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THE HALOGENATION OF TOLUENE WITH SULPHURYL CHLORIDE AND DICHLORINE IN THE PRESENCE OF TRANSITION METAL COMPLEXES

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Summary

A detailed study has been made of the halogenation of toluene in the presence of a range of transition metal complexes. Both side-chain and ring chlorination are observed, the favoured route depending on the metal complex. Side-chain halogenation, in the presence of $[M(PPh_3)_4]$ and $[MCl_2(PPh_3)_2]$ (M = Pd, Pt), has been shown to proceed by a free radical chain reaction in which the metal complex acts solely as an initiator. In the presence of, $[M_2(CO)_{10}]$ (M = Mn, Re), $[Re_2(CO)_8(PPh_3)_2]$, $[Fe_2(CO)_4(\eta\text{-}cp)_2]$ and $[Mo_2(CO)_6(\eta\text{-}cp)_2]$, ring chlorinated products are formed by a Friedel–Crafts mechanism.

We have recently been engaged in studies of the addition of halocarbons to alkenes and methathesis reactions between saturated hydrocarbons and halocarbons in the presence of transition metal complexes. The addition reactions follow "redox-catalysed" mechanisms of the type outlined in Scheme 1 [1,2], while the metathesis reactions are free radical chain processes in which the metal complex acts simply as an initiator (Scheme 2) [3].

There are few reports in the literature of other reactions which could proceed by either metal catalysed or radical chain routes and which may involve metal–radical interactions, thereby modifying the normal reactivity patterns of the free radicals. One such process is the chlorination of alkyl aromatics by sulphuryl chloride in the presence of metal complexes which was reported by Matsumoto and co-workers [4]. The use of SO_2Cl_2 as a halogenating agent was first reported by Kharasch and

$[M] + CCl_4 \rightarrow [MCl] + CCl_3^{\cdot}$

$CCl_3^{\cdot} + RCH{=}CH_2 \rightarrow R\dot{C}HCH_2CCl_3$

$R\dot{C}HCH_2Cl_3 + [MCl] \rightarrow RCHClCH_2CCl_3 + [M]$

SCHEME 1. [M] represents a metal complex.

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$[M] + CCl_4 \rightarrow [MCl] + CCl_3^{\bullet}$

$CCl_3^{\bullet} + RH \rightarrow CHCl_3 + R^{\bullet}$

$R^{\bullet} + CCl_4 \rightarrow RCl + CCl_3^{\bullet}$

$2CCl_3^{\bullet} \rightarrow C_2Cl_6$

SCHEME 2. [M] represents a metal complex.

Brown [5], who found that excellent yields of chloroalkanes and chlorobenzyls could be obtained from SO_2Cl_2 and alkanes or toluenes respectively in the presence of organic peroxides. The main problem with these peroxide-initiated chain reactions, from a preparative point of view, is the formation of significant quantities of polychlorinated products. Thus, cyclohexane undergoes 98% conversion to a mixture of $C_6H_{11}Cl$ and $C_6H_{10}Cl_2$ (9/1 ratio) and toluene gives $PhCH_2Cl$ and $PhCHCl_2$ (73/27 ratio, under similar conditions to those used for reactions employing $[Pd(PPh_3)_4]$ (vide infra)).

Matsumoto et al. reported that the use of $[Pd(PPh_3)_4]$ in place of the peroxide initiator led to much more selective chlorination of toluenes. Thus, toluene, itself is reported to undergo 82% conversion to $PhCH_2Cl$ and $PhCHCl_2$ (98/2 ratio). Furthermore, in the case of toluene, no ring chlorinated products were reported, although such compounds were produced in small amounts ($< 5\%$), together with a substantial yield of *m*-$ClC_6H_4CH_2Cl$, from *m*-$ClC_6H_4CH_3$. Use of $[PdCl_2(PPh_3)_2]$ in analogous reactions led to a 62% conversion of toluene into $PhCH_2Cl$, $PhCHCl_2$ and $CH_3C_6H_4Cl$ (86/1/13 ratio). $[NiCl_2(PPh_3)_2]$ produced comparable yields of side chain chlorinated products with less ring chlorination. $[RuCl_2(PPh_3)_3]$ and $[RhCl(PPh_3)_3]$ both gave almost equal amounts of $PhCH_2Cl$ and $CH_3C_6H_4Cl$.

In view of this enhanced specificity in reactions between toluenes and SO_2Cl_2 in the presence of some of the above metal complexes compared to those using peroxide initiators, we were anxious to explore these reactions in more detail.

During the course of this study we found that SO_2Cl_2 was a particularly effective reagent for the high yield synthesis of some chlorometal carbonyls from dimeric metal carbonyl precursors. These results have been published in preliminary form [6].

Experimental

All reactions were carried out under dry oxygen-free nitrogen. All solvents and reagents were purified by standard techniques before use, and particular care was taken to ensure that organic reagents were free from peroxides. Solvents were thoroughly degassed by at least three freeze-pump-thaw cycles immediately prior to use. Transfer of solvents between vessels and all other manipulations were carried out with rigorous exclusion of air.

Infrared spectra were recorded on a Perkin–Elmer 457 spectrometer. GLC analyses were performed on either an F.I.D. equipped Pye 204, or Perkin–Elmer Sigma 3B chromatographs linked to a Spectra-Physics Autolab Minigrator. Quantification of product yields were accomplished by means of a 2 m, $\frac{1}{4}$ inch, 5% OV17 on Chromosorb W80-100 mesh column (column T 70°C, injector T 150°C, detector T 200°C, nitrogen flow rate 30 cm^3 min^{-1}) using the Pye 204 instrument. Analysis of chlorotoluene isomer ratios was performed on 25 m. OV101 capillary column (column, T 70°C, detector T 150°C, injector T 200°C). Quantification of reaction products was achieved with the aid of chlorocyclohexane as internal standard. Response factors were measured on three separate occasions during the course of each set of analyses.

$[Cr(CO)_6]$, $[Mn_2(CO)_{10}]$, $[Re_2(CO)_{10}]$ and $[Fe_2(CO)_4(\eta\text{-}Cp)_2]$ were supplied by Strem Chemicals and were recrystallised prior to use. $[Pd(PPh_3)_4]$ was supplied by Johnson–Matthey Chemicals Ltd and was used as received. $[Mo_2(CO)_6(\eta\text{-}cp)_2]$ [7], $[Pt(PPh_3)_4$ [8], *cis-* and *trans-*$[PtCl_2(PPh_3)_2]$ [9,10], $[RuCl_2(PPh_3)_3]$ [11], $[Os(CO)_3(PPh_3)_2]$ [12] and $[RhCl(PPh_3)_3]$ [13] were prepared by literature methods.

[ReCl(CO)₅]

A dichloromethane (20 cm^3) solution of $Re_2(CO)_{10}$ (0.22 g, 3.4×10^{-4} mol) was treated with SO_2Cl_2 (1 cm^3, 1.2×10^{-2} mol) at room temperature with stirring. Reaction was rapid as evidenced by an immediate effervescence which subsided after about 2 min, however, the solution was stirred for about 30 min at room temperature. Infrared spectroscopy of the solution at this stage show only carbonyl absorption bands for $[ReCl(CO)_5]$. Removal of the solvent and excess SO_2Cl_2 under vacuum produced a white solid, which was washed with ethanol and dried in vacuo. (0.24 g, 97% yield. Analysis; found: C, 16.70; Cl, 9.90. C_5ClO_5Re calcd.: C, 16.58; Cl; 9.81%).

[MnCl(CO)₅]

A procedure identical to that described above for $[ReCl(CO)_5]$ was used which employed $[Mn_2(CO)_{10}]$ (0.27 g, 6.9×10^{-4} mol). $[MnCl(CO)_5]$ was obtained as a yellow crystalline solid (0.29 g, 91% yield. Analysis; found: C, 26.40; Cl, 15.40. C_5ClMnO_5 calcd.: C, 26.10; Cl 15.40%).

[FeCl(CO)₂(η-Cp)]

$[Fe_2(CO)_4(\eta\text{-}Cp)_2]$ (0.25 g, 1.2×10^{-3} mol) was dissolved in trichloromethane (20 cm^3) and treated with SO_2Cl_2 (1 cm^3, 1.2×10^{-2} mol) at room temperature. A rapid reaction ensued, as indicated by the effervescence of the solution, but the mixture was stirred at room temperature for 30 min. The solution was then pumped to dryness, redissolved in trichloromethane and then filtered. Removal of the solvent left a red-brown residue which was recrystallised from a trichloromethane/petroleum ether mixture (88/15) (0.16 g, 54% yield, Analysis; found: C, 39.71; H, 2.20; Cl, 16.95. $C_7H_5ClFeO_2$ calcd.: C, 39.53; M, 2.35; Cl, 16.71%).

Reaction between [Re₂(CO)₈(PPh₃)₂] and SO₂Cl₂

Addition of SO_2Cl_2 (1 cm^3, 1.2×10^{-2} mol) to a solution of $[Re_2(CO)_8(PPh_3)_2]$ (0.25 g, 2.2×10^{-4} mol) in trichloromethane (25 cm^3) resulted in a rapid reaction which turned the initially colourless solution yellow. The reaction mixture was then stirred for 20 min to ensure completion. The infrared spectrum of the solution at this stage showed carbonyl stretching frequencies assignable to *cis-* and *trans-*$[ReCl(CO)_4(PPh_3)]$. Removal of the solvent under reduced pressure and recrystallisation of a portion of residue from benzene/petroleum ether afforded pure *trans-*$[ReCl(CO)_4PPh_3]$ (ν(CO), 1990 cm^{-1} (C_6H_6 solution). Analysis; found: C, 44.63; H, 2.50; Cl, 6.01; P. 5.23. $C_{22}H_{15}ClO_4PRe$ calcd.: C, 44.32; H, 2.52; Cl, 5.96; P, 5.20%). Recrystallisation of the remaining reaction mixture from tetrachloromethane gave *cis-*$[ReCl(CO)_4PPh_3]$ (ν(CO), 2105(w), 2015(m) 2002(s), 1946(m) cm^{-1} (CCl_4 solution).

When the reaction between $[Re_2(CO)_8(PPh_3)_2]$ and SO_2Cl_2 was performed at 0°C or in C_6H_6, a larger proportion of the *trans*-isomer was formed.

Isomerisation of trans-[ReCl(CO)$_4$(PPh$_3$)]

A sample of *trans*-$[ReCl(CO)_4(PPh_3)]$ was dissolved in dichloromethane and the solution refluxed. The infrared spectrum of this solution was monitored periodically and complete isomerisation to the *cis*-form was achieved in 35 min.

Reaction of [Pt(PPh$_3$)$_4$] with SO$_2$Cl$_2$

$[Pt(PPh_3)_4]$ (0.2 g, 1.6×10^{-4} mol) was dissolved in toluene (20 cm^3) and SO_2Cl_2 (2 cm^3, 2.5×10^{-2} mol) added to the stirred solution at room temperature. A yellow solid was immediately precipitated. After 20 min, the precipitate was removed by filtration. Infrared spectroscopy showed this to be a mixture of *cis*-$[PtCl_2(PPh_3)_2]$ (ν(Pt–Cl), 321(sh), 317, 293, 279 cm^{-1}) and *trans*-$[PtCl_2(PPh_3)_2]$ (ν(Pt–Cl), 340 cm^{-1}) [14]. The *trans*-isomer was extracted from this mixture with benzene, leaving the white *cis*-form undissolved. The benzene solution was reduced in volume under vacuum and the yellow *trans*-complex precipitated by the addition of methanol. This was recrystallised from benzene.

Reaction between $[Pt(PPh_3)_4]$ and SO_2Cl_2 in toluene at 120°C in a sealed tube yielded a golden-yellow solid indentified as *trans*-$[PtCl_4(PPh_3)_2]$ (ν(Pt–Cl), 330, 325 cm^{-1}. Analysis; found: C, 50.31. H, 3.50; Cl, 16.78; P, 7.03. $C_{36}H_{30}Cl_4P_2Pt$ calcd.: C, 50.17, H, 3.48; Cl, 16.49; P, 7.20%).

Reaction of [Pd(PPh$_3$)$_4$] and SO$_2$Cl$_2$

$[Pd(PPh_3)_4]$ (0.2 g, 1.7×10^{-4} mol) was dissolved in toluene and SO_2Cl_2 (2 cm^3, 2.5×10^{-3} mol) added to the stirred solution at room temperature. A rapid reaction ensued with the solution attaining an orange colour. After 20 min, stirring was ceased and the solvent was removed under reduced pressure. A red oily solid (I) was formed which was recrystallised from ethanol. (Analysis; found: C, 48.00; H, 4.10; C, 19.43; P, 5.81; Pd, 18.6; O, 3.01%. M.p., 130–133°C).

When the above reaction is performed as detailed above, but employing SO_2Cl_2 (1.0 cm^3, 1.2×10^{-2} mol) the products are the above red compound and $[PdCl_2(PPh_3)_2]$. This mixture can be separated by treatment with ethanol, $[PdCl_2(PPh_3)_2]$ being insoluble. In the presence of a greater excess of SO_2Cl_2, the mixture is converted entirely to the red compound.

Reaction of I with piperidine

Compound I (0.1 g) was dissolved in dichloromethane (20 cm^3) and piperidine (1 cm^3, 1.0×10^{-2} mol) added to the stirred solution at room temperature. The orange solution immediately turned yellow and after 10 min the solvent was removed under reduced pressure. The residue was recrystallised from ethanol to afford yellow crystals of $[PdCl_2(C_5H_{11}N)_2]$ (Analysis; found: C, 34.81; H, 6.49; N, 8.00; Cl, 19.83. $C_{10}H_{22}Cl_2N_{11}Pd$ calcd.: C, 34.54; H, 6.33; N, 8.06; Cl, 20.44%. NMR data: δ 1.6 (5H) (CH_2NHCH_2), 3.1 ppm (6 H) ($CH_2CH_2CH_2$). Mass spectral data: M/z 348 ($PdCl_2(NC_5H_{11})_2^+$), 313 ($PdCl(C_5H_{11}N)_2^+$), 278 ($Pd(C_5H_{11}N)_2^+$), 191 ($Pd(C_5H_{11}N)^+$), 85 ($C_5H_{11}N^+$) (based on ^{108}Pd and ^{35}Cl)).

Typical conditions for reactions between toluene and sulphuryl chloride in the presence of metal complexes

(a) Sealed tube reactions *. The metal complex (4×10^{-5} mol), toluene (9.2 g, 0.1 mol) and SO_2Cl_2 (3.4 g, 2.5×10^{-2} mol) were placed in a thick walled glass ampule with a restriction at the neck to facilitate sealing. The reaction mixture was degassed by three freeze-pump-thaw cycles and the tube was sealed under vacuum. The tube was then placed in a steel bomb which was heated in an oven (i.e. in the dark) to the desired temperature (100 or 120 °C) for the desired time (20 min, 2 or 20 h). After reaction the tube was frozen in liquid nitrogen and broken open. After thawing, the reaction mixture was analysed.

(b) Reflux reactions. The metal complex (4×10^{-5} mol), toluene (9.2 g, 0.1 mol) and SO_2Cl_2 (3.4 g, 2.5×10^{-2} mol) were placed in a round bottomed flask and degassed by three freeze-pump-thaw cycles. The apparatus was entirely wrapped in aluminium foil to exclude daylight and the mixture refluxed by heating in an oil bath at 100 or 112°C. After the appropriate time the solution was cooled and analysed.

Typical conditions for reactions between toluene and dichlorine in the presence of metal complexes

(a) Reflux reactions. The transition metal complex (4×10^{-5} mol) was dissolved in toluene (9.2 g, 0.1 mol) and placed in a round-bottomed flask fitted with an inlet bleed from a dichlorine cylinder and a reflux condenser. The apparatus was entirely wrapped in aluminium foil to exclude daylight and the mixture degassed by three freeze-pump-thaw cycles. A slow stream of dichlorine gas was then bubbled through the solution while it was refluxed for 20 min. After reaction, the solution was flushed with dinitrogen, allowed to cool and analysed.

(b) Low temperature reactions. The reaction mixture (amounts as in (a)) was placed in a round-bottomed flask, wrapped in foil and degassed as above. This was then cooled to 0 °C and a slow stream of dichlorine gas bubbled through the solution for 60 s. The solution was then stirred for 20 min before dichlorine was bubbled through the solution for a second 60 s period. The mixture was then stirred for a further 30 min after which it was flushed with dinitrogen and analysed.

Results and discussion

(a) General considerations

This study has been principally concerned with the role of transition metal complexes in promoting the side chain chlorination of toluene by SO_2Cl_2. As will become apparent in the following discussion, a number of the complexes employed also promote ring chlorination. It will be shown that toluene has proved to be a particularly useful substrate in that the site of halogenation, ring or side chain, acts as a guide to the reaction mechanism. Thus, the formation of $PhCH_2Cl$ is character-

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* **IMPORTANT: Potential hazard.** On a number of occasions in the early part of this study tubes, even when constructed from thick walled glass tubing, exploded in the oven. We believe the risk of explosion depends markedly on the quality of the seal at the neck. In later reactions, tubes were placed in stainless steel screw cap bombs which were heated in the oven. We recommend that this procedure always be followed for sealed tube reactions. No problems were encountered with reflux reactions.

istic of a free radical or metal-modified free radical reaction while production of *ortho*- and *para*-$ClC_6H_4CH_3$ arises as a consequence of an ionic mechanism [5,15] Reactions performed under the conditions used in these studies confirmed these generalisations. Thus, reaction between toluene and SO_2Cl_2 in the presence of di-t-butyl peroxide yielded only $PhCH_2Cl$, with no evidence for ring chlorination and reaction in the presence of the well-known Friedel–Crafts catalyst, $[FeCl_3]$ gave only *ortho*- and *para*-chlorotoluene. In the absence of either initiator or catalyst, a small amount of $PhCH_2Cl$ (< 4%) was formed. This presumably arose as a consequence of thermal homolysis of SO_2Cl_2 at 120°C.

By way of comparison with reactions involving toluene and SO_2Cl_2 in the presence of metal complexes, some similar reactions between toluene and dichlorine were investigated.

(b) Reactions in the presence of $[M(PPh_3)_4]$, $[MCl_2(PPh_3)_2]$ (M = Pd, Pt) and related complexes

Matsumoto and co-workers [4] reported excellent yields of benzyl chloride from the reaction between toluene and SO_2Cl_2 in the presence of $[Pd(PPh_3)_4]$ (molar ratios ranging from 1/2/0.002 to 1/4/0.002) in refluxing benzene for 2 to 5 h. Our attempts to repeat this work were not entirely successful. In our hands, reactions carried out under the conditions used previously gave 41% conversion of toluene to $PhCH_2Cl$ (cf. 80% conversion previously reported). The most favourable conversion obtained in the present work was 50%, achieved using the molar ratios, 1/2/0.008. However, in this reaction both $PhCHCl_2$ (2%) and chlorotoluenes (3%) were formed. Others have encountered similar difficulties in attempting high yield chlorination of toluenes using this method [16].

In our subsequent studies of the reaction mechanism we employed molar ratios of $1/0.25/4 \times 10^{-4}$ (toluene/SO_2Cl_2/metal complex) and performed reactions in the absence of any solvent either under reflux or in sealed tubes heated to 100 or 120°C. Solvents were dispensed with, in order to obviate any possibility of their

TABLE 1

REACTIONS BETWEEN $PhCH_3$ AND SO_2Cl_2 IN THE PRESENCE OF VARIOUS METAL COMPLEXES [a]

Complex	Reaction temperature (°C)	Chlorotoluene yield (%)	Benzyl chloride yield (%)
$[Pt(PPh_3)_4]$	120	12.8	84.6
	100	12.2	84.0
$[PtCl_2(PPh_3)_2]$	120	15.5	80.9
	100	29.5	66.4
$[Pd(PPh_3)_4]$	120	12.4	80.2
	100	13.4	79.0
$[PdCl_2(PPh_3)_2]$	120	13.3	78.8
	100	19.2	74.1
$[RuCl_2(PPh_3)_3]$	120	93.3	3.3
	100	86.8	1.3
$[RhCl(PPh_3)_3]$	120	56.0	32.3
	100	61.9	22.1

[a] All reactions were performed for 120 min in sealed tubes.

chlorination. All reactions were carried out with the total exclusion of light. The results of these reactions are shown in Tables 1 and 2. In these tables yields are presented with respect to the amount SO_2Cl_2 charged to the reaction, as this is the reagent of lowest concentration. This does not, of course, represent preparative conditions, where SO_2Cl_2 would be in excess and yields would be calculated with respect to toluene. It does however, allow comparison of the efficiency of use of SO_2Cl_2.

Several points are immediately obvious from Tables 1 and 2. High utilisation of SO_2Cl_2 was achieved in both reflux and sealed tube reactions for all metal complexes. The yield of ring chlorinated products in reflux reactions employing $[M(PPh_3)_4]$ and $[MCl_2(PPh_3)_2]$ (M = Pd, Pt) was low (< 5%) and in all cases no $PhCHCl_2$ was observed. Analogous reaction in sealed tubes gave a greater proportion of chlorotoluenes. We ascribe this to the continued presence of HCl in the sealed tube reactions, a compound which is known to promote the electrophilic chlorination of aromatic rings [15]. It also appears likely that in reactions involving $[M(PPh_3)_4]$, the majority of the $PhCH_2Cl$ was formed in a reaction promoted by $[MCl_2(PPh_3)_2]$, as the former reacted rapidly with SO_2Cl_2 to yield the latter (vide infra), and that the slightly higher proportion of $PhCH_2Cl$ formed in the presence of $[M(PPh_3)_4]$ reflected the fact that conversion of this complex into $[MCl_2(PPh_3)_2]$ played a part in promoting side-chain chlorination.

$[RuCl_2(PPh_3)_3]$ played a different role to $[MCl_2(PPh_3)_2]$ (M = Pd, Pt), giving very high yields of chlorotoluenes. Clearly this compound, or a ruthenuim(III) compound formed by its interaction with SO_2Cl_2, shows activity very simlar to that of iron chlorides. After reaction, the ruthenuim was present in the form of the metal. In order to ascertain that this was not the effective catalyst, a sample was recovered from the reaction under anaerobic conditions and recharged to a fresh reaction. Subsequent analysis showed that no chlorotoluenes had been formed, but a small amount of benzyl chloride was present. This initiation of a free radical reaction between toluene and SO_2Cl_2 was presumably responsible, at least in part, for the benzyl chloride formed in the presence of $[RuCl_2(PPh_3)_3]$. $[RhCl(PPh_3)_3]$ showed behaviour intermediate between $[MCl_2(PPh_3)_2]$ and $[RuCl_2(PPh_3)_3]$. In all cases, except $[RuCl_2(PPh_3)_3]$, the yield of benzyl chloride was decreased and the yield of

TABLE 2

REACTION BETWEEN $PhCH_3$ AND SO_2Cl_2 IN THE PRESENCE OF PLATINUM AND PALLADIUM COMPLEXES [a]

Complex	Reaction conditions	Chlorotoluene yield (%)	Benzyl chloride yield (%)
$[Pt(PPh_3)_4]$	S.T.	10.2	86.5
	Reflux	2.1	92.8
$[PtCl_2(PPh_3)_2]$	S.T.	16.1	82.5
	Reflux	4.5	90.7
$[Pd(PPh_3)_4]$	S.T.	11.3	86.7
	Reflux	2.8	89.7
$[PdCl_2(PPh_3)_2]$	S.T.	15.7	79.8
	Reflux	5.2	89.8

[a] Reactions were performed at 120°C for 20 min under either sealed tube (S.T.) or reflux reactions conditions.

TABLE 3

REACTIONS BETWEEN $PhCH_3$ AND SO_2Cl_2 IN THE PRESENCE OF $PtCl_2(PPh_3)_2$

Amount of $[PtCl_2(PPh_3)_2]$ (mol × 10^6)	Amount of $PhCH_2Cl$ (mmol)	Ratio of $[PhCH_2Cl]/[PtCl_2(PPh_3)_2]^{1/2}$
10.54	8.55	2.63
7.61	7.20	2.61
5.05	5.96	2.65
2.72	4.31	2.61

chlorotoluenes increased at lower temperature, with the overall conversion to chlorinated products remaining almost constant.

In an effort to gain an insight into the mechanism of formation of benzyl chloride in the presence of $[MCl_2(PPh_3)_2]$, a series of reactions were carried out employing $[PtCl_2(PPh_3)_2]$, the results of which are detailed in Table 3. In these experiments the amount of $[PtCl_2(PPh_3)_2]$ charged to sealed tube reactions was varied, while the quantities of reactants and the reaction conditions were kept strictly constant. By using very low concentrations of metal complex and performing the reactions at 100°C for only 30 min, these reactions did not go to completion and thus the effect of the variation of the concentration of metal complex on the yield of benzyl chloride could be investigated. From these reactions, it was found that the ratio $[C_6H_5CH_2Cl]/[PtCl_2(PPh_3)_2]^{1/2}$ was constant. Although such reactions do not serve as rigorous kinetic experiments, they do provide a guide to the order of reaction with respect to the complex. In our related study of the reaction of cyclohexane with CCl_4 in the presence of $[Re_2(CO)_{10}]$ [3], which has been shown to be half order in metal complex by a detailed kinetic study, this technique of using sealed tube reactions as detailed above has proved effective in giving a guide to the reaction order with respect to $[Re_2(CO)_{10}]$. This technique can only be applied to studies involving variations in the metal complex and is not applicable to measurements of the orders of reaction with respect to the reactants. Nevertheless, the order with respect to the complex is mechanistically helpful in this case.

We believe two mechanisms are worthy of consideration for reactions of this type. These are a radical chain process in which the metal complex acts simply as an

$$[M] + SO_2Cl_2 \xrightarrow{k_1} [MCl] + SO_2Cl^{\bullet}$$

$$[MCl] + SO_2Cl_2 \xrightarrow{k_2} [MCl_2] + SO_2Cl^{\bullet}$$

$$SO_2Cl^{\bullet} + PhCH_3 \xrightarrow{k_3} PhCH_2^{\bullet} + SO_2 + HCl$$

$$PhCH_2^{\bullet} + SO_2Cl_2 \xrightarrow{k_4} PhCH_2Cl + SO_2Cl^{\bullet}$$

$$2PhCH_2^{\bullet} \xrightarrow{k_5} PhCH_2CH_2Ph$$

$$2SO_2Cl^{\bullet} \xrightarrow{k_6} 2SO_2 + Cl_2$$

SCHEME 3. [M] represents $[PdCl_2(PPh_3)_2]$.

$[M] + SO_2Cl_2 \rightarrow [MCl] + SO_2Cl^{\bullet}$

$SO_2Cl^{\bullet} + PhCH_3 \rightarrow PhCH_2^{\bullet} + SO_2 + HCl$

$PhCH_2^{\bullet} + [MCl] \rightarrow PhCH_2Cl + [M]$

SCHEME 4. [M] represents $[PdCl_2(PPh_3)_2]$.

initiator (Scheme 3) and a redox-catalysed process (Scheme 4). The exact form of the rate expression for Scheme 3 depends on whether both the first and second reactions are included in generating $SO_2Cl^{\bullet}$ radicals or if only the first reaction is considered. However, both sequences give rise to the same orders of reaction. The nature of the termination processes is also important, in that, taking account of only benzyl radical coupling leads to the rate expression given in eq. 1, where K is a composite second order rate constant. If termination occurs through $SO_2Cl^{\bullet}$ coupling, the rate expression is that given in eq. 2. Scheme 4 gives rise to the rate expression given eq. 3.

$$\text{Rate} = k[M]^{1/2}[SO_2Cl_2]^{3/2} \qquad (1)$$

$$\text{Rate} = k[M]^{1/2}[SO_2Cl_2]^{1/2}[PhCH_3] \qquad (2)$$

$$\text{Rate} = k[M][SO_2Cl_2] \qquad (3)$$

It can be seen that the order with respect to the metal complex clearly differentiates between the radical chain and redox-catalysed mechanisms and that the results contained in Table 3 indicate that the former mechanism obtains.

A similar study of variation in yield of $PhCH_2Cl$ with variation in $[PdCl_2(PPh_3)_2]$ concentration has not been undertaken, since the nature of the $[PdCl_2(PPh_3)_2]/SO_2Cl_2$ reaction is not clear (vide infra). Similarly, the results of such studies using $[M(PPh_3)_4]$ are difficult to interpret since $[MCl_2(PPh_3)_2]$ is rapidly formed by reaction of the zero-valent complex with SO_2Cl_2 and the dichlorides are efficient initiators of the chlorination reaction. Nevertheless, such a study was carried out using $[Pd(PPh_3)_4]$, since this was the compound mainly employed by Matsumoto [4]. It can be seen from Table 4 that the ratio $[PhCH_2Cl]/[Pd(PPh_3)_4]^{1/2}$ is also constant, however, this may be fortuitous. It remains noteworthy that yields of $PhCH_2Cl$ were slightly higher when $[M(PPh_3)_4]$ was used instead of $[MCl_2(PPh_3)_2]$ (M = Pd or Pt) and presumably the extra amount of this product arose as a consequence of a free radical reaction initiated as as result of the reaction between $[M(PPh_3)_4]$ and SO_2Cl_2.

TABLE 4

REACTIONS BETWEEN $PhCH_3$ AND SO_2Cl_2 IN THE PRESENCE OF $Pd(PPh_3)_4$

Amount of $[Pd(PPh_3)_4]$ (mol × 10^6)	Amount of $PhCH_2Cl$ (mmol)	Ratio of $[PhCH_2Cl]/[Pd(PPh_3)_4]^{1/2}$
9.61	11.13	3.59
5.28	7.89	3.43
2.77	5.80	3.48

(c) Reactions between both $[M(PPh_3)_4]$ and $[MCl_2(PPh_3)_2]$ (M = Pd, Pt) and SO_2Cl_2: the nature of the initiation processes

(i) $[M(PPh_3)_4]$ (M = Pd, Pt). Reaction between $[Pt(PPh_3)_4]$ and SO_2Cl_2 at room temperature resulted in the rapid formation of a yellow solid which was separated into two components. Infrared spectroscopy showed these to be the known compounds, *cis*- and *trans*-$[PtCl_2(PPh_3)_2]$. This represents a novel and convenient route to the *trans*-complex. We do not have evidence as to the nature of the initial interaction between $[Pt(PPh_3)_4]$ and SO_2Cl_2, but suggest a charge transfer process is likely (Scheme 5). Others have found that platinum(0) complexes form charge transfer complexes with acceptors such as TCNE and quinones [17] and, furthermore, oxidative addition of alkyl halides to $[Pt(PPh_3)_3]$ is also believed to be initiated by charge transfer [18].

The reaction between $[Pd(PPh_3)_4]$ and SO_2Cl_2 is more complex. In the presence of excess SO_2Cl_2, a red solid was formed which has not been positively characterised. Elemental analysis suggested the partial empirical formula $[PdPCl_3O]$. There was no evidence for the presence of sulphur. The ^1H NMR spectrum of this compound showed only absorptions in the aromatic region (centred at δ 8.08 ppm) and the infrared spectrum showed a number of differences to that of $[PdCl_2(PPh_3)_2]$. These are illustrated in Fig. 1. On the basis of this evidence, we have been unable to advance a formula for this compound.

The red compound reacted with piperidine under mild conditions to yield $[PdCl_2(piperidine)_2]$. When $[Pd(PPh_3)_4]$ was treated with a lower molar ratio of SO_2Cl_2, a mixture of the red compound and $[PdCl_2(PPh_3)_2]$ was formed. Furthermore, treatment of $[PdCl_2(PPh_3)_2]$ with SO_2Cl_2 yielded the red compound. On the basis of these findings we can make the following comments about the reaction between $[Pd(PPh_3)_4]$ and SO_2Cl_2. Firstly, the initial reaction is analogous to that observed with $[Pt(PPh_3)_4]$: formation of $[PdCl_2(PPh_3)_2]$. Secondly, reaction of the red compound with piperdine suggests it also contains palladium(II) unless piperidine is acting as a reducing agent, but it is not $[PdCl_2(PPh_3)]_2$, which is known to yield $[PdCl_2(PPh_3)(piperidine)]$ when treated with piperidine [19]. The infrared spectrum is somewhat atypical of those compounds containing coordinated PPh_3, neither it is consistent with coordinated $OPPh_3$. This compound remains unidentified. Despite this difficulty, the identification of $[PdCl_2(PPh_3)_2]$ as the initial product from the reaction between $[Pd(PPh_3)_4]$ and SO_2Cl_2 suggests a similar mode of initiation to that proposed for the analogous platinum(0) complex.

(ii) $[PtCl_2(PPh_3)_2]$. There was no reaction between $[PtCl_2(PPh_3)_2]$ and SO_2Cl_2 at room temperature, however, reaction at 120°C or reaction between $[Pt(PPh_3)_4]$ and SO_2Cl_2 at 120°C gave *trans*-$[PtCl_4(PPh_3)_2]$. The *trans*-geometry was inferred from infrared data, since this compound gave a single strong absorption at 330 cm^{-1} with a shoulder at 325 cm^{-1}. This is directly analogous to that of *trans*-

$$[Pt(PPh_3)_n] + SO_2Cl_2 \rightarrow [Pt(PPh_3)_n]^{\dot{+}} + SO_2Cl_2^{\dot{-}}$$

$$SO_2Cl_2^{\dot{-}} \rightarrow SO_2Cl^{\cdot} + Cl^-$$

$$[Pt(PPh_3)_n]^{\dot{+}} + Cl^- \rightarrow [PtCl(PPh_3)_n]$$

$$[PtCl(PPh_3)_n] + SO_2Cl_2 \rightarrow [PtCl_2(PPh_3)_2] + SO_2Cl^{\cdot} + (n-2)PPh_3$$

SCHEME 5. $n = 3$ or 4.

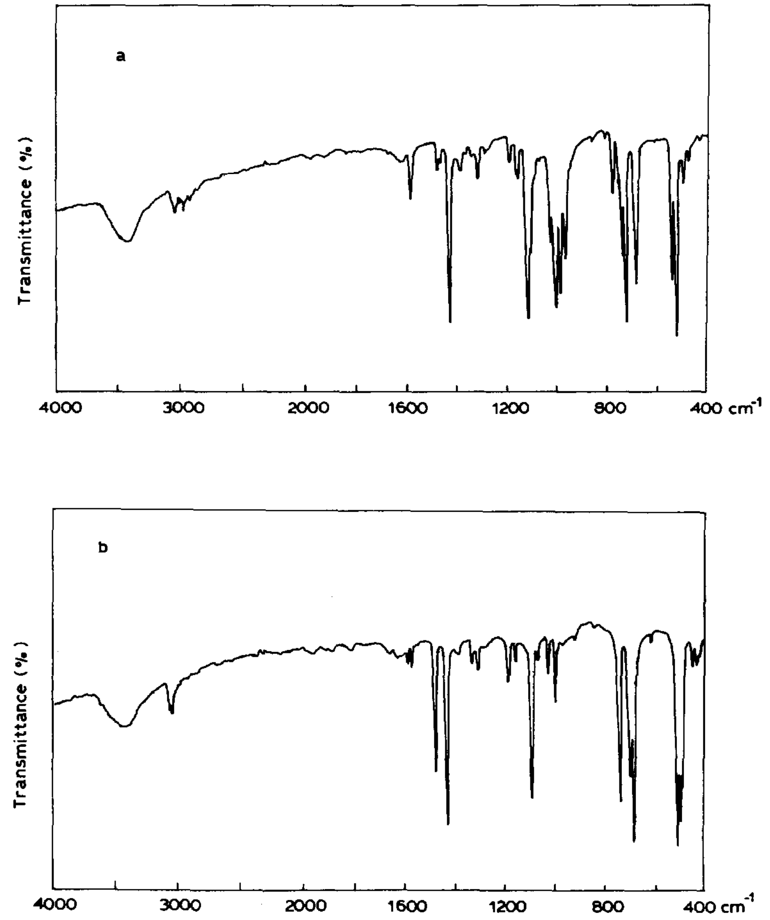

Fig. 1. Infrared spectra (KBr discs) of (a) red compound produced by reaction between $[Pd(PPh_3)_4]$ and SO_2Cl_2 and (b) $[PdCl_2(PPh_3)_2]$.

$[PtCl_4(PEt_3)_2]$, which showed bands at 340 and 334 cm^{-1} (shoulder) [20]. *trans*-$[PtCl_4(PPh_3)_2]$ does not appear to have been reported previously. On the basis of these findings, the role of $[PtCl_2(PPh_3)_2]$ in initiating the radical chain reaction is presumably similar to that of $[M(PPh_3)_4]$ and is outlined in Scheme 6. Once again, we propose charge transfer as the initial mode of interaction between the metal complex and SO_2Cl_2. We are, however, unable to rule out the possibility that formation of $[PtCl_4(PPh_3)_2]$ occurs via an oxidative addition reaction proceeding by a free radical mechanism (Scheme 7), in which reaction of $[PtCl_3(PPh_3)_2]$ with

$[PtCl_2(PPh_3)] + SO_2Cl_2 \rightarrow [PtCl_2(PPh_3)_2]^{+\cdot} + SO_2Cl_2^{-\cdot}$
$SO_2Cl_2^{-\cdot} \rightarrow SO_2Cl^{\cdot} + Cl^-$
$[PtCl_2(PPh_3)_2]^{+\cdot} + Cl^- \rightarrow [PtCl_3(PPh_3)_2]$
$[PtCl_3(PPh_3)_2] + SO_2Cl_2 \rightarrow [PtCl_4(PPh_3)_2] + SO_2Cl^{\cdot}$
SCHEME 6

$[PtCl_2(PPh_3)_2] + SO_2Cl_2 \rightarrow [PtCl_3(PPh_3)_2] + SO_2Cl^\cdot$

$[PtCl_3(PPh_3)_2] + SO_2Cl^\cdot \rightarrow [PtCl_3(SO_2Cl)(PPh_3)_2]$

$[PtCl_3(SO_2Cl)(PPh_3)_2] \rightarrow [PtCl_4(PPh_3)_2] + SO_2$

SCHEME 7

$SO_2Cl^\cdot$ competes with initiation of benzyl chloride-forming chains by that radical. In this context it is noteworthy that oxidative addition of *para*-$MeC_6H_4SO_2Cl$ to $[PtMe_2L_2]$ ($L = PMe_2Ph$; $L_2 = Ph_2PCH_2CH_2PPh_2$) giving $[PtMe_2Cl(SO_2R)L_2]$ has been shown by spin trapping experiments to follow a radical mechanism analogous to that outlined in Scheme 7 [18]. Furthermore, the related complex, $[PtCl(SO_2R)(PPh_3)_2]$ undergoes SO_2 extrusion to give $[PtR(Cl)(PPh_3)_2]$ [21].

Finally we can exclude radical chain initiation by reductive elimination from either $[PtCl_4(PPh_3)_2]$ or $[PtCl_2(PPh_3)_2]$ (eq. 4 and 5), since heating either compound in toluene at 120°C for 2 h did not give rise to either $PhCH_2Cl$ or $(PhCH_2)_2$, products which would indicate the occurrence of free radical reactions.

$$[PtCl_4(PPh_3)_2] \rightarrow [PtCl_2(PPh_3)_2] + 2Cl^\cdot \qquad (4)$$

$$[PtCl_2(PPh_3)_2] \rightarrow [Pt(PPh_3)_2] + 2Cl^\cdot \qquad (5)$$

(d) Reactions between toluene and SO_2Cl_2 in the presence of metal carbonyl complexes

The results of reactions between toluene and SO_2Cl_2 in the presence of various metal carbonyl complexes is reported in Table 5. These reactions were carried out under conditions similar to those discussed in section (b) (toluene/SO_2Cl_2/metal complex $1/0.9/6 \times 10^{-4}$). A number of features are immediately obvious from these results. Firstly, only $[Cr(CO)_6]$ gives rise to appreciable amounts of benzyl chloride and in this case the yield is poor compared to that from reactions initiated by palladium or platinum complexes. Secondly, all complexes examined gave poor to moderate yields of chlorotoluenes. Thirdly, while the *ortho/para* ratio for chlorotoluenes varies from 1.5 to 2.8, depending on the metal complex and the

TABLE 5

REACTIONS OF $PhCH_3$ AND SO_2Cl_2 IN THE PRESENCE OF SOME METAL CARBONYL COMPLEXES

Complex	Reaction conditions [a]	Product yields (%)			*o/p* ratio
		o-$CH_3C_6H_4Cl$	*p*-$CH_3C_6H_4Cl$	$C_6H_5CH_2Cl$	
$[Cr(CO)_6]$	100 (S) 20	0.7	0.3	13.0	2.3
	120 (S) 20	5.6	3.4	25.6	1.6
$[Mn_2(CO)_{10}]$	100 (S) 20	7.7	3.2	5.7	2.4
$[Re_2(CO)_{10}]$	100 (S) 20	19.9	8.0	0.3	2.5
	120 (S) 18	20.8	13.3	0	1.6
	70 (R) 18	18.9	6.8	0.1	2.7
	70 (R) 24	42.0	15.7	0.2	2.8
$[Re(CO)_5Cl]$	120 (S) 18	29.0	19.6	0	1.5
$[Re_2(CO)_8(PPh_3)_2]$	70 (R) 18	8.9	3.6	0.6	2.5
$[Fe_2(CO)_4(\eta\text{-cp})_2]$	100 (R) 20	28.1	16.6	0	1.7
$[Mo_2(CO)_6(\eta\text{-cp})_2]$	100 (S) 20	16.3	7.9	0	2.1

[a] The entries in the column represent reaction temperatures, reaction conditions (sealed tube (S) or reflux (R) and reaction time (h).

conditions, these values are in the range typical of reactions in the presence of the usual Friedel–Crafts catalysts [15]. As will be discussed in section (e) reactions between some of these metal carbonyl complexes and SO_2Cl_2 at low temperatures gave good yields of chloro derivatives. However, under the more vigorous conditions employed in these reactions, no carbonyl-containing metal compounds were recovered at the end of the reactions. The metal-containing products appeared to be chlorides in all cases, however, detailed identification of these compounds was not undertaken because of the difficulty of removing the last traces of SO_2Cl_2 from the reaction products. This rendered analytical data meaningless.

It is clear that in these reactions, the metal carbonyls or the metal halides derived from them were behaving as Friedel–Crafts catalysts. In order to assess which of these two species were the effective catalyst, a reaction employing $Re_2(CO)_{10}$ was carried out at 120°C for 18 h in a sealed tube. This gave a 34% yield of chlorotoluenes. At the end of this time, all volatile materials were removed from the reaction vessel, leaving a green-black residue, tentatively identified as $[ReCl_6]$. Fresh portions of toluene and SO_2Cl_2 were added to this residue and the reaction repeated. In this case a further 19% of chlorotoluenes was formed indicating that the metal chloride plays a very substantial role in catalysis. We were unable to discern any trends amongst the yields of chlorotoluenes produced by the various carbonyl compounds.

(e) Low temperature reactions between some metal carbonyls and SO_2Cl_2: a convenient route to chlorometal carbonyls

When SO_2Cl_2 was added to a solution of either $[Mn_2(CO)_{10}]$ or $[Re_2(CO)_{10}]$ in either benzene or dichloromethane at room temperature, $[MCl(CO)_5]$ (M = Mn or Re, respectively) was formed in greater than 90% isolated yield. These reactions represent extremely convenient syntheses of analytically pure samples of the chlorometal carbonyls and have advantages over the previous syntheses of these molecules [22]. Similar reaction of $[Re_2(CO)_8(PPh_3)_2]$ and SO_2Cl_2 at room temperature lead to formation of a mixture of *cis*- and *trans*-$[ReCl(CO)_4PPh_3]$. Removal of the solvent from this mixture and recrystallisation of the residue from benzene/petroleum ether allowed isolation of a pure sample of the *trans* isomer. Recrystallisation of the remaining residue from CCl_4 afforded pure *cis*-$[ReCl(CO)_4PPh_3]$. When the reaction between $[Re_2(CO)_8(PPh_3)_2]$ and SO_2Cl_2 was performed at 0°C, the same mixture was produced, but the *trans* isomer was formed in greater proportions. However, lowering the reaction temperature to −78°C, did not further increase the proportion of the *trans* form in the product mixture. The *trans* isomer was also favoured in reactions carried out in benzene rather than dichloromethane. This represents the first report of *trans*-$[ReCl(CO)_4PPh_3]$, although the bromo analogue is well known [23] When a solution of the *trans*-chloro complex in $CHCl_3$ was refluxed, complete conversion to the *cis* isomer occurred in 40 min. The corresponding *trans–cis* isomerisation of the bromo analogue took two hours [23].

Reaction between $[Fe_2(CO)_4(\eta\text{-}Cp)_2]$ and SO_2Cl_2 proceeded rapidly at room temperature in $CHCl_3$, affording $[FeCl(CO)_2(\eta\text{-}Cp)]$ as the major product, together with $[Fe(CO)_3(\eta\text{-}Cp)][FeCl_4]$. The relative amounts of these two products depends markedly on the solvent employed, the chloro complex predominating in chlorinated solvents, whereas the salt was favoured in benzene. Full details of these studies will be reported elsewhere [24]. Both $[Mo_2(CO)_6(\eta\text{-}Cp)_2]$ and $[Cr(CO)_6]$

TABLE 6

REACTION BETWEEN $PhCH_3$ AND Cl_2 IN THE PRESENCE OF PLATINUM AND PALLADIUM COMPLEXES [a]

Catalyst	Moles of chlorotoluene $\times 10^3$	Moles of benzyl chloride $\times 10^3$
$Pt(PPh_3)_4$	0.9	48.7
$Pd(PPh_3)_4$	1.4	45.8
$PtCl_2(PPh_3)_2$	1.4	42.2
$PdCl_2(PPh_3)_2$	1.3	44.4

[a] Reaction temperature: 120°C.

underwent total decarbonylation when treated with SO_2Cl_2 at either room temperature or 0°C.

(f) Reactions between toluene and dichlorine in the presence of transition metal complexes

By way of comparison with the reactions between toluene and SO_2Cl_2 discussed above, similar reactions were performed employing chlorine. Two series of reactions were carried out. In the first, a toluene solution of the metal complex (4×10^{-5} mol) was heated to 120°C and then a slow stream of dichlorine gas was bubbled through this solution for 20 min. In all cases investigated, benzyl chloride was formed, the yields (based on toluene charged) are shown in Table 6 and are in the range, 40–50%. In addition, chlorotoluenes (1.0–1.5%) and $PhCHCl_2$ (up to 6%) were produced.

In the second series, reactions were performed at low temperatures (−10 to 0°C). The results of these reactions are shown in Table 7 and in all cases chlorotoluene formation was preferred. It is noteworthy from the last two entries, that in the absence of metal complexes, low temperature reactions between dichlorine and toluene favoured free radical products. However, at these temperatures all the metal complexes investigated acted as Friedel–Crafts catalysts.

TABLE 7

REACTIONS BETWEEN $PhCH_3$ AND Cl_2 IN THE PRESENCE OF SOME METAL COMPLEXES [a]

Complex	Moles of complex ($\times 10^4$)	Moles of chlorotoluene ($\times 10^3$)	Moles of benzyl chloride ($\times 10^3$)
$[Os(CO)_3(PPh_3)_2]$	1.3	13.6	0.3
$[Pt(PPh_3)_4]$	1.8	15.6	0.8
$[PtCl_2(PPh_3)_2]$	0.4	14.0	0.6
$[Re(CO)_5Cl]$	11.6	15.2	0.3
$[Mn_2(CO)_{10}]$	5.3	19.3	0.8
$[Re_2(CO)_{10}]$	3.1	5.2	2.4
–	–	1.5	8.6
–	–	3.8	6.6

[a] Reaction temperature: 0°C.

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