Mechanistic Studies of Some Oxidative-addition Reactions: Free-radical Pathways in the Pt^0–RX, Pt^0–PhBr, and Pt^{II}–$R'SO_2X$ Reactions (R = Alkyl, R′ = Aryl, X = Halide) and in the Related Rhodium(I) or Iridium(I) Systems

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Spin-trapping studies, using R′NO (R′ = Bu^t or C_6HMe_4-2,3,5,6), have been carried out on: (i) various Pt^0–alkyl halide (RX) systems, *e.g.* $[P(PR''_3)_n]$ (R″ = Et or Ph, *n* = 3 or 4)–MeI; (ii) a number of Pt^{II}–sulphonyl or acyl halide reactions, *e.g.* *cis*-$[PtMe_2(PMe_2Ph)_2]$–*p*-$MeC_6H_4SO_2X$; and (iii) several Rh^I– or Ir^I–alkyl halide additions. In most cases the appropriate nitroxyl spin adduct $R(R')\dot{N}O$ or $R'(p\text{-}MeC_6H_4SO_2)\dot{N}O$ [but not $R(R'''CO)\dot{N}O$] is observed by e.s.r. spectroscopy. *In conjunction with appropriate control experiments*, this leads to the unequivocal conclusion that free radicals are implicated in systems (i) (X = Cl, Br, or I) and (ii) (X = Cl or Br). By means of the nitrone $PhCH{=}N(O)Bu^t$, a platinum(I) complex has been trapped during the course of the $[Pt(C_2H_4)(PPh_3)_2]$–EtI reaction; its formulation as $[Pt\{CH(Ph)\dot{N}O(Bu^t)\}I(PPh_3)_2]$ is based on e.s.r. data. Trityl chloride adds to $[Pt(PPh_3)_3]$ [but not so rapidly to a rhodium(I) or iridium(I) substrate] to give $Ph_3\dot{C}$ and $[PtCl_2(PMe_2Ph)_2]$; Ph_2CHBr and $[Pt(PPh_3)_3]$ give $(Ph_2CH)_2$ as the principal organic product. Galvinoxyl inhibits the addition of *p*-$MeC_6H_4SO_2Cl$ to $[PtMe_2(PMe_2Ph)_2]$. Azobis(isobutyronitrile) under photolysis catalyses the oxidative addition of PhBr to $[Pt(PPh_3)_3]$. Whereas the addition of MeI to $[Pt(PPh_3)_3]$ in benzene leads exclusively to the 1 : 1 adduct, in tetrahydrofuran by far the major product is $[PtI_2(PPh_3)_2]$. It is concluded that reactive halides RX add to a platinum(0) substrate *via* a geminate radical pair $[Pt^IL_n(X)] + R^\bullet$, whereas with less reactive halides, or in the sulphonyl halide–Pt^{II} addition, a radical-chain mechanism is operative.

THE mechanism of the oxidative addition of an alkyl halide to a low-oxidation-state metal complex continues to attract considerable interest. Early suggestions favoured an S_N2 displacement at carbon or a cyclic three-centre transition state, whereas more recent work has implicated free radicals.

We have reviewed developments up to the end of 1975;[1] relevant work since then includes the identification of radicals in the reaction of an alkyl halide with *cis*-$[Mo(CO)_2(Me_2PCH_2CH_2PMe_2)_2]$,[2] *trans*-$[Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$,[3] $[Fe(\eta\text{-}C_5H_5)(MgBr)(Ph_2PCH_2CH_2PPh_2)]$,[4] $SnMe_3^-$,[5a] $Na[Fe(\eta\text{-}C_5H_5)(CO)_2]$,[5b] or SnX_2 [X = $CH(SiMe_3)_2$ or $N(SiMe_3)_2$].[6,7] Otsuka and Ataka[8] suggested a radical-chain mechanism involving metal-centred radicals, rather than organic radicals, for additions to $[Rh(CNR)_4]^+$; Osborn[9a] has provided an account of his work on additions to Rh^I, Ir^I, Pd^0, and Pt^0 and Stille and co-workers have summarised their studies[9b] especially on palladium(0) systems and provided new data.[9c] Pearson and Poulas[9d] propose a modified S_N2 mechanism for addition of allylic halides to *trans*-$[Ir(CO)Cl(PPh_3)_2]$.

In 1973 we proposed a non-chain radical mechanism for additions to Pt^0,[10] a key feature of which was a rate-determining homolytic abstraction of halogen by the metal(0) complex. We now report in detail on this work, with some extensions to systems of Rh^I, Ir^I, and Pt^{II}. An important aspect of this study has been the use of spin trapping, an e.s.r. procedure whereby a reactive free radical $R^\bullet$ is trapped by a nitroso-compound R′NO, and identified by the e.s.r. spectrum of the resultant nitroxyl, $R(R')\dot{N}O$. This technique has been reviewed,[11] as has some of its recent applications in organometallic chemistry.[1] In this paper, R′ = 2,3,5,6-tetramethylphenyl and, additionally, for experiments with $[Pt(PPh_3)_3]$, R′ = Bu^t.

RESULTS

(*a*) *Spin-trapping Experiments*.—(*i*) *Oxidative addition to a platinum*(0) *complex*. Table 1(*a*) lists the various combinations of a platinum(0) complex and an alkyl halide which were monitored by spin trapping. In each case the addition

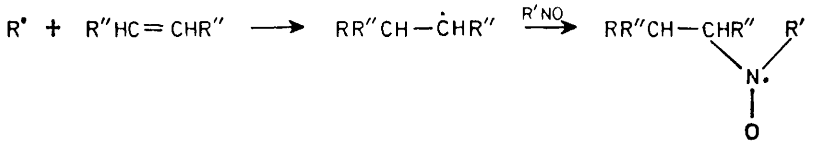
TABLE 1

Oxidative-addition reactions monitored by e.s.r. spin trapping[a]

(*a*) $Pt^0 \longrightarrow Pt^{II}$	Addendum
$[Pt(PPh_3)_n]$ (*n* = 3 or 4)	CH_3I, CD_3I, EtI, Pr^nI, Pr^nBr, $PhCH_2Br$, or Ph_2CHBr
$[Pt(C_2H_4)(PPh_3)_2]$	MeI, EtI[b], Pr^nI, or $PhCH_2Br$
$[Pt(PEt_3)_n]$ (*n* = 3 or 4)	MeI, EtI, Pr^nI, or $PhCH_2Br$
$[Pt(PhCH{=}CHPh)(PEt_3)_2]$	MeI or $PhCH_2Br$
$[Pt(cod)_2]$	MeI, EtI, or $PhCH_2Br$
(*b*) Rh^I, $Ir^I \longrightarrow Rh^{III}$, Ir^{III}	
$[RhCl(PPh_3)_3]$	MeI, $PhCH_2Br$, or Ph_2CHBr
trans-$[Ir(CO)Cl(PPh_3)_2]$	MeI, $PhCH_2Br$, or Ph_2CHBr
(*c*) $Pt^{II} \longrightarrow Pt^{IV}$	
cis-$[PtL_2R_2]$	
R = Me, L = PMe_2Ph	*p*-$MeC_6H_4SO_2X$ (X = Cl or Br), PhCOCl, or MeCOX (X = Cl or Br)[c]
R = Me, L = ½ $Ph_2PCH_2CH_2PPh_2$	*p*-$MeC_6H_4SO_2X$ (X = Cl or Br)
R = Me, L = PEt_3	*p*-$MeC_6H_4SO_2Br$ or PhCOCl[c]
R = Me, L = PPh_3	*p*-$MeC_6H_4SO_2Br$
R = CH_2Ph, L = PPr^n_3	*p*-$MeC_6H_4SO_2Br$
R = Et, L = PMe_2Ph	MeCOBr[c]

[a] Spin trap, R′NO = 2,3,5,6-tetramethyl-1-nitrosobenzene (nd) in each case; additionally, R′NO = Bu^tNO for experiments with $[Pt(PPh_3)_3]$. [b] In this instance, the nitrone $PhCH{=}N(O)Bu^t$ was also used in order to trap a platinum(I) complex (by Dr. P. I. Riley). [c] The acyl halide experiments did *not* lead to spin-trapped $R\dot{C}O$, *i.e.* the acyl nitroxide; with MeCOX and nitrosodurene, the nitroxyl radical $Me(C_6HMe_4\text{-}2,3,5,6)NO$ was detected.

of an alkyl halide to a benzene solution of the metal complex $[Pt(PPh_3)_n]$ (n = 3 or 4), $[Pt(C_2H_4)(PPh_3)_2]$, or $[Pt(PEt_3)_n]$ (n = 3 or 4) in the presence of a spin trap R′NO (or, in one case, a nitrone) gave an e.s.r. spectrum readily assignable to the nitroxyl spin adduct R(R′)ṄO; e.s.r. coupling constants are listed in Table 2, and a typical spectrum is shown in the Figure. The quality of the spectrum indicates that the Pt^0 + RX + R′NO combination may have some potential for generating nitroxyl radicals for e.s.r. studies. For the olefin complexes $[Pt(PhCH{=}CHPh)(PEt_3)_2]$ or $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) a six-line (equal-intensity) spectrum was observed, indicating splitting by a single hydrogen α to nitrogen. This is assigned to the spin adduct (1), formed by attack of the alkyl radical on the liberated olefin, equation (i) (R″CH=CHR″ = stilbene or octa-1,5-diene). A similar situation occurs in the reaction of $[PtMe_2(bipy)]$ (bipy = 2,2′-bipyridyl) with diethyl fumarate in the presence of Bu^tNO, where the adduct $MeCH(CO_2Et)CH(CO_2Et)(Bu^t)$-ṄO is observed.[12]


(i)

(1)

$$R^{\bullet} + R''HC{=}CHR'' \longrightarrow RR''CH-\dot{C}HR'' \xrightarrow{R'NO} RR''CH-CHR''(R')N(\dot{O})$$

TABLE 2

E.s.r. parameters for the spin adducts observed during the Pt^0—Pt^{II} and Pt^{II}—Pt^{IV} reactions [a]

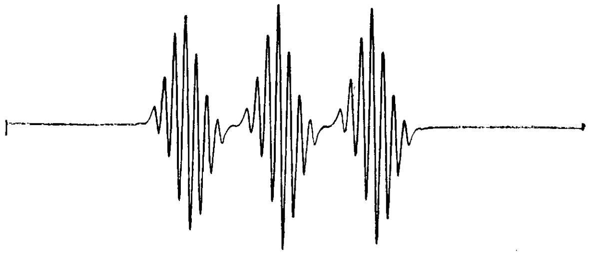
Nitroxyl	$\alpha(^{14}N)$/mT	$\alpha(^{1}H)$/mT
(*a*) Alkyl nitrosodurene radicals		
Me	1.370	1.216
Et	1.368	1.101
CD_3	1.370	
Pr^n	1.361	0.703
CH_2Ph	1.367	0.802
$CHPh_2$	1.374	0.143
$O_2SC_6H_4Me$-*p*	1.13	
(*b*) Aminyl oxide radicals, R(R′)ṄO		
$Me(Bu^t)$	1.52	1.31
$Et(Bu^t)$	1.52	1.04
$Pr^i(Bu^t)$	1.68	1.80
$PhCH_2(Bu^t)$	1.46	0.74
(*c*) $[Pt\{CHPhN(O)Bu^t\}I(PPh_3)_2]$ [b]	1.50	0.34

[a] All spectra were recorded at *ca.* 20 °C (in benzene) under an inert atmosphere. [b] See (2). Experiment of Dr. P. I. Riley using the nitrone $PhCH{=}N(O)Bu^t$ gave $g_{av.}$ 2.013, and $\alpha(^{195}Pt)$ 3.0 mT; *cf.* [13] $[Pt\{CHPhN(O)Bu^t\}(MeO_2CC{\equiv}CCO_2Me)Cl(PEt_3)_2]$, see (3), for which $g_{av.}$ 2.013, $\alpha(N^{14})$ 1.432, $\alpha(^{1}H)$ 0.41, and $\alpha(^{195}Pt)$ 0.66 mT.

The spin-trapping experiments were carried out with Schlenk-tube and syringe techniques, and hence involved traces of air. For the $[Pt(PPh_3)_3]$–MeI reaction two further experiments were carried out: (a) with rigorous exclusion of air, and (b) with air-saturated MeI. Both experiments gave clean e.s.r. signals for Me(R′)ṄO, of almost identical signal strength. The spin-trapping reaction with $[Pt(PPh_3)_3]$ and MeI was also carried out in CH_2Cl_2 with the same result as in benzene.

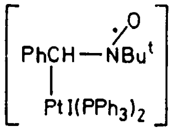
The addition of ethyl iodide to ethylenebis(triphenylphosphine)platinum(0) in the presence of the nitrone $PhCH{=}N(O)Bu^t$ as spin trap in benzene at ambient temperature gave a signal attributed to the spin-trapped platinum(I) complex (2), with g = 2.013, and the hyperfine coupling constants (to ^1H, ^{14}N, and ^{195}Pt) shown in Table 2. The identification is based on a comparison with data obtained on another platinum(I) species, trapped using the same nitrone, from the system *trans*-$[PtCl(H)(PEt_3)_2]$–$MeO_2CC{\equiv}CCO_2Me$ in benzene at 70 °C; the strong e.s.r. signal, g = 2.013, was ascribed to the spin adduct (3).[13] The smaller ^{195}Pt hyperfine coupling in (2) compared with (3) is attributed to the higher basicity of PEt_3 compared with PPh_3 and the ability of the acetylene to behave as a π acceptor.

(*ii*) *Oxidative additions to a complex of* Rh^I *or* Ir^I. The reactions examined are listed in Table 1(*b*). With a Rh^I : R′NO ratio of 10 : 1, no signal for the Me or $PhCH_2$ spin adduct was observed, either immediately after mixing or after 40 min, and for Ph_2CHBr only a very weak signal was found. With a Rh^I : R′NO ratio of 1 : 10, no signal for the Me adduct was detected, but the adducts of $Ph\dot{C}H_2$ or $Ph_2\dot{C}H$ were observed. In the case of Ir^I, with a ten-fold molar excess of R′NO, similar results were obtained: no signal with MeI, but positive results with $PhCH_2Br$ or Ph_2CHBr.



E.s.r. spectrum of $Bu^t(CD_3)\dot{N}O$ generated by the addition of CD_3I (1 mol) to $[Pt(PPh_3)_3]$ (1 mol) in the presence of Bu^tNO (*ca.* 0.4 mol) in benzene at 20 °C (*ca.* 5 × 10^{-2} mol dm^{-3} in Pt)

(*iii*) *Oxidative additions to a platinum*(II) *complex.* As an extension to the above work, the addition of a sulphonyl halide, RSO_2X, to a square-planar complex of Pt^{II} was examined. Complexes of the type $[PtL_2R_2]$ (R = alkyl, L = a tertiary phosphine) were used; the ready addition of *p*-$MeC_6H_4SO_2Cl$ to *cis*-$[PtMe_2(PMe_2Ph)_2]$ to give the corresponding octahedral dimethylplatinum(IV) compound had been reported.[14a] The reactions monitored are listed in Table 1(*c*), and were carried out by allowing equimolar amounts of platinum substrate and sulphonyl halide in benzene to warm up from 5 to 30 °C in the presence of R′NO. E.s.r. spectra were recorded over this period. In each case a strong three-line signal for $RSO_2(R')\dot{N}O$ was detected. For the system *p*-$MeC_6H_4SO_2Br$ and *cis*-$[PtL_2R_2]$ (R = Me, L = PEt_3, or PMe_2Ph) a very weak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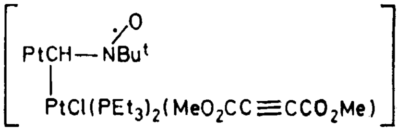
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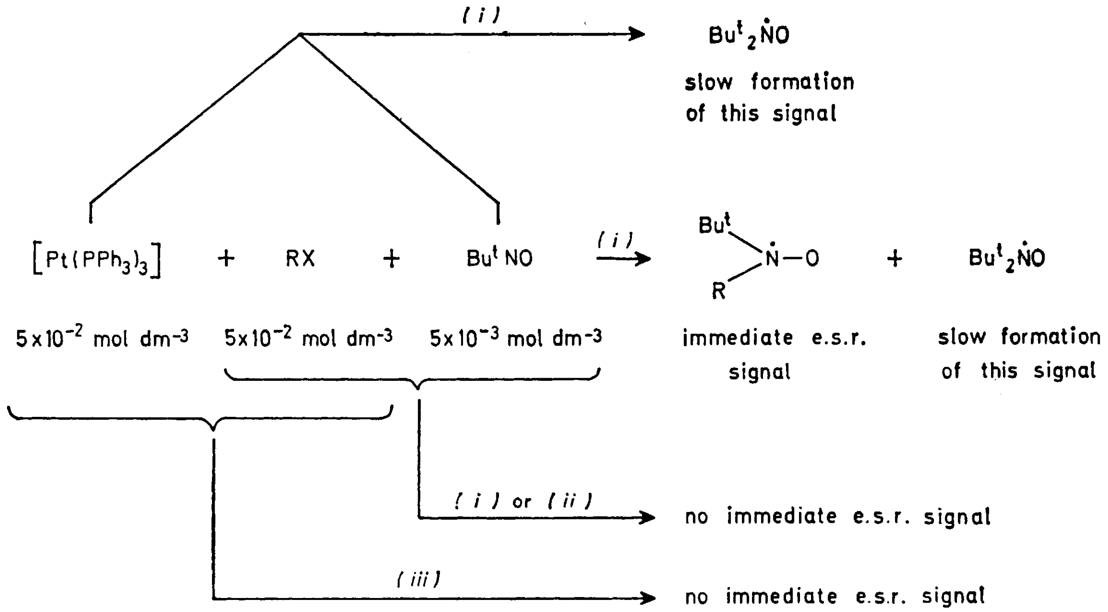
signal characteristic of $\mathrm{Me(R')\dot{N}O}$ was observed at low temperature; this signal soon collapsed, leaving the normal strong spectrum of $\mathrm{RSO_2(R')\dot{N}O}$. The spin trapping of $\mathrm{Me^{\bullet}}$ may indicate that an S_H2 reaction (bimolecular homolytic substitution, see ref. 14*b* for a demonstration of this reaction type, using *cis*-$[\mathrm{PtL_2R_2}]$ complexes) is taking place. Spin trapping of sulphonyl radicals was not known prior to this study, but the identity of the spin adduct was confirmed (a) by an alternative method of generation [irradiation of a mixture of $\mathrm{(Bu^tO)_2}$, $\mathrm{SiEt_3H}$, *p*-$\mathrm{MeC_6H_4SO_2Br}$, and R′NO, *cf.* ref. 15], and (b) an independent report which appeared during the course of this work.[16]

The acyl spin adduct was not detected in the *cis*-$[\mathrm{PtMe_2(PMe_2Ph)_2}]$–MeCOX (X = Cl or Br) system, but even under ambient conditions $\mathrm{Me(R')\dot{N}O}$ (R′NO = nitrosodurene) was observed. For the acetyl chloride system the initial $\mathrm{Me(R')\dot{N}O}$ signal collapsed at *ca.* 40 °C and gradually a new $\mathrm{Me(R')\dot{N}O}$ signal appeared. In the corresponding PhCOCl reaction, radical products were not detected.

(*b*) *Control Experiments*.—It is important in work of this kind to establish, as far as possible, that the observed radicals are produced exclusively by the reaction under investigation. It was therefore necessary to examine (for addition to a complex of $\mathrm{Pt^0}$, $\mathrm{Rh^I}$, or $\mathrm{Ir^I}$), by e.s.r. spectroscopy, the combination of the spin trap with (a) metal complex reagent, (b) alkyl halide, and (c) metal complex product. For (b) and (c), no e.s.r. signals were detectable under conditions of high gain (amplification), either immediately after mixing or after 0.5 h. For (a), it was found that $[\mathrm{Pt(PPh_3)_3}]$ appeared to accelerate the decomposition of $\mathrm{Bu^tNO}$ to $\mathrm{Bu^t_2\dot{N}O}$, and to cause the formation of broad very weak signals when compared to the formation of $\mathrm{R(R')\dot{N}O}$. The results for the $\mathrm{Pt^0}$–RX system are summarised in Scheme 1. The complex $[\mathrm{RhCl(PPh_3)_3}]$ and R′NO gave a very weak signal, detectable only after 0.5 h, and *trans*-$[\mathrm{Ir(CO)Cl(PPh_3)_2}]$ and R′NO gave no detectable signal. For additions to a platinum(II) complex, no signal was detected from (i) *cis*-$[\mathrm{PtL_2R_2}]$ + R′NO [*cf.* control experiment (c) in the additions to $\mathrm{Pt^0}$], (ii) *p*-$\mathrm{MeC_6H_4SO_2X}$ (X = Cl or Br) and R′NO, or (iii) the platinum(IV) products and R′NO. It was found that *p*-$\mathrm{MeC_6H_4SO_2I}$ and R′NO alone generated a clean signal for *p*-$\mathrm{MeC_6H_4SO_2(R')\dot{N}O}$, and that u.v. irradiation of *cis*-$[\mathrm{PtL_2R_2}]$ with R′NO gave $\mathrm{Me(R')\dot{N}O}$. Thus use of the iodide was avoided, and exposure to direct light minimised. The results are summarised in Schemes 1 and 2.

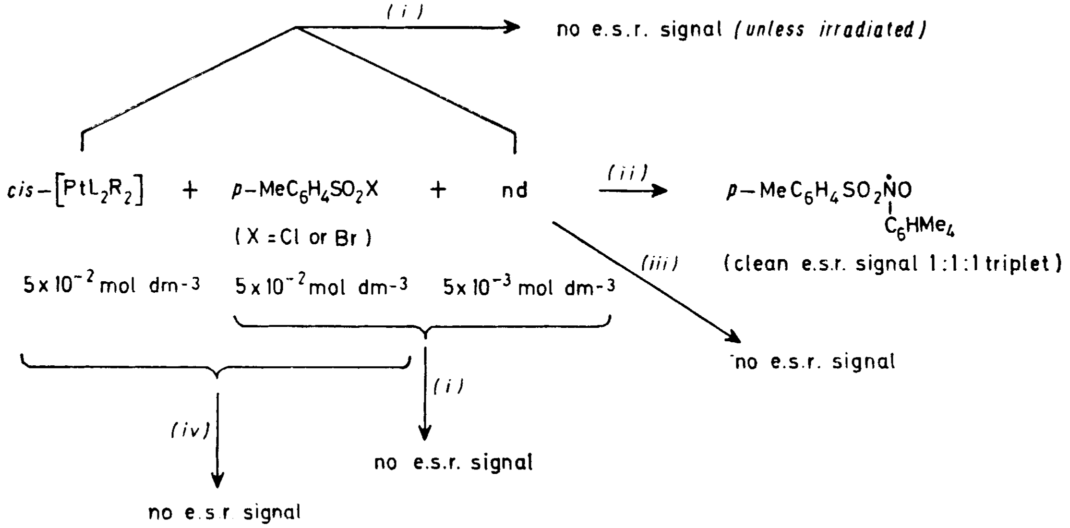


SCHEME 1 The $[\mathrm{Pt(PPh_3)_3}]$, RX, $\mathrm{Bu^tNO}$ system: summary of e.s.r. results (R = $\mathrm{CH_3}$, $\mathrm{CD_3}$, Et, or $\mathrm{CH_2Ph}$). Additionally, $[\mathrm{Pt(C_2H_4)(PPh_3)_2}]$ + EtI + PhCH=N(O)Bu^t in $\mathrm{C_6H_6}$ at 20 °C gave an e.s.r. signal attributed to the platinum(I) nitroxyl (2). (*i*) $\mathrm{C_6H_6}$, 20 °C, in the dark; (*ii*) + $\mathrm{PPh_3}$ (5×10^{-2} mol dm^{-3}), $\mathrm{C_6H_6}$, 20 °C, in the dark; (*iii*) as in (*i*) + excess of RX until no further colour change, then as in (*ii*) + Bu^{t}NO

(*c*) *Other E.S.R. Experiments*.—The reaction of $\mathrm{Ph_3CCl}$ with each complex of $\mathrm{Rh^I}$, $\mathrm{Ir^I}$, or $\mathrm{Pt^0}$ was also investigated by e.s.r. spectroscopy, since the $\mathrm{Ph_3C^{\bullet}}$ radical is stable, and thus requires no spin trap for its observation. The compound $\mathrm{Ph_3CCl}$ in benzene does not give an e.s.r. signal; addition of 1 equivalent of $[\mathrm{Pt(PPh_3)_3}]$ (both the metal complex and organic halide were *ca.* 5×10^{-2} mol dm^{-3}) gave an immediate strong spectrum of $\mathrm{Ph_3C^{\bullet}}$. The concentration of the radical was estimated to be in the range 10^{-3}—10^{-2} mol dm^{-3}. This apparent 10% yield is explained by the fact that $\mathrm{Ph_3C^{\bullet}}$ is in equilibrium with a diamagnetic dimeric form [17] which at the concentrations used is *ca.* 10% dissociated.[18] Each complex of $\mathrm{Rh^I}$ or $\mathrm{Ir^I}$ also reacted with $\mathrm{Ph_3CCl}$ to give $\mathrm{Ph_3C^{\bullet}}$, although not as quickly as did $[\mathrm{Pt(PPh_3)_3}]$.

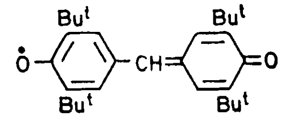
An attempt was made to detect a radical directly from an alkyl halide and $[\mathrm{Pt(PPh_3)_3}]$, using allyl bromide in toluene at low temperature. The allyl radical is relatively persistent and gives only a five-line spectrum; toluene becomes viscous at low temperature which hinders radical recombination. No signals were detected, but insufficient solubility of $[\mathrm{Pt(PPh_3)_3}]$ was probably a limiting factor.

The interaction of the stable trityl radical, $\mathrm{Ph_3C^{\bullet}}$ (prepared from $\mathrm{Ph_3CCl}$ and Zn in benzene) and $[\mathrm{Pt(PPh_3)_3}]$, $[\mathrm{RhCl(PPh_3)_3}]$, or *trans*-$[\mathrm{Ir(CO)Cl(PPh_3)_2}]$ was examined, in order to see whether any evidence for a $[\mathrm{LM{-}CPh_3}]^{\bullet}$ species could be found. No change in the e.s.r. spectrum of $Ph_3C^{\bullet}$ was observed on the addition of the complex of Pt^0, Rh^I, or Ir^I, although in the last case some increase in resolution occurred with time.



SCHEME 2 The $[PtL_2R_2]$, p-$MeC_6H_4SO_2X$, nitrosodurene (nd) system: summary of e.s.r. results. For L (= tertiary phosphine) and R see Table 1. (*i*) C_6H_6, 20 °C, 30 min; (*ii*) C_6H_6, 20 °C, 20 min, in the dark; (*iii*) C_6H_6, PPh_3, (5×10^{-3} mol dm^{-3}), 20 °C, 30 min; (*iv*) formation of platinum(IV) adduct followed by nd in C_6H_6, 20 °C, 30 min

(*d*) *Experiments with Galvinoxyl* (4), *a Free-radical Inhibitor*.—Galvinoxyl ($G\dot{O}$) has been found to inhibit the addition of certain alkyl halides to some complexes of Rh^I, Ir^I, Pd^0, or Pt^0, this being evidence for a radical-chain mechanism.[19] In the present work, the addition of p-$MeC_6H_4SO_2X$ (X = Cl or Br) to *cis*-$[PtMe_2(PMe_2Ph)_2]$ in the presence or absence of $G\dot{O}$ was monitored by ^1H n.m.r., the *Me*–P resonance being characteristic and different for the metal reagent and metal product. It was found that the reaction of the platinum substrate with p-$MeC_6H_4SO_2Cl$ was completely inhibited by *ca.* 1% $G\dot{O}$ in diethyl ether, and predominantly inhibited in benzene, under conditions in which the reaction proceeded to completion in the absence of $G\dot{O}$. In contrast, the reaction of the same substrate with p-$MeC_6H_4SO_2Br$ in benzene was not inhibited by $G\dot{O}$, and only slightly inhibited in ether. While the observation of inhibition is evidence for a radical-chain reaction, the lack of inhibition for the bromide is not evidence for a non-chain mechanism.



(4)

(*e*) *Some Preparative-scale Experiments* (*including Solvent Participation*).—It was important to know whether the presence of the spin trap altered the nature of the major product of the oxidative addition. Treatment of MeI with $[Pt(PPh_3)_4]$ has been reported to give $[PtMe(I)(PPh_3)_2]$ in *ca.* 70% yield.[20] This reaction was carried out with Bu^tNO or R′NO present, and in the presence or absence of benzene. The latter variation provides parallels to both the literature reaction and the spin-trapping experiments. The results are summarised in equations (ii)—(iv) (nd = nitrosodurene).

Comparison of the *ca.* 60% yield for reactions (iii) and (iv) with the yield of *ca.* 70% found for reaction (ii) indicates that the presence of the spin trap in the low concentration used does not significantly alter the stoicheiometry of the reaction. The separate question of the exact influence of the spin trap on the yield was not investigated. Experiments addressed to this problem would require information on the amount of spin trap present as the active monomer, and the efficiency of the spin-trapping step.

Experiments by Dr. P. P. Power illustrate an interesting solvent influence on the course of oxidative addition of methyl iodide to $[Pt(PPh_3)_3]$. Thus, whereas in benzene only the 1 : 1 adduct $[PtMe(I)(PPh_3)_2]$ is formed, in tetrahydrofuran (thf) as solvent only a trace of this is found, the major product being $[PtI_2(PPh_3)_2]$, equation (v) (relative mol ratios being shown in parentheses).[7]

The reaction of $[Pt(PPh_3)_3]$ with 1 equivalent of Ph_3CCl yielded a yellow solution (containing $Ph_3C^{\bullet}$, by e.s.r.) and a white precipitate. The latter was identified by i.r. spectroscopy as *cis*-$[PtCl_2(PPh_3)_2]$, equation (vi). The report [21] (without details) that Ph_3CBr oxidatively adds to $[Pt(PPh_3)_4]$ to give $[PtBr(CPh_3)(PPh_3)_2]$ therefore requires checking.

$$[Pt(PPh_3)_3] + \text{excess of MeI} \xrightarrow{\text{no solvent}} [PtMe(I)(PPh_3)_2] \quad \text{(ii)}$$
$$68\% \text{ (ref. 20)}$$

$$[Pt(PPh_3)_3] + \text{excess of MeI} + \frac{1}{10}\,Bu^tNO \xrightarrow{\text{benzene}} [PtMe(I)(PPh_3)_2] \quad \text{(iii)}$$
$$62\%$$

$$[Pt(PPh_3)_3] + \text{excess of MeI} + \frac{1}{10}\,\text{nd} \xrightarrow{\text{no solvent}} [PtMe(I)(PPh_3)_2] \quad \text{(iv)}$$
$$62\%$$

Free radicals typically give rise to products derived from combination, disproportionation, rearrangement, or atom abstraction. Characterisation of such compounds provides good evidence for radical intermediates. It was decided to examine the organic products of the reaction between Ph_2CHBr and $[Pt(PPh_3)_3]$ since (i) dimerisation is the major decomposition pathway for $Ph_2\dot{C}H$, and (ii) the reaction between Ph_2CHBr and $[Pt(PPh_3)_3]$ was found to yield $[PtBr_2(PPh_3)_2]$ and hence the yield of the organic fragment was expected to be stoicheiometric. Combined g.l.c.–mass spectrometric analyses of the supernatant solution after the reaction of $[Pt(PPh_3)_3]$ with Ph_2CHBr revealed that the major volatile components were $(Ph_2CH)_2$ and PPh_3. Much smaller amounts of $(Ph)_2$, Ph_2CH_2, and $(PhCH_2)_2$ were also detected. A solution of pure Ph_2CHBr did not contain any of these compounds. The presence of the dimer $(Ph_2CH)_2$ lends support to the postulate of radical

$$2[Pt(PPh_3)_3] + 2Ph_3CCl \longrightarrow [PtCl_2(PPh_3)_2] + [Pt(PPh_3)_3] + PPh_3 + 2Ph_3C^{\bullet} \quad \text{(vi)}$$

formation; such a species would not be formed if Ph_2CH^+ or Ph_2CH^- were intermediates.

$$[Pt(PPh_3)_3] + 2MeI \begin{cases} \xrightarrow[-[PMePh_3]I]{C_6H_6} [PtMe(I)(PPh_3)_2] \\ \qquad\qquad \text{(sole product)} \\ \xrightarrow[-[PMePh_3]I]{thf} [PtMe(I)(PPh_3)_2] + [PtI_2(PPh_3)_2] \\ \qquad\qquad (<1\%) \qquad\qquad\qquad (>19\%) \end{cases} \quad \text{(v)}$$

(*f*) *Optical-activity Experiments*.—These were carried out in part by Dr. M. J. S. Gynane. A *ca.* 0.01 mol dm^{-3} solution of $[Pt(C_2H_4)(PPh_3)_2]$ in benzene was added to (+)-2-chloro-octane at 20 °C. The mixture was set aside at this temperature for 24 h, whereafter the organic matter was removed *in vacuo*. Fractional distillation yielded (+)-2-chloro-octane of identical optical purity to the starting material. Similar results were obtained with 2-iodo-octane (see Experimental section).

(*g*) *A Catalysis Experiment*.—Dr. P. P. Power showed that azobis(isobutyronitrile) (aibn) under photolysis acts as a catalyst for the oxidative addition of bromobenzene to $[Pt(PPh_3)_3]$. Thus, mixing the latter with an 8 mol equivalent of PhBr in benzene (*ca.* 2×10^{-1} mol dm^{-3}) gave *cis*-$[PtBr(Ph)(PPh_3)_2]$ (>70%) and PPh_3 in *ca.* 40 h at 20 °C. In the presence of aibn (*ca.* 6×10^{-3} mol dm^{-3}) under photolysis (250-W medium-pressure Hg lamp) after *ca.* 5 h the reaction was *ca.* 30% complete, and in the absence of aibn *ca.* 20% complete [equation (vii)]. These data were obtained from three pairs (*i.e.* with or without aibn) of experiments, and each yield was within 2% of the quoted mean. The results were obtained gravimetrically, the 1 : 1 adduct being the only insoluble component in the

$$[Pt(PPh_3)_3] \xrightarrow[20°C,\ 5\ h]{8PhBr\ in\ C_6H_6} \begin{cases} \xrightarrow{aibn,\ h\nu} 30\% \text{ of } 1:1 \text{ adduct} \\ \xrightarrow{dark} 20\% \text{ of } 1:1 \text{ adduct} \end{cases} \quad \text{(vii)}$$

system. In control experiments, the reaction of $[Pt(PPh_3)_3]$ (*ca.* 0.33 mmol) with PhBr (*ca.* 30 mmol) in C_6H_6 (10 cm^3) was allowed to proceed for 16 h at 20°C (a) with and (b) without irradiation; there was only a slight (*ca.* 10%) rate enhancement for (a) compared with (b) in contrast to (c) the *ca.* 50% for aibn and irradiation.

(*h*) *Some Attempted CIDNP Experiments*.—Table 3 lists combinations of alkyl halide and metal complex which were examined by n.m.r. spectroscopy in an attempt to detect CIDNP effects. (Some of these experiments were carried out by Dr. M. J. S. Gynane, using either ^1H or ^{13}C Fourier-transform techniques, under the guidance of Dr. C. Brown at the University of Kent.) In no case was such an effect found, but this is not evidence for the absence of radical intermediates. In closely related systems, $[M(PEt_3)_3]$ (M = Pd or Pt)–Pr^iI or $[Pt(PEt_3)_3]$–$PhCH_2Br$, CIDNP has been found; in these cases the metal product was the dihalide, *cis*-$[M(PEt_3)_2X_2]$.[22]

DISCUSSION

A major feature of this work is the use of the spin-trapping technique to provide the first example [10] of e.s.r. evidence for the intermediacy of free radicals in oxidative additions to a low-oxidation-state metal complex. Although the control experiments described above have eliminated, as far as is possible, alternative sources for the generation of radicals, two important questions remain. These are (i) whether the presence of a spin trap induces a radical mechanism, and (ii) whether the observed radicals reflect only a minor pathway. With regard to (i), the fact that nitroxyls were not detected in every experiment strongly suggests that the presence of a spin trap does not cause a radical mechanism to operate. For example, no signal was found under conditions of high gain for the addition of MeI to a complex of Rh^I or Ir^I. Furthermore, the experiments with Ph_3CCl and Ph_2CHBr clearly indicate that a low-oxidation-state metal complex is capable of homolytically abstracting a halogen atom from an organic halide in the absence of a spin trap.

TABLE 3

Attempted ^1H n.m.r. CIDNP experiments *

Substrate	Addendum
$[Pt(PPh_3)_3]$	CH_3I, Pr^iBr, Pr^iI
$[Pt(C_2H_4)(PPh_3)_2]$	CH_3I, $PhCH_2Br$
$[Pt(PEt_3)_n]$ (n = 3 or 4)	CH_3I, Pr^iBr

* All experiments were carried out at *ca.* 30 °C in sealed n.m.r. tubes with benzene as solvent.

Question (ii) is more difficult to answer. The intensity of the e.s.r. signals is of little use due to uncertainties regarding (a) the amount of spin trap (a dimer in the solid state) present as the active monomer in solution, and (b) the efficiency of the trapping step. However, some evidence is available which supports the assumption that the nitroxyl signals obtained represent more than a minor pathway. A spin-trapping experiment with CCl_4 and $[Pt(PPh_3)_3]$ gave a signal for $(Cl_3C)R'\dot{N}O$ which was *ca.* 100-fold weaker than that obtained with MeI under the same conditions. Although the difference is partly due to the more rapid decay of $Cl_3C(R)\dot{N}O$ compared with $Me(R)\dot{N}O$, it was clear that CCl_4 generated a much weaker signal than MeI. This observation correlates well with some results obtained by Bamford *et al.*[23] on the combination $[Pt(PPh_3)_4] + CCl_4$ as an initiator for the free-radical polymerisation of certain vinyl monomers; a kinetic analysis of the polymerisation showed that only a small amount of the platinum complex reacted with CCl_4 to produce $\dot{C}Cl_3$ radicals (which initiate the polymerisation). Thus the spin-trapping result (a weak signal) is consistent with the kinetic analysis (minor reaction pathway). From this we extrapolate that the much stronger signals obtained with MeI or the other halides reflect a more dominant pathway.

On the basis of some of the above results we have proposed[10] the non-chain radical mechanism of equations (viii)—(x) for the oxidative addition to Pt^0. Step (ix) is a homolytic abstraction of a halogen atom to generate a halogenoplatinum(I) intermediate and a radical $R^{\bullet}$.

$$[Pt(PPh_3)_n]\ (n = 3 \text{ or } 4) \rightleftharpoons [Pt(PPh_3)_2] + 1 \text{ or } 2\ PPh_3 \qquad \text{(viii)}$$

$$[Pt^0(PPh_3)_2] + RX \rightleftharpoons \underset{(5)}{[Pt^I(PPh_3)_2X]} + R^{\bullet} \qquad \text{(ix)}$$

$$R^{\bullet} + \underset{(5)}{[Pt^I(PPh_3)_2X]} \longrightarrow [Pt^{II}(PPh_3)_2RX)] \qquad \text{(x)}$$

This was assumed to be rate-determining, to be consistent with the observed second-order kinetics (first order in metal complex and alkyl halide concentration respectively) often found for these reactions.[1] The second attractive feature is that formation of the dihalogeno-complex, *i.e.* $[PtL_2X_2]$, is neatly explained by the process (xi) and likewise the occurrence of the hydrido-complex $[Pt(H)L_2X]$ is explained as derived from the common platinum(I) intermediate by hydrogen abstraction.

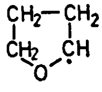
$$\underset{(5)}{[Pt^I(PPh_3)_2X]} + RX \longrightarrow [Pt(PPh_3)_2X_2] + R^{\bullet} \qquad \text{(xi)}$$

In the light of our more recent results, the mechanism receives both support and modification. The platinum(I) intermediate (5) gains credence from the spin-trapping experiment using the nitrone, the platinum(I) spin adduct (2) being reasonably formulated on the basis of the prior art relating to an analogue (3).[13] The fact that (+)-2-chloro-octane is not racemised by prolonged contact with a catalytic quantity of $[Pt(C_2H_4)(PPh_3)_2]$ makes it unlikely that the reverse of equation (ix) is fast enough to have any significance in competing with (x); however, halogen-atom abstraction from a paramagnetic halogenometal complex (*e.g.* $CuBr_2$) and $R^{\bullet}$ is known.[24] Furthermore, it is likely that, from the data on a molybdenum(0) system,[2] there may be an extra step involving initial electron transfer; equation (ix) may thus be replaced by (xii) and (xiii), with uncertainty as to whether platinum-free X^- has an independent existence.

$$[Pt(PPh_3)_2] + RX \longrightarrow [Pt^I(PPh_3)_2]^{\bullet +}[RX]^{\bullet -} \qquad \text{(xii)}$$

$$[Pt^I(PPh_3)_2]^{\bullet +}[RX]^{\bullet -} \longrightarrow \underset{(5)}{[Pt^I(PPh_3)_2X]} + R^{\bullet} \qquad \text{(xiii)}$$

The observation[7] that use of thf as a solvent instead of benzene promotes the formation of $[PtL_2X_2]$ at the expense of $[PtL_2R(X)]$ may then be interpreted by assuming that the reactive radical $R^{\bullet}$ readily abstracts a hydrogen atom from thf to generate the radical (6); this bulky radical then combines less readily with $[Pt^I(PPh_3)_nX]$ and hence dihalide formation is increasingly (compared with C_6H_6 as solvent) favourable; abstraction of an α-hydrogen atom of thf was first discussed in a transition-metal context in ref. 3. Likewise, most secondary alkyl halides react with $[Pt(PPh_3)_n]$ ($n = 3$ or 4) to give the platinum(II) dihalide, and in terms of the above mechanism we interpret this to mean that the corresponding secondary alkyl radical $R^{\bullet}$ does not effectively compete with the fast halogen-abstraction reaction (xi).



(6)

The demonstration that PhBr oxidatively adds to $[Pt(PPh_3)_3]$[7] makes it virtually inevitable that at least in this system a free-radical pathway is appropriate, since nucleophilic polar displacement of halide from an unactivated halogenoarene has no precedent.

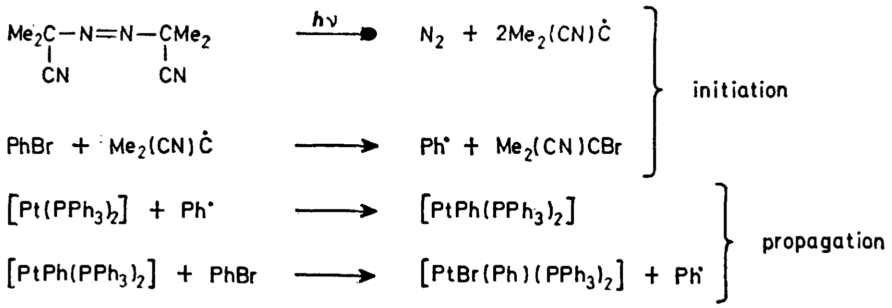
Although we have not established the identity of the metal products in the additions to complexes of Rh^I or Ir^I, our results show that these substrates can also readily abstract a halogen atom from RX. In the case of addition to a platinum(II) complex, free radicals are implicated by the spin-trapping experiments, and inhibition by 1% of galvinoxyl is evidence that a chain mechanism is occurring.

Two types of chain mechanism have been suggested for related oxidative additions; one by Osborn and coworkers[19a] involving a paramagnetic $[ML_nR]$ species as an intermediate, and the other[8] involving a paramagnetic $[ML_nX]$ complex. The former proposal initially required an unknown initiator, but has since been modified[19b] to incorporate equations (ix)—(xi) (see ref. 1 for a more detailed discussion). The second type of chain mechanism has also implicated a reaction analogous to that of (ix), as the initiating step. It therefore seems that homolytic halogen abstraction of the type shown in equation (xiv) [possibly preceded by a one-electron transfer, as in equation (xii)][2,25] is a key organometallic reaction. Thus it provides (a) the first step in a radical non-chain mechanism, (b) a route to side products, and (c) the initiator for a chain mechanism with the paramagnetic $[ML_nR]$ as chain carrier.

$$[ML_n] + RX \longrightarrow [ML_nX] + R^{\bullet} \qquad \text{(xiv)}$$

A distinction between the chain and the non-chain mechanism is the nature of the intermediate paramagnetic metal complex, which for the $[Pt(PPh_3)_3]$–RX system is $[Pt(PPh_3)_nX]$ and $[Pt(PPh_3)_nR]$ ($n = 2$ or 3), respectively. In a related system, a $Sn^{II} \longrightarrow Sn^{IV}$ oxidative addition with $Sn[CH(SiMe_3)_2]_2$ as substrate, the tin(III) radical is sufficiently persistent to be observed by direct e.s.r. observation and appears to be the tin(III) halide.[6] Although a platinum(I) intermediate, (2), has been intercepted in the reaction pathway, it cannot be ruled out that in place of an iodide ligand in (2) there may be an ethyl group. A further difference between the chain and non-chain mechanism may lie in the kinetics. The latter is readily consistent with second-order characteristics, but the former less obviously so (but see ref. 26).

Catalysis by a radical initiator provides evidence of the possibility of a chain mechanism. The results in the [Pt(PPh$_3$)$_3$]–PhBr system using aibn under photolysis as catalyst, as well as the EtBr catalysis noted in the Sn[CH(SiMe$_3$)$_2$]$_2$–PhBr system,[7] suggest the chain mechanism of Scheme 3 for the catalysed reaction. This is similar to that proposed originally for an Ir^{I} ⟶ Ir^{III} oxidative addition.[19a] It gains further support from the inhibition noted for the addition of MeCHBrCO$_2$Et to [Pt(PEt$_3$)$_3$] by galvinoxyl or duroquinone.[19c] We pointed out [7] that these scavengers react with the platinum(0) substrate, but now believe that this does not invalidate the conclusion because even a small molar proportion of the inhibitor suppresses the reaction.



SCHEME 3 Proposed radical-chain mechanism for the aibn-catalysed photochemical addition of PhBr to [Pt(PPh$_3$)$_3$]

It is instructive to compare the oxidative addition of an alkyl halide to a platinum(0) substrate with that of a palladium(0) analogue. Spin-trapping experiments have been carried out for the addition of PhCH$_2$Cl or PhMeCH$_2$Br to [Pd(PPh$_3$)$_4$] using Bu^{t}NO.[27] Nitroxyls R(Bu^t)ṄO were generated, but it was shown that the metal 1 : 1 adduct [PdCl(PPh$_3$)$_2$R] itself produced the nitroxyl by reaction with Bu^{t}NO. The inference by Stille and co-workers [9b,c,27] that these results reflect on the validity of ours in the Pt^0–RX system is incorrect because, as Scheme 1 clearly demonstrates, similar control experiments in the latter case exclude the possibility that the nitroxyl is derived from the platinum(II) product. Additionally, there was no i.r. or ^{1}H n.m.r. indication of any interaction upon mixing between Bu^{t}NO and [Pt(PPh$_3$)$_n$] (n = 3 or 4) or [Pt(PPh$_3$)$_2$R(X)]. The difference between the Pd and Pt systems is not surprising in view of the greater lability of the Pd–C than Pt–C bonds. Thus *cis*-[PtMe$_2$(PEt$_3$)$_2$] may be distilled at 85 °C (10^{-4} mmHg),[20,*] but the palladium analogue is completely decomposed at 100 °C, and palladium(II) alkyls with PPh$_3$ as a ligand are even less stable, *e.g.* *cis*-[PdMe$_2$(PPh$_3$)$_2$] decomposes at 35—40 °C in solution.[28]

Conclusions.—One-electron processes are becoming increasingly important in the reactions of low-valent organotransition-metal complexes.[1,24] In the context of oxidative additions, various mechanisms (S$_N$2, three-centre, radical) have been proposed, and some may even operate concurrently, but the occurrence of the concerted three-centre process for alkyl halide addition (whether polarised or not) is without firm evidence.[1] There is unlikely to be a universally valid mechanism for all combinations of low-oxidation-state metal substrate and halogenohydrocarbon addendum. However, for additions to a platinum(0) complex, radical pathways are clearly established. With reactive halides, such as EtI, the non-chain process of equations (ix)—(xiii) is paramount, whereas with less reactive halides, and especially with a radical initiator, the chain mechanism of Scheme 2 is operative, as is probably the case for RSO$_2$Cl additions to a platinum(II) substrate.

The use of the spin-trapping technique has provided the first e.s.r. evidence for the intermediacy of free radicals in oxidative-addition reactions, and leads to the suggestion that equation (xiv) is an important process (possibly proceeding *via* a one-electron transfer) in the interaction of a low-valent metal complex and an organic halide.

EXPERIMENTAL

E.s.r. spectroscopic experiments were carried out in quartz 4 mm tubes fitted with ground-glass joints to permit manipulation of air-sensitive compounds. Solvents were dried and distilled before use. Unless otherwise stated, manipulations were carried out under argon or dinitrogen and with degassed pure solvents (typically using five freeze–thaw cycles). 2-Methyl-2-nitrosopropane [29] (Bu^{t}NO) and 2,3,5,6-tetramethyl-1-nitrosobenzene [30] (nitrosodurene, nd) were prepared as described in the literature. Solutions of known concentration of alkyl halide, metal complex, and nitroso-compound [or PhCH=N(O)Bu^t] were transferred by syringe to the e.s.r. tube, amounts being measured by volume. Experiments with Bu^{t}NO were carried out with protection from light. Details on the CIDNP experiments, aibn catalysis, and solvent effects are in the Results section.

Oxidative Addition of Methyl Iodide to Tris(triphenyl-

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[*] Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

phosphine)platinum(0) *in the Presence of* 2-*Methyl*-2-*nitrosopropane or Nitrosodurene.*—This was carried out according to the literature method [20] for the same reaction in the absence of spin trap or solvent.

(*a*) *In the presence of* 2-*methyl*-2-*nitrosopropane and benzene.* Tris(triphenylphosphine)platinum(0) (0.59 g, 0.6 mmol) was dissolved in benzene (*ca.* 5 cm^3) and the solution protected from light. To this was added a solution of 2-methyl-2-nitrosopropane (0.005 2 g, 0.06 mmol) in methyl iodide (5 cm^3). The combined solutions were stirred at ambient temperature for 3 h, whereafter volatiles were removed. The residue was refluxed in methanol (*ca.* 15 cm^3) and the mixture filtered. Crystallisation of the solid product from hot benzene afforded white crystals (0.312 2 g, 62%) of *trans*-iodo(methyl)bis(triphenylphosphine)platinum(II), m.p. 269.5—271 °C (decomp.) (open capillary) [lit.,[20] 270—274 °C (decomp.) (Koffler hot stage)] (Found: C, 51.8; H, 4.0. Calc. for $C_{37}H_{33}IP_2Pt$: C, 51.6; H, 3.9%).

(*b*) *In the presence of nitrosodurene and in the absence of solvent.* Nitrosodurene (0.007 4 g, 0.05 mmol) was dissolved in methyl iodide (*ca.* 3 cm^3) and the solution added to solid [Pt(PPh$_3$)$_3$] (0.45 g, 0.46 mmol). The resultant solution was stirred at ambient temperature; after 0.25 h the solution had lightened but a yellow colour remained. Methyl iodide (2 cm^3) was added and stirring was continued for 0.75 h. The work-up was as described in the preceding experiment, yielding white crystals (0.242 g, 62%), m.p. 271.5—273 °C (decomp.) (Found: C, 51.5; H, 3.9%).

Reactions of Tris(*triphenylphosphine*)*platinum*(0).—(*a*) *With chlorotriphenylmethane.* Tris(triphenylphosphine)platinum(0) (0.175 g, 0.178 mmol) was dissolved in benzene (*ca.* 3 cm^3); chlorotriphenylmethane in benzene was added (0.175 mmol, 3.5 cm^3 of a 5×10^{-2} mol dm^{-3} solution). The solution was stirred at ambient temperature for 2 h over which time the yellow colour remained and a fine white precipitate formed. The e.s.r. spectrum of the supernatant solution was recorded. The precipitate was filtered off, washed with a little cold benzene, and dried (high vacuum ambient temperature). Infrared spectroscopy identified the product as *cis*-dichlorobis(triphenylphosphine)platinum(II) (0.065 g, 92%).

(*b*) *With bromodiphenylmethane.* Tris(triphenylphosphine)platinum(0) (0.252 g, 0.257 mmol) was dissolved in benzene (*ca.* 5 cm^3) to give a yellow solution, and bromodiphenylmethane (0.062 g, 0.252 mmol) was added. The solution was stirred for 1 h at ambient temperature during which time a white precipitate formed and the yellow colour remained. A sample of the solution was analysed by g.l.c.–mass spectrometry. In a separate experiment, involving excess of bromodiphenylmethane, the precipitate was isolated, recrystallised (CH_2Cl_2–EtOH), and identified as the pale cream powder, *cis*-dibromobis(triphenylphosphine)platinum(II) (Found: C, 48.5; H, 3.4. Calc. for $C_{36}H_{30}Br_2P_2Pt$: C, 49.2; H, 3.4%).

The Lack of Influence on the Optical Rotation of (+)-2-*Halogeno-octane by a Trace of Tris*(*triphenylphosphine*)*platinum*(0).—(+)-2-Iodo-octane (0.229 g, 0.95 mmol) was dissolved in benzene (7.734 g) and the rotation measured, α_m (benzene, 25 °C, 589 nm) = +41.7 (c = 2.61).* An aliquot (3 cm^3) of this solution was added to [Pt(PPh$_3$)$_3$] (0.015 g, 0.015 2 mmol, 5% with respect to 2-iodo-octane) and the resultant solution stirred overnight at ambient temperature. Volatiles were removed and their rotation and n.m.r. spectra measured. The rotation of the stock solution of 2-iodo-octane was unchanged after leaving overnight. Similar results were obtained by Dr. M. J. S. Gynane on the (+)-2-chloro-octane–[Pt(C$_2$H$_4$)(PPh$_3$)$_2$] system.

Bromobis(*dimethylphenylphosphine*)*dimethyl*(*toluene*-p-*sulphonyl*)*platinum*(IV).— *cis*-Bis(dimethylphenylphosphine)dimethylplatinum(II) (0.504 g, 1.00 mmol) was dissolved in diethyl ether (2 cm^3). To this solution was added a solution of toluene-*p*-sulphonyl bromide (0.236 g, 1.00 mmol) in diethyl ether (1 cm^3) *via* a syringe. A yellow colour developed immediately upon mixing, and very quickly faded as a cream precipitate was formed. After filtration, washing with diethyl ether and hexane, and drying *in vacuo*, white crystals were obtained of the title *product* (0.59 g, 80%), m.p. 139—141 °C (Found: C, 40.9; H, 4.9. $C_{25}H_{35}BrO_2P_2PtS$ requires C, 40.8; H, 4.8%).

Bis(*dimethylphenylphosphine*)*iododimethyl*(*toluene*-p-*sulphonyl*)*platinum*(IV).— *cis*-Bis(dimethylphenylphosphine)dimethylplatinum(II) (0.153 g, 0.31 mmol) in benzene (2 cm^3) was added dropwise to solid toluene-*p*-sulphonyl iodide (0.087 g, 0.31 mmol) at −25 °C. The mixture was allowed to warm to 50 °C during 2 h. Benzene was removed *in vacuo*, to produce a pale yellow, oily solid. After triturating with diethyl ether and hexane, filtration and drying *in vacuo* yielded the pale yellow title *compound* (0.20 g, 83%), m.p. 132—143 °C (decomp.) (Found: C, 39.2; H, 4.7. $C_{25}H_{35}IO_2P_2PtS$ requires C, 38.8; H, 4.6%).

Chloro-(p-*chlorobenzenesulphonyl*)*bis*(*dimethylphenylphosphine*)*dimethylplatinum*(IV).—Dry recrystallised *p*-chlorobenzenesulphonyl chloride (0.203 g, 0.96 mmol) in diethyl ether (2 cm^3) was added with stirring to a solution of *cis*-bis(dimethylphenylphosphine)dimethylplatinum(II) (0.278 g, 0.55 mmol) in the same solvent (3 cm^3). The mixture was stirred for 0.5 h, gradually forming a white crystalline precipitate. After filtration, washing with cold diethyl ether and hexane, and drying *in vacuo*, the title product (0.175 g, 45%) was formed as a white microcrystalline powder, m.p. 133—135 °C (decomp.). Further characterisation was carried out only by ^{1}H n.m.r. spectroscopy.

Reaction between cis-*Bis*(*dimethylphenylphosphine*)*dimethylplatinum*(II) *and Methanesulphonyl Chloride.*—The chloride (0.092 g, 0.80 mmol) in diethyl ether (2 cm^3) was added by syringe to a solution of *cis*-bis(dimethylphenylphosphine)dimethylplatinum(II) (0.201 g, 0.40 mmol) in diethyl ether (3 cm^3). After stirring for 0.5 h, ether was removed *in vacuo*, and the oily residue so produced was recrystallised from ether–hexane (1 : 1) at −70 °C, filtered off, and dried *in vacuo* to produce white crystals. Proton n.m.r. spectroscopy suggested that the product may be the platinum(IV) addition complex and this was indicated by analysis (Found: C, 35.8; H, 5.0. Calc. for $C_{29}H_{31}ClO_2PPtS$: C, 37.0; H, 5.0%). Phosphorus-31 n.m.r. data suggested the presence of a *cis*–*trans* mixture.

Formation of trans-*Bromobis*(*dimethylphenylphosphine*)p-*tolylplatinum*(II) *by Thermal Decomposition of Bromobis*(*dimethylphenylphosphine*)*dimethyl*-p-(*toluene*-p-*sulphonyl*)-*platinum*(IV).— Bromobis(dimethylphenylphosphine)dimethyl(toluene-*p*-sulphonyl)platinum(IV) (0.113 g, 0.15 mmol) was dissolved in dry degassed benzene (5 cm^3) and refluxed for 3.5 h. Benzene was removed *in vacuo*; the cream coloured residue was washed with cold hexane, filtered off, and dried *in vacuo* to give the platinum(II) dibromide as a white powder (0.072 g, 73%), m.p. 136—138 °C (Found: C, 42.8; H, 4.7. Calc. for $C_{23}H_{29}BrP_2Pt$: C,

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* $\alpha_m(t,\lambda) = [\alpha]^t_\lambda$, the units being ° cm^3 dm^{-1} g^{-1}. Units of concentration c are g dm^{-3}.

43.0; H, 4.6%). Further characterisation was carried out by ^{1}H n.m.r. spectroscopy.

Formation of trans-*Bromobis(dimethylphenylphosphine)-methylplatinum*(II) *by Thermal Decomposition of Acetylbromobis(dimethylphenylphosphine)dimethylplatinum*(IV).—Acetylbromobis(dimethylphenylphosphine) dimethylplatinum(IV) (0.075 g, 0.13 mmol) was dissolved in a deuteriochloroform–dichloromethane mixture, degassed thoroughly, sealed in an n.m.r. tube, and the ^{1}H n.m.r. spectrum was recorded. The solution was then heated to 80 °C for 2 h, and further characterisation was carried out by ^{1}H n.m.r. and i.r., which showed that the white powder obtained by removal of solvent *in vacuo* was the bromo(methyl)platinum(II) complex.

Thermal Decomposition of Acetylchlorobis(dimethylphenylphosphine)dimethylplatinum(IV), *an N.M.R. Experiment.*—The title compound (0.059 g, 0.094 mmol) was dissolved in dry deuteriochloroform and the ^{1}H n.m.r. spectrum was recorded. Deuteriochloroform was removed *in vacuo*, and the oily residue was triturated with hexane and dried *in vacuo*. Characterisation was carried out by ^{1}H n.m.r. after dissolving the white crystalline residue in deuteriochloroform; as in the previous experiment, the product was identified as *trans*-chlorobis(dimethylphenylphosphine)-methylplatinum(II).

Galvinoxyl Reactions.—The reactions of *cis*-[$PtMe_2(PMe_2Ph)_2$] and *p*-$MeC_6H_4SO_2X$ (X = Cl or Br) or MeCOX (X = Cl or Br) were carried out by intimately mixing the platinum(II) substrate and galvinoxyl (1—5% molar with respect to Pt^{II}) and dissolving the mixture in benzene or diethyl ether. The compound *p*-$MeC_6H_4SO_2X$ or MeCOX in the same solvent was then added and the mixture was stirred for 0.5 h [*i.e.* the time taken completely to form platinum(IV) adducts in the absence of galvinoxyl]. Solvent was then removed *in vacuo*, and the residue was dissolved in $CDCl_3$ (with CH_2Cl_2 as an internal standard) and the ^{1}H n.m.r. spectrum of the mixture was recorded. Comparison of the ^{1}H n.m.r. of the mixture and of the appropriate platinum(II) starting material and platinum(IV) product (especially in the P–Me region) indicated whether inhibition had occurred.

Thus it was observed that the P–Me region of *cis*-[$PtMe_2(PMe_2Ph)_2$]–*p*-$MeC_6H_4SO_2Cl$ (1% galvinoxyl) or *cis*-[$PtMe_2(PMe_2Ph)_2]_0$MeCOCl (1% galvinoxyl) was similar to that of the P–Me region of the starting material, *cis*-[$PtMe_2(PMe_2Ph)_2$] (*i.e.* the P–Me region is a predominant doublet with 'virtual' coupling). However, the P–Me region of *cis*-[$PtMe_2(PMe_2Ph)_2$]–*p*-$MeC_6H_4SO_2Br$ (or MeCOBr) (1% galvinoxyl) resembled that of the platinum(IV) products (*i.e.* complex multiplet), and this reaction is therefore not inhibited.

Reaction of cis-*Bis(dimethylphenylphosphine)diethylplatinum*(II) *and Acetyl Chloride.*—Acetyl chloride (0.019 g, 0.25 mmol) in OEt_2 (1 cm^3) was added *via* a syringe to *cis*-bis(dimethylphenylphosphine)diethylplatinum(II) (0.107 g, 0.20 mmol) in a diethyl ether–benzene mixture (1 : 1) (7 cm^3). The mixture was stirred vigorously for 0.75 h; solvent was removed *in vacuo*, and the white residue was thoroughly washed with cold diethyl ether, filtered off, and dried *in vacuo* to give the product as a cream powder. This was identified as *chlorobis(dimethylphenylphosphine)-ethylplatinum*(II) (0.084 g, 78%), m.p. 106—108 °C, by i.r. [absence of ν(C=O)] and analysis (Found: C, 40.3; H, 5.1. $C_{18}H_{27}ClP_2Pt$ requires C, 40.4; H, 5.1%).

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