependence of the rate on the concentration of alkyl halide (Figure 2). The overall second-order rate constants obtained are given in Table 1.

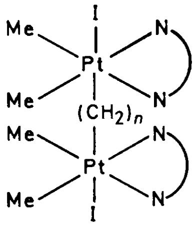
The kinetic results suggested that the S_N2 mechanism of oxidative addition, involving rate-determining displacement of iodide from the alkyl halide by the nucleophilic platinum centre of (**1**), was involved.[10,11] The kinetic data are not consistent with a free-radical chain mechanism, and this mechanism is also ruled out by the lack of incorporation of oxygen or activated alkenes in the products when reactions were carried out in the presence of these reagents.[15,18]



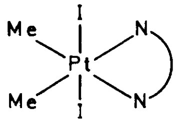
	R	X
(**2a**)	Me	I
(**2b**)	Et	I
(**2c**)	Pr	I
(**2d**)	Bu	I
(**2e**)	C$_5$H$_{11}$	I
(**2f**)	CH$_2$CH$_2$CHCH$_2$	Br
(**2g**)	CH$_2$=CHCH$_2$CH$_2$	Br



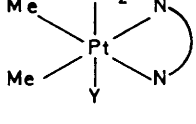
	n
(**3a**)	3
(**3b**)	4
(**3c**)	5
(**3d**)	2

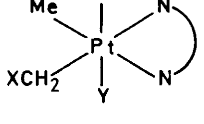


	n
(**4a**)	3
(**4b**)	4
(**4c**)	5
(**4d**)	2



(**5**)





(**6a**) X = Y = I (**7a**)
(**6b**) X = Cl, Y = I (**7b**)
(**6c**) X = Y = Cl (**7c**)

Table 1. Second-order rate constants for reactions of complex (**1**) in acetone at 25 °C

Reagent	10^3k_2/dm^3 mol^{-1} s^{-1}	Reagent	$10^3k_2'$/dm^3 mol^{-1} s^{-1}
MeI	$(69 \pm 5) \times 10^3$		
EtI	69 ± 4		
Pr^{n}I	34 ± 2		
Bu^{n}I	39 ± 2		
$CH_3(CH_2)_4I$	44 ± 3		
CH_2I_2	*a*	(**6a**)	*b*
$I(CH_2)_2I$	11 700[c]	(**3d**)	*d*
$I(CH_2)_3I$	130 ± 10	(**3a**)	190 ± 9
$I(CH_2)_4I$	100 ± 10	(**3b**)	85 ± 5
$I(CH_2)_5I$	84 ± 4	(**3c**)	88 ± 5

[a] Very small in the early stages. [b] No reaction. [c] Refers to the approximate rate of disappearance of the band at 472.7 nm in the u.v.–visible spectrum. The reaction does not occur by the S_N2 mechanism. See text for a discussion. [d] Not measured but presumed to be very large.

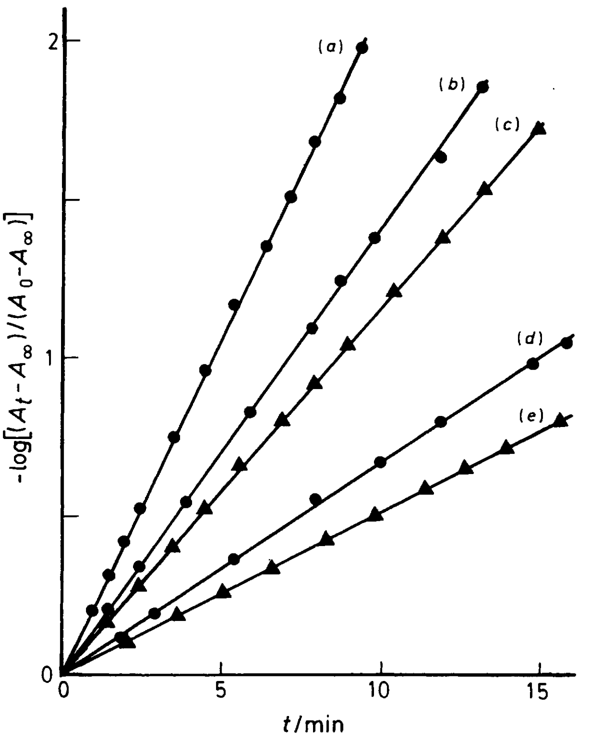


Figure 1. First-order plots for the reaction of complex (**1**) with alkyl halides in acetone at 25 °C: (*a*) $I(CH_2)_4I$, 7.5×10^{-2}; (*b*) $I(CH_2)_4I$, 5×10^{-2}; (*c*) EtI, 7.5×10^{-2}; (*d*) $I(CH_2)_4I$, 2.5×10^{-2}; (*e*) EtI, 2.5×10^{-2} mol dm^{-3}

It is more difficult to rule out a radical non-chain mechanism, since this would also give second-order kinetics.[21] The observation that alkenes such as acrylonitrile, when present during the reaction, are not incorporated in the products (**2**) rules out out the intermediacy of free alkyl radicals[18] but does not preclude the intermediacy of caged radical pairs $[\mathrm{PtIMe_2(phen)}]^{\bullet}\mathrm{R}^{\bullet}$ which then collapse to give (**2**). In order to test for this mechanism, the reaction of (**1**) with cyclopropylmethyl bromide was studied. The reaction gave only (**2f**) as product. If the cyclopropylmethyl radical were formed, it would undergo ring opening to give the but-3-enyl radical[22] with a first-order rate constant, $k \approx 10^8$ s^{-1}. This would then give the product (**2g**), which was not observed. Complex (**2g**) is stable and can be prepared by reaction of but-3-enyl bromide with complex (**1**).[23] This result is most easily rationalized in terms of the S_N2 mechanism. For the radical non-chain mechanism to be correct, the intermediate $[\mathrm{PtBrMe_2(phen)}]^{\bullet}\mathrm{CH_2CH_2CHCH_2}^{\bullet}$ must collapse to product (**2f**) with a rate constant much greater than 10^8 s^{-1}. Further evidence against this radical mechanism is obtained from the relative rates of reaction with different alkyl iodides, RI, which follow the series R = Me $\gg$ Et $\gg$ Pr^i, the opposite of the expected series for a radical non-chain mechanism but the expected series for the S_N2 mechanism.

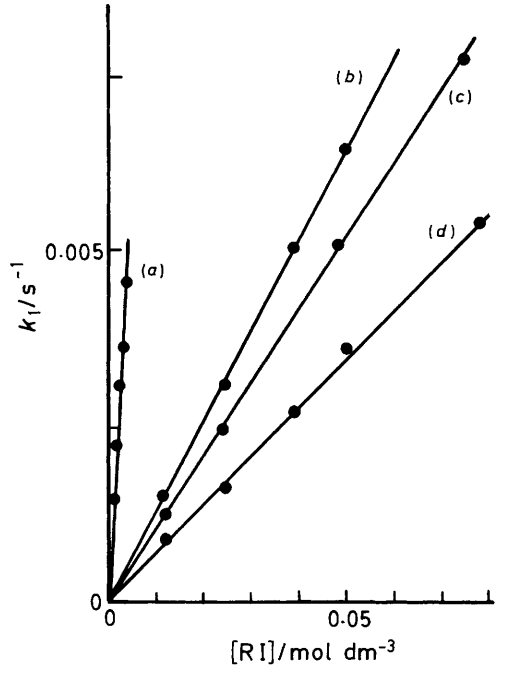


Figure 2. Plots of first-order rate constants (k_1/s^{-1} or, for MeI only, $0.02k_1$/s^{-1}) for the reaction of complex (**1**) with alkyl halides in acetone at 25 °C *versus* concentration of alkyl halide: (*a*) MeI; (*b*) $I(CH_2)_3I$; (*c*) $I(CH_2)_4I$; (*d*) EtI

If we take the S_N2 mechanism to be correct, it is interesting to compare the rate constants obtained with more conventional nucleophiles than (**1**). A series of average relative rates has been proposed[19] to be Me:Et:Pr:Bu = 30:1:0.4:0.4 whereas we observe this series for complex (**1**) as nucleophile to be 1 000:1:0.5:0.6.[24] The large decrease in rate between MeI and EtI for reaction with complex (**1**) is presumably due to steric effects in the reaction with the bulky nucleophile (**1**). Since square-planar complexes with tertiary phosphine ligands are much more sterically hindered than (**1**), it is not surprising that these complexes usually fail to undergo oxidative addition with ethyl iodide, and other primary alkyl halides, by the S_N2 mechanism. Usually a free radical mechanism is observed for such reactions when they occur at all.[1,23]

Di-iodoalkanes, $I(CH_2)_nI$ *with* n = 3—5.—The di-iodoalkanes $I(CH_2)_nI$ with n = 1 or 2 react with complex (**1**) in a more complex way than when n = 3—5 and these reactions are treated later. Reaction of complex (**1**) with a large excess of $I(CH_2)_nI$, n = 3—5, gave the products (**3**). These reactions followed good second-order kinetics (Figures 1 and 2), as for the simple alkyl iodides, and the rates were not affected by light or by radical scavengers or initiators. The reactions thus probably occur by the S_N2 mechanism and the second-order rate constants are given in Table 1. It can be seen that the distant iodo substituent has a small activating effect on the rate of reaction when n = 3, and that this effect falls off as the length of

Table 2. Product ratio for the reaction between complex (**1**) and CH_2I_2 at 20 °C

Conditions	10^3[PtMe$_2$(phen)] (mol dm^{-3})	10^2[CH$_2$I$_2$] (mol dm^{-3})	Solvent	Product ratio* {(**6a**) + (**7a**)}/(**5**)
Excess of CH_2I_2, dark	8.2	20.6	Acetone	2.2
Excess of CH_2I_2, diffuse light	8.2	20.6	Acetone	2.3
1:1 Molar ratio, dark	9.4	0.94	Acetone	1.2
1:1 Molar ratio, diffuse light	9.4	0.94	Acetone	1.4
1:1 Molar ratio, galvinoxyl present, diffuse light	5.8	0.58	Acetone	0.94
1:1 Molar ratio, diffuse light	8.6	0.86	CH_2Cl_2	3.4

* Average of two runs; reproducibility in all cases was ±10%.

the alkyl chain increases and is absent when $n = 5$. The activating effect is given by the ratio $0.5k_2\{I(CH_2)_nI\}/k_2\{H(CH_2)_nI\} = 1.9$, 1.3, and 0.95 when $n = 3$, 4, and 5 respectively.

Reaction of complex (**1**) with (**3**) gave the corresponding bridging polymethylene derivatives (**4**).[18] The rates of these reactions were monitored in the usual way using a large excess of the derivative (**3**). Again good second-order kinetics were observed and tests for free-radical mechanisms were negative, indicating the S_N2 mechanism. The rate constants are given in Table 1. The distant platinum centre of (**3**) has an activating effect on the rate of reaction. Since there is no statistical effect in this case, the activating effect is given by $k_2\{(3)\}/k_2\{H(CH_2)_nI\} = 5.6$, 2.2, and 2.0 when $n = 3$, 4, and 5 respectively. Again the effect decreases with increasing chain length. This appears to be the first measurement of the neighbouring-group effect of a transition-metal atom on the rate of oxidative addition.[19] A much greater effect by a neighbouring rhodium centre was proposed but this has recently been retracted.[24,25] The present work suggests a fairly small, but still significant, activating effect when $n = 3$.[19]

Di-iodomethane and Chloroiodomethane.—Reaction of di-iodomethane with complex (**1**) gave a mixture of (**5**), (**6a**), and (**7a**). Initially, the *cis* isomer (**7a**) was formed but this isomerized slowly to (**6a**), as monitored by n.m.r. spectroscopy.[12] Chloroiodomethane with (**1**) gave a mixture of (**5**), (**6b**), and (**7b**) and small amounts of (**6c**) and (**7c**). A similar halogen scrambling has been observed previously in reactions with platinum(0) complexes and was considered indicative of a free-radical reaction.[26]

The kinetics of the reaction of (**1**) with CH_2Cl_2 in acetone solution were complex. An initial induction period was followed by a rapid reaction, indicative of a free-radical chain reaction. Confirmation was obtained by the observation that the reaction was retarded by the free-radical scavenger galvinoxyl [2,6-di-t-butyl-α-(3,5-di-t-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-*p*-tolyloxy] [an independent experiment showed that galvinoxyl failed to react with (**1**)], and this reagent also gave an increase in the yield of the product (**5**) (Table 2).[27] The rate of reaction was greatly increased by irradiation of the solution, as was observed previously with the free-radical chain reaction of (**1**) with Pr^{i}I,[17,18] but the product ratio {(**6a**) + (**7a**)}/(**5**) was not significantly affected.

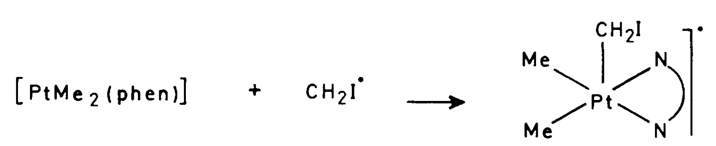
The above data are rationalized in terms of the following free-radical chain mechanism. The initiation steps are thought to involve iodine atom-abstraction steps [equations (1) and (2)],

$$[PtMe_2(phen)] + CH_2I_2 \longrightarrow [PtIMe_2(phen)]^{\bullet} + CH_2I^{\bullet} \quad (1)$$

$$[PtIMe_2(phen)]^{\bullet} + CH_2I_2 \longrightarrow [PtI_2Me_2(phen)] + CH_2I^{\bullet} \quad (2)$$

and reaction (1) occurs much more rapidly when the solution is irradiated. The chain reaction then occurs by the sequence of reactions (3)—(5).

The isomerization step of equation (4) is suggested in order to



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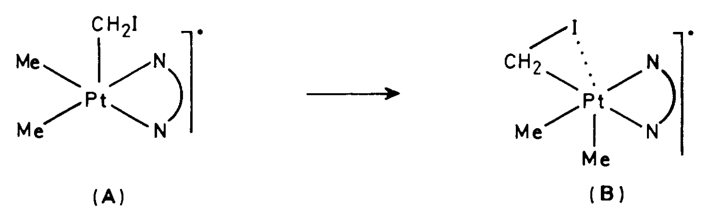

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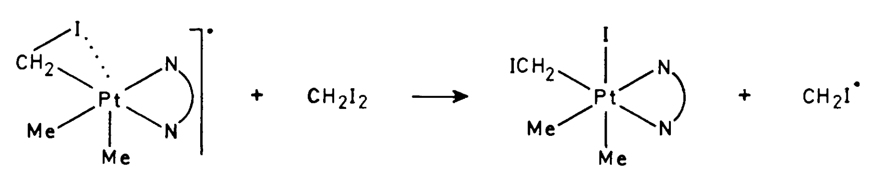

(5)

rationalize the unusual *cis* stereochemistry of the oxidative addition. Most oxidative additions to platinum(II), whether they occur by the free-radical chain mechanism or the S_N2 mechanism, give *trans* oxidative addition.[2–19] Both proposed platinum(III) radical intermediates (**A**) and (**B**) [equation (4)] have the favoured *fac*-trialkylplatinum stereochemistry, but (**B**) allows an intramolecular I ··· Pt interaction which may give added stability. We considered the possibility that the iodine atom of (**B**) could be completely transferred to platinum to give the carbon-centred radical [PtIMe$_2$(CH$_2$)(phen)], which could then abstract an iodine atom from CH_2I_2 to complete the chain reaction. However, in this mechanism CH_2ClI should give mostly [PtClMe$_2$(CH$_2$I)(phen)] as product, rather than the observed major product [PtIMe$_2$(CH$_2$Cl)(phen], (**6b**) and (**7b**), and so the mechanism is disproved.

The radical chain is obviously a short one since significant amounts of complex (**5**) were formed in all cases, and a contribution from a radical non-chain mechanism[28] cannot be ruled out. Complex (**5**) is not formed by decomposition of (**6**) or (**7**), which are stable under the reaction conditions.[12] A very similar radical-chain mechanism has been proposed for the photochemical oxidative addition of CH_2Cl_2 to [Pt(thpy)$_2$], where thpy = 2-(2-thienyl)pyridine.[28]

Why is the S_N2 mechanism not followed in the reaction of complex (**1**) with CH_2I_2? The major factor is probably the low reactivity of CH_2I_2 to nucleophilic substitution reactions.[29] In addition, free-radical reactions of CH_2I_2 may be initiated by electron transfer from platinum to give $[CH_2I_2]^-$, and this reaction is more favourable than for the monoiodoalkanes.[21,30]

The failure of the complexes (**6**) and (**7**) to react with (**1**) to give Pt$_2$(μ-CH$_2$) complexes is clearly due to steric hindrance. The C–X bond in halogenomethylplatinum complexes is known to be activated towards nucleophilic substitution,[31–33] but the bulky nucleophile (**1**) cannot approach the carbon atom as shown by a study of molecular models.

1,2-Di-iodoethane.—Complex (**1**) reacts rapidly with 1,2-di-iodomethane to give some ethylene and a mixture of complexes (**5**) and (**4d**).[12] Attempts to detect intermediates by n.m.r. spectroscopy were unsuccessful. The formation of (**4d**) must involve the intermediacy of (**3d**), but the platinum atom presumably activates the C–I bond of (**3d**) to such a great extent that this complex cannot be detected.[34]

The kinetics of the above reaction was complex. The reaction rate was accelerated by light and retarded by the free-radical scavenger galvinoxyl, suggesting that a radical mechanism was involved. The dark reaction, using an excess of 1,2-di-iodoethane, followed approximate first-order kinetics for about 50% of the reaction and then occurred faster than expected for a true first-order reaction. From plots at different concentrations of $C_2H_4I_2$ a 'second-order' rate constant was obtained and is given in Table 1. This indicates only the higher reactivity of $C_2H_4I_2$ when compared to either CH_2I_2 or $C_3H_6I_2$, since the mechanism is almost certainly not S_N2.

The mechanism of the above reaction is uncertain. It is likely that it resembles that for the CH_2I_2 reaction, except that the presumed intermediate (**3d**) reacts very rapidly with complex (**1**) to give (**4d**).

Conclusions

Complex (**1**) reacts with primary alkyl iodides by the S_N2 mechanism to give complexes (**2**). The same mechanism is involved in reactions of di-iodoalkanes I(CH$_2$)$_n$I with (**1**) to give (**3**) when n = 3—5, but when n = 1 or 2 a free-radical mechanism is observed instead.

The C–I bond of complex (**3a**), containing the Pt(CH$_2$)$_3$I group, is activated by the neighbouring platinum atom, and readily undergoes further oxidative addition to complex (**1**) to give the μ-polymethylene derivative (**4a**). Similar reactions occur with (**3b**) or (**3c**) to give (**4b**) or (**4c**) but the activating effect of the neighbouring platinum atom is much less. It is likely that a much greater activating effect is present for the Pt(CH$_2$)$_2$I group, but this could not be measured since the required complex (**3d**) could not be obtained.

Experimental

U.v.–visible spectra were recorded on either a Cary 118 spectrophotometer fitted with a thermostatted cell compartment or a Hewlett Packard 8450A diode-array spectrophotometer. Photolysis experiments were performed using a model 9741-50 Cole Parmer low-noise illuminator (λ 400—800 nm), in conjunction with the HP8450A spectrophotometer as described elsewhere.[15] Most of the synthetic work has been described previously.[12]

[PtBrMe$_2$(CH$_2$CHCH$_2$CH$_2$)(phen)].—Excess of cyclopropylmethyl bromide (0.25 cm^3) was added to a solution of [PtMe$_2$(phen)] (0.08 g) in acetone (20 cm^3). After several hours a pale yellow solution developed. The solvent was removed under vacuum and the solid residue was redissolved in CH_2Cl_2 (5 cm^3). The product was recovered by precipitation using pentane (15 cm^3). ^{1}H N.m.r. data in CDCl$_3$: 1.66 [s, ^2J(PtH) = 71.5, MePt], 1.36 [d, ^2J(PtH) = 70 Hz, CH$_2$Pt], −0.58, −0.83 (m, br, CHCH$_2$CH$_2$).

Kinetic Studies of the Reaction of Primary Alkyl Iodides with Complex (**1**).—(*a*) *Determination of rate constants.* A solution of EtI in acetone (30.0 cm^3, 1.0 × 10^{-1} mol dm^{-3}), was added to a solution of [PtMe$_2$(phen)] in acetone (10.0 cm^3, 2.0 × 10^{-3} mol dm^{-3}). The two solutions were thoroughly mixed and a sample quickly transferred to a 1-cm quartz cuvette held in the cell compartment of a Cary 118 spectrophotometer at 25 °C. The decay of the metal-to-ligand charge-transfer band at 472 nm was measured with time. The process was repeated using a constant concentration of complex (**1**), but varying that of EtI. A plot of $\ln[A_t - A_\infty)/(A_0 - A_\infty)]$ *vs.* time gave a good straight line in each case, and from these plots the overall second-order rate constants were determined (Table 1). In a similar fashion the second-order rate constants for the reaction of Pr^{n}I, Bu^{n}I, and CH$_3$(CH$_2$)$_4$I with complex (**1**) were calculated. In the case of MeI the reaction was very rapid and so the fast-scanning Hewlett Packard spectrophotometer was used; the initial concentrations of (**1**) and MeI (added by microsyringe to the cuvette, followed by rapid mixing) were also lower in order to give measurable rates while keeping the concentration of MeI at least seven times that of (**1**) (see Figure 2).

(*b*) *Reaction in the presence of olefin.* To an acetone solution (20 cm^3) containing [PtMe$_2$(phen)] (0.04 g) and freshly distilled acrolein (acrylaldehyde) (1 cm^3) was added an excess of MeI (0.5 cm^3). The solution rapidly turned pale yellow and the solid product was recovered by precipitation using pentane. It was identified as [PtIMe$_3$(phen)]. In a similar fashion EtI was treated with (**1**) in the presence of acrylonitrile, the sole product being [PtIMe$_2$Et(phen)].

Kinetics Studies of the Reaction of CH_2I_2 *with Complex* (**1**).—(*a*) A solution containing a mixture of [PtMe$_2$(phen)] (2.5 × 10^{-4} mol dm^{-3}) and CH_2I_2 (2.0 × 10^{-3} mol dm^{-3}) was made up in acetone and a portion quickly transferred to a 1-cm quartz cuvette in the cell compartment of a Cary 118 spectrophotometer. The reaction was monitored by following the decay of the band at 472 nm with time. An induction period of about 3 min was observed followed by a rapid reaction.

(*b*) *Photolysis of the reaction solution.* A solution, of the same concentrations as described above, was prepared in acetone. The u.v.–visible spectrum was recorded (325—600 nm) in diffuse daylight using the Hewlett Packard spectrophotometer (Figure 2). After a period of 15 min the sample was photolysed from above for 5 s. The band at 473 nm decayed almost instantaneously.

(*c*) *Effect of galvinoxyl.* A solution of [PtMe$_2$(phen)] (1.0×10^{-4} mol dm^{-3}) and CH$_2$I$_2$ (4.0×10^{-3} mol dm^{-3}) in acetone was allowed to react in a 1-cm quartz cuvette placed in the Hewlett Packard spectrophotometer. The absorbance at 473 nm was monitored with time. An induction period was observed followed by a rapid decay of the band. At this point a small volume of galvinoxyl [0.1 cm^3, 10% molar ratio with respect to (**1**)] was added. The reaction was also followed by ^{1}H n.m.r. spectroscopy. A solution of [PtMe$_2$(phen)] (0.015 g) in CH$_2$Cl$_2$ (1 cm^3) was placed in an n.m.r. tube and to it was added CH$_2$I$_2$ (0.003 cm^3, 1:1 molar ratio). N.m.r. spectra were recorded over a period of 15 min and finally after 2 h. The procedure was repeated but now in the presence of galvinoxyl (6% molar amount). The reaction was retarded by a factor of about 5.

(*d*) *Product ratio from the reaction.* A series of experiments were performed in acetone, for the reaction of complex (**1**) with CH$_2$I$_2$. The relative concentrations of each reagent were varied and the reactions were performed in the dark and in diffuse daylight. The relative amount of [PtIMe$_2$(CH$_2$I)(phen)] to [PtI$_2$Me$_2$(phen)] was measured by comparing the integral due to the MePt signal, from these complexes, in the ^{1}H n.m.r. spectrum of the reaction product (Table 2). A further experiment was performed in diffuse daylight for a 1:1 molar ratio of reagents, in the presence of galvinoxyl. Finally a reaction was performed using CH$_2$Cl$_2$ as solvent. The results were reproducible to ±10%.

Kinetic Studies of the Reaction of I(CH$_2$)$_2$I *with Complex* (**1**).—(*a*) *Determination of the overall rate.* The reaction between [PtMe$_2$(phen)] (5×10^{-5} mol dm^{-3}) and I(CH$_2$)$_2$I (1.0×10^{-3} mol dm^{-3}) in acetone was followed by monitoring the decay with time of the band due to complex (**1**) at 473 nm in the u.v.–visible spectrum. A plot of $\ln(A_t - A_\infty)$ *vs.* time was linear for about 50% completion of the reaction. The procedure was repeated for the same concentration of (**1**) but varying the concentration of I(CH$_2$)$_2$I. Using the linear portion of these plots an overall 'second-order' rate constant was determined for the reaction (Table 1).

(*b*) *Determination of the rate constant for the formation of* [PtIMe$_2${(CH$_2$)$_n$I}(phen)], n = 3—5. To a solution of [PtMe$_2$(phen)] (2.0×10^{-3} mol dm^{-3}) in acetone (10.0 cm^3) was added a solution of I(CH$_2$)$_4$I (1.0×10^{-4} mol dm^{-3}) in acetone (30.0 cm^3). A sample of the reaction mixture was quickly transferred to a 1-cm quartz cuvette which was placed in the thermostatically controlled (25 °C) cell compartment of a Cary 118 spectrophotometer. The absorbance at 473 nm was recorded with time and a graph of $\log [(A_t - A_\infty)/(A_0 - A_\infty)]$ *vs.* time gave a good straight line. The procedure was repeated using the same concentration of complex (**1**) whilst varying the concentration of I(CH$_2$)$_4$I. From such plots the overall second-order rate constant for this reaction was determined (Table 1). In a similar way the rate constants were determined for the reaction of I(CH$_2$)$_3$I and I(CH$_2$)$_5$I with complex (**1**).

(*c*) *Determination of the rate constant for the formation of* [{PtIMe$_2$(phen)}$_2${μ-(CH$_2$)$_n$}], n = 3—5. To a solution of [PtMe$_2$(phen)] (2.0×10^{-4} mol dm^{-3}) in acetone (10.0 cm^3) was added a solution of [PtIMe$_2${(CH$_2$)$_5$I}(phen)] (2.0×10^{-3} mol dm^{-3}) in acetone (10.0 cm^3). The decay of the band at 473 nm of a sample of this reaction mixture was monitored with time and at a temperature of 25 °C. A graph of $\log [(A_t - A_\infty)/(A_0 - A_\infty)]$ *vs.* time gave a good straight line. The procedure was repeated using the same concentration of complex (**1**) whilst varying the concentration of [PtIMe$_2${(CH$_2$)$_5$I}(phen)]. From such plots the overall second-order rate constant for the reaction was determined. The same procedure was used to determine the rate constant for the reaction of [PtMe$_2$(phen)] with [PtIMe$_2${(CH$_2$)$_n$I}(phen)], n = 3 or 4.

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