Unsaturated σ-Hydrocarbyl Transition-metal Complexes. Part 2.[1] Synthesis and Reactions of Vinylplatinum Complexes and a Comparison with Analogous Fluorovinyl and Alkynyl Complexes †

By **Christine J. Cardin, David J. Cardin,** and **Michael F. Lappert,*** School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

Alkenyl ($CH=CH_2$ or $CF=CF_2$) or alkynyl ($C\equiv CPh$) derivatives of trimethyltin are shown to be superior to lithium or magnesium reagents for the synthesis of corresponding mono-organoplatinum(II) species by metathesis (L =

$$SnMe_3R + cis\text{-}[PtCl_2L_2] \longrightarrow trans\text{-}[PtRClL_2] + SnMe_3Cl$$

tertiary phosphine). The reactivity order for $SnMe_3R$ is R = $C\equiv CPh$ > $CF=CF_2$ > $CH=CH_2$. This order is also found for oxidative addition of $SnMe_3R$ to Pt^0 to give *cis*-$[PtRL_2(SnMe_3)]$. When the latter complex (R = $CH=CH_2$) reacts with X_2 or MeX further oxidative addition occurs exclusively at the platinum centre. Aromatic isonitriles (R′NC)co-ordinate to the platinum and give insertion products *trans*-$[Pt\{C(CH=CH_2)=NR'\}ClL_2]$ on heating or carbene complexes with NBu^nH_2. The alkynyl *trans*-$[Pt(C\equiv CPh)ClL_2]$ also forms 1 : 1 adducts with R′NC and carbene complexes therefrom, but no insertion products. Spectroscopic data for the new complexes are presented.

THIS paper forms the second part of a series dealing with transition-metal alkenyl and alkynyl (hydrocarbyl) complexes.[1] The series has as the important objectives of (*i*) an assessment of the *trans* influence of carbon ligands with *sp* or sp^2 ligating C atoms, and (*ii*) an investigation of the chemistry of unsaturated σ-hydrocarbyl and related derivatives of platinum-(II) and -(IV). The principal evidence with regard to *trans* influence comes from the two crystal-structure determinations which form Parts 3 [2] and 4 [3] of this series. In Part 4 we also summarise some pertinent spectroscopic results and discuss the influence of hybridisation on the *trans* influence of carbon ligands. Reliable results on an sp^3 ligand (CH_2SiMe_3) are available for comparison.[4]

In particular we are concerned with the possible effects on *trans* influence of α-unsaturation in hydrocarbyl ligands arising through a potential p_π–d_π overlap between C_α and Pt. Although such overlap is well documented for carbon bonded to more electronegative heteroatoms, leading to lowered *trans* influence, the effect has not been examined for σ-unsaturated hydrocarbyl ligands. The data are discussed in detail in Part 4, but in summary the changes in *trans* influence are small and for Pt^{II} decrease in the series CH_2SiMe_3 > $C\equiv CPh \simeq CH=CH_2$, with only small differences between the *sp* and sp^2 ligand. The extent of multiple bonding as judged by Pt–C bond lengths is also small. A preliminary communication has appeared.[5]

Much interest has been shown in recent years in alkenyl complexes of the late transition metals,[6-13] but these studies have utilised substituted alkenyls almost exclusively, and few results on the ' pure ' vinyl group as a ligand have been reported. Our interest is in the reactivity and bonding of the ' pure ' vinyl group when attached to a transition metal. Additionally, we have compared the three σ-unsaturated ligands $CH=CH_2$, $CF=CF_2$, and $C\equiv CPh$ (*i*) as their $SnMe_3$ derivatives in the synthesis of platinum(II) organometallics by either (*a*) metathesis or (*b*) oxidative addition [equation (1), L =

$$\begin{tikzcd} cis\text{-}[PtCl_2L_2] \arrow[r, "(a)"] & {} & \\ & {[PtR(X)L_2]} \arrow[ul, phantom, "X = Cl"] & {[PtL_n]} \arrow[l, "(b)\ n = 3 \text{ or } 4", "X = SnMe_3"'] \end{tikzcd} \quad (1)$$

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† No reprints available.

[1] Part 1, B. Çetinkaya, M. F. Lappert, J. McMeeking, and D. Palmer, *J.C.S. Dalton*, 1973, 1202.

[2] Part 3, C. J. Cardin and K. W. Muir, *J.C.S. Dalton*, in press.

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phosphine], and (*ii*) as their platinum(II) derivatives, with regard to reactivity and bonding. As to (*ii*), a feature of these platinum(II) complexes is that they are unsaturated with respect to two centres: the metal and the ligand. There are reports of double-bond reactivity in substituted platinum(II) alkenyls,[7,10] but none concerning the vinyl group itself.

The utility of SnMe$_3$R [*cf.* equation (1)] has previously (see also ref. 5) been explored for several unsaturated species, (*a*) as group transfer reagents [R = C$_5$H$_5$,[14] C$_3$H$_5$,[15] N=CX$_2$ (X = Ph,[16] Bu^t,[16] or CF$_3$,[16-18]), aryl,[19] and C≡CPh (for Rh^{I} or Ir^{I} only) [1]] and (*b*) as oxidative addenda {R = C$_5$H$_5$,[14] H,[20] or C≡CPh [as in equation (1b) and also for Mo^0, Co^0, Rh^{I}, or Ir^{I} substrates] [1]}. (Reactions of SnMe$_3$Cl with some platinum(0) substrates were formerly thought to proceed *via* Sn–Cl cleavage, but have recently been shown to involve insertion of Pt into the Sn–C bond.[21a]) We shall show that the reactivity order for SnMe$_3$R with respect to both (*a*) and (*b*) decreases in the order R = C≡CPh > CF=CF$_2$ > CH=CH$_2$, and hence appears to be directly related to the stability of the derived anion R$^-$ and the ionicity of the Sn–R bond.

Although the first transition-metal vinyl complex was reported in 1964,[21b] the number described since then has been low,[8,11,22-25] except for cobalt complexes related to vitamin B$_{12}$.[26] The paucity of characterised compounds appears to be due, not to their instability, but to the failure of the obvious synthetic routes with unsubstituted starting materials. Thus, acetylene inserts only exceptionally into the M–H bond,[24] although activated acetylenes such as F$_3$C–C≡C–CF$_3$ insert readily into a wide variety of M–H bonds.[27] Similarly, there is only a single report of the use of MgBr(CH=CH$_2$) to prepare a vinyl complex,[23] and no account of the use of lithium reagents.

TABLE 1

Selected data for the new complexes

				Analytical data (%)					Selected i.r. data [a]		Mass spectra [b]	
		Reaction		Found		Calc.						
Complex	Yield (%)	time (*t*/h)	M.p. (θ_c/°C)	C	H	C	H	Other elements	ν(C=C) or ν(C—C)	ν(Pt–Cl)	Found (calc.)	Reaction type [c]
trans-[Pt(CH=CH$_2$)Cl(PMe$_2$Ph)$_2$]	32	7	127—128	40.6	4.8	40.5	4.7		1 564	284	533 (533)	A
trans-[Pt(CH=CH$_2$)Cl(PEt$_2$Ph)$_2$]	50	60	108	44.7	5.7	44.8	5.6		1 568	270	589 (589)	A
trans-[Pt(CH=CH$_2$)Cl(PMePh$_2$)$_2$]	3	24	142—144	51.0	4.5	51.1	4.4		1 568	278	657 (657)	A
trans-[Pt(CF=CF$_2$)Cl(PEt$_2$Ph)$_2$]	20	12	97—99	41.4	4.8	41.0	4.7		1 713	285	643 (643)	A
trans-[Pt(CF=CF$_2$)$_2$(PEt$_2$Ph)$_2$]	15	12	109—112	42.0	4.4	41.8	4.4		1 722, 1 713		689 (689)	A
trans-[Pt(CF=CF$_2$)Cl(PMe$_2$Ph)$_2$]	20	1	155—158	36.2	4.2	36.5	4.4		1 715		587 (587)	A
trans-[Pt(C≡CPh)Cl(PEt$_2$Ph)$_2$]	90	24	108	50.8	5.2	50.6	5.3	*d*	2 120		663 (663)	A
trans-[Pt(C≡CPh)Cl(PMePh$_2$)$_2$]	30	5	193—195	55.9	4.3	55.9	4.0	*e*	2 130		731 (731)	A
trans-[PtBr(CH=CH$_2$)(PMe$_2$Ph)$_2$]	10	3	114	37.4	4.5	37.4	4.8	*f*	1 564		578 (577)	B
cis-[Pt(CF=CF$_2$)(PPh$_3$)$_2$(SnMe$_3$)]	76	15	171—174 (decomp.)	51.1	4.3	51.1	4.1	*g*	1 708		717 (717)	C
trans-[Pt(CF=CF$_2$)(PMe$_2$Ph)$_2$(SnMe$_3$)]	2	15	140—141	35.3	4.3	35.2	4.4		1 653			C
trans-[PtBr(CH=CH$_2$)(PEt$_2$Ph)$_2$]	90	12	104	41.1	5.4	41.7	5.3	*h*	1 567		633 (633)	D
trans-[Pt(CH=CH$_2$)I(PEt$_2$Ph)$_2$]	85	12	95—97	38.3	5.0	38.7	4.9	*i*	1 567		681 (681)	D
[Pt(CH=CH$_2$)Cl$_3$(PEt$_2$Ph)$_2$]	90	0.5	175—178 (decomp.)	40.0	5.3	40.0	5.0	*j*	1 592	328, 255	*k*	E
[PtBr$_3$(CH=CH$_2$)(PEt$_2$Ph)$_2$]	85	0.5	167—169 (decomp.)	33.4	4.2	33.2	4.2	*l*	1 590		*k*	E
[PtBr$_2$Me(CH=CH$_2$)(PEt$_2$Ph)$_2$]	40	*m*	115—118	38.0	5.1	37.9	5.0		1 575		*k*	E
[PtMe(CH=CH$_2$)I$_2$(PEt$_2$Ph)$_2$]	50	*m*	129—131	34.0	4.7	33.6	4.4		1 575		*k*	E
[PtBr$_2$(CH=CH$_2$)Cl(PEt$_2$Ph)$_2$]	80	1	170	34.5	4.2	34.8	4.4		1 585	255		E
[PtBrMe(CH=CH$_2$)I(PMe$_2$Ph)$_2$]	60	*m*	159—161	31.4	4.0	31.7	3.9		1 572		725 (719)	E
trans-[Pt{C(CH=CH$_2$)=NC$_6$H$_4$OMe-*p*}Cl(PEt$_2$Ph)$_2$]	70	1	113—115	49.9	5.9	49.8	5.6	*n*	1 537	260	760 (760)	F
trans-[Pt(CH=CH$_2$)(CNC$_6$H$_4$OMe-*p*)(PEt$_2$Ph)$_2$][PF$_6$]	60	0.5	98—100	44.2	5.1	43.3	4.8	*o*	1 564	*p*	679 (687)	F
trans-[Pt(CH=CH$_2$){C(NHBu^n)NHC$_6$H$_4$OMe-*p*}(PEt$_2$Ph)$_2$][PF$_6$]	85	0.5	129	46.1	5.8	45.1	5.7	*q*	1 568	*r*	722 (722)	F
[Pt(C≡CPh)(CNC$_6$H$_4$OMe-*p*)(PMePh$_2$)][PF$_6$]	60	0.5	114	51.7	3.7	51.9	3.7	*s*	2 145	*t*	902 (902)	F
[Pt(C≡CPh){C(NHBu^n)NHC$_6$H$_4$OMe-*p*}(PMePh$_2$)][PF$_6$]	50	0.5	192—194	52.8	5.0	52.7	4.7	*u*	2 130	*v*	797 (827)	F
[PtMe(CH=CH$_2$)ClI(PMe$_2$Ph)$_2$]	50	*m*	174	33.8	4.0	33.7	4.2				675 (675)	E

[a] As Nujol mull. [b] *m/e* Values for parent ions. [c] A = SnMe$_3$Cl elimination; B = Grignard reagent; C = oxidative addition to Pt^0; D = metathesis from chloride; E = oxidative addition to Pt; and F = see text. [d] P, 9.2 (calc.: 9.3%). [e] Cl, 5.1 (calc.: 4.9%). [f] P, 10.1 (calc.: 10.5%); Br, 13.7 (calc.: 13.8%). [g] F, 5.8 (calc.: 5.9%); P, 6.2 (calc.: 6.4%). [h] Br, 12.7 (calc.: 12.6%). [i] I, 18.8 (calc.: 18.6%); P, 8.9 (calc.: 9.1%). [j] Cl, 16.3 (calc.: 16.1%); P, 9.2 (calc.: 9.4%). [k] No molecular ion obtained, highest peak is that due to [PtX$_2$L$_2$]$^+$. [l] Br, 30.4 (calc.: 30.2%); P, 7.8 (calc.: 7.8%). [m] *ca.* 4 weeks. [n] N, 2.0 (calc.: 1.9%). [o] N, 1.7 (calc.: 1.7%). [p] ν(C≡N) at 2 185 cm^{-1}. [q] N, 3.3 (calc.: 3.1%). [r] ν(N–H) at 3 440 and 3 550 cm^{-1}. [s] N, 1.4 (calc.: 1.4%). [t] ν(C≡N) at 2 145 cm^{-1}. [u] N, 2.6 (calc.: 2.7%). [v] ν(N–H) at 3 400 and 3 328 cm^{-1}.

RESULTS AND DISCUSSION

The new complexes prepared are recorded in Table 1. All gave satisfactory analyses and nearly all a molecular-ion peak in the mass spectrometer.

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Synthesis of Vinylplatinum(II) *Complexes and of Fluorovinyl or Alkynyl Analogues*.—The reagent $SnMe_3(CH{=}CH_2)$ did not add oxidatively to the d^{10} species $[Pt(CH_2{=}CH_2)(PPh_3)_2]$, $[Pt(PPh_3)_3]$, or $[Pt(PPh_3)_4]$, or to the d^8 complexes $[Ir(CO)Cl(PPh_3)_2]$ or $[RhCl(PPh_3)_3]$. This is in contrast to the alkynyl $SnMe_3(C{\equiv}CPh)$ which adds [as in equation (1b)] readily to all these complexes,[1] and to $SnMe_3(CF{=}CF_2)$ which is intermediate in reactivity (see below).

However, *cis*-dichlorobis(phosphine)platinum(II) complexes did undergo metathetical exchange reactions with the vinyltin compound, with $SnMe_3Cl$ elimination as in equation (1a). Only a single vinyl group is introduced by this method. Prolonged heating under reflux was required in order to give satisfactory yields (Table 1) and it was essential to use an excess of the tin reagent. A convenient practical feature of this preparation is that all the tin compounds involved are hexane-soluble and were readily extracted during work-up of the reaction mixture; side reactions involving the tin reagent, such as polymerisation, did not occur. In contrast, using $Sn(CH{=}CH_2)_4$, although monovinyl complexes of platinum were isolated after extended heating under reflux, decomposition of $Sn(CH{=}CH_2)_4$ appeared to take place, giving products not readily removed by hexane extraction and reducing the usefulness of the reaction. Vinyl-lithium or the vinyl Grignard reagents also gave extensive side reactions: vinyl-lithium yielded only polymeric material on reaction with the same platinum(II) dihalides. Vinylmagnesium bromide gave a low yield (8%) of *trans*-$[PtBr(CH{=}CH_2)(PMe_2Ph)_2]$ with *cis*-$[PtCl_2(PMe_2Ph)_2]$, and this mixture had to be separated by chromatography from the large amount of high-molecular-weight material. A small quantity of *trans*-$[PtBrH(PMe_2Ph)_2]$ was also present in one reaction; this may have been formed as shown in (2) (*cf.* ref. 28). Because vinylplatinum(II) complexes withstand long periods of reflux with $SnMe_3(CH{=}CH_2)$ during their preparation (sometimes >24 h: see Table 1), formation of the platinum hydride by direct elimination of acetylene seems unlikely. On the other hand, it is possible that the reducing action of the Grignard reagent is directly responsible for the side reaction.[2,9]

$$\left.\begin{array}{l} cis\text{-}[PtCl_2(PMe_2Ph)_2] + MgBr(CH{=}CH_2) \longrightarrow \\ \qquad\qquad [PtCl(MgBr)(PMe_2Ph)_2] + CH_2{=}CHCl \\ [PtCl(MgBr)(PMe_2Ph)_2] + [NH_4]Cl \longrightarrow \\ \qquad\qquad\qquad [PtClH(PMe_2Ph)_2] \\ [PtClH(PMe_2Ph)_2] + Br^- \xrightarrow{\text{trace of } PMe_2Ph} \\ \qquad\qquad\qquad trans\text{-}[PtBrH(PMe_2Ph)_2] \end{array}\right\} (2)$$

Alkynyl or fluorovinyl derivatives of Pt^{II} were easily prepared using the appropriate tin reagents, and the extent of substitution at Pt was readily controlled by the stoicheiometry of the reaction. These exchanges of halide and R require only short reflux times and again have the practical advantage of ready isolation of products. The length of refluxing time required to give essentially complete reaction thus leads to the reactivity order for $SnMe_3R$ of (R=) $C{\equiv}CPh > CF{=}CF_2 > CH{=}CH_2$, which appears to correlate with the likely extent of polarisation of the Sn–C bond. It is noteworthy that we found no reaction between an excess of $SnMe_3(CH_2SiMe_3)$ and *cis*-$[PtCl_2(PMe_2Ph)_2]$ on prolonged heating under reflux in tetrahydrofuran (thf). This tin compound was also inactive with regard to oxidative addition at Pt^0.

All the new complexes prepared in this way are of *trans* stereochemistry as judged by the resonance patterns of the phosphine alkyl group in the ^1H n.m.r. spectrum,[30] and in three cases the stereochemistry was established by *X*-ray crystallography: *trans*-$[PtCl(CH{=}CH_2)(PEt_2Ph)_2]$,[2] *trans*-$[PtCl(C{\equiv}CPh)(PEt_2Ph)_2]$,[3] and *trans*-$[Pt(CF{=}CF_2)_2(PEt_2Ph)_2]$.[31]

Reactivity of Vinylplatinum Complexes.—Here there are several points of interest: (*a*) the possible activation or deactivation of the double bond when bonded to platinum; (*b*) the nature of the M–C bond in comparison with M-alkyl or M-alkynyl bonds, including their relative *trans* effect or influence and the ease of cleavage of these bonds; (*c*) the possibility of ligand-rearrangement reactions involving the vinyl group; and (*d*) the nature of addition reactions to substrates which possess dual centres (C=C and Pt^{II}) of unsaturation. The reactions are summarised in Scheme 1.

Reactions with halogens were studied using $[PtX(CH{=}CH_2)(PEt_2Ph)_2]$ (X = Cl, Br, or I) prepared from the chloro-complex and LiBr or NaI in acetone. One equivalent of chlorine in benzene when added to *trans*-$[Pt(CH{=}CH_2)Cl(PEt_2Ph)_2]$ gave a high yield of the trichloro-complex $[Pt(CH{=}CH_2)Cl_3(PEt_2Ph)_2]$ without displacement of, or addition to, the vinyl group. A similar result has been reported for chloro-substituted vinyl complexes.[7] The new platinum(IV) vinyl complex had ^1H and ^{13}C n.m.r. spectroscopic features which show clearly the change in oxidation state of the metal (Tables 2 and 3). Similarly, oxidative addition at the metal centre was the sole reaction when *trans*-$[PtBr(CH{=}CH_2)(PEt_2Ph)_2]$ was treated with bromine (1 equivalent), with rapid decolourisation of the added bromine. However, on addition of iodine (1 equivalent) to *trans*-$[Pt(CH{=}CH_2)I(PEt_2Ph)_2]$ and stirring, evaporation of solvent gave a mixture of deep red needles and yellow prisms. Attempted manual separation, and subsequent recrystallisation of the red needles, gave chiefly a further quantity of yellow prisms identified as *trans*-$[PtI_2(PEt_2Ph)_2]$. The red needles are therefore presumed to be the addition product $[Pt(CH{=}CH_2)I_3(PEt_2Ph)_2]$ from which vinyl iodide elimination readily occurred. (A related elimination is reported in ref. 32.) The reaction of a further equivalent of bromine with $[PtBr_3(CH{=}CH_2)(PEt_2Ph)_2]$ gave only *trans*-$[PtBr_2(PEt_2Ph)_2]$, with no evidence for

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[28] *cf.* H. Felkin and P. J. Knowles, *J. Organometallic Chem.*, 1972, **37**, C147.

[29] See, for example, M. R. Collier, M. F. Lappert, and R. Pearce, *J.C.S. Dalton*, 1973, 445 and refs. therein.

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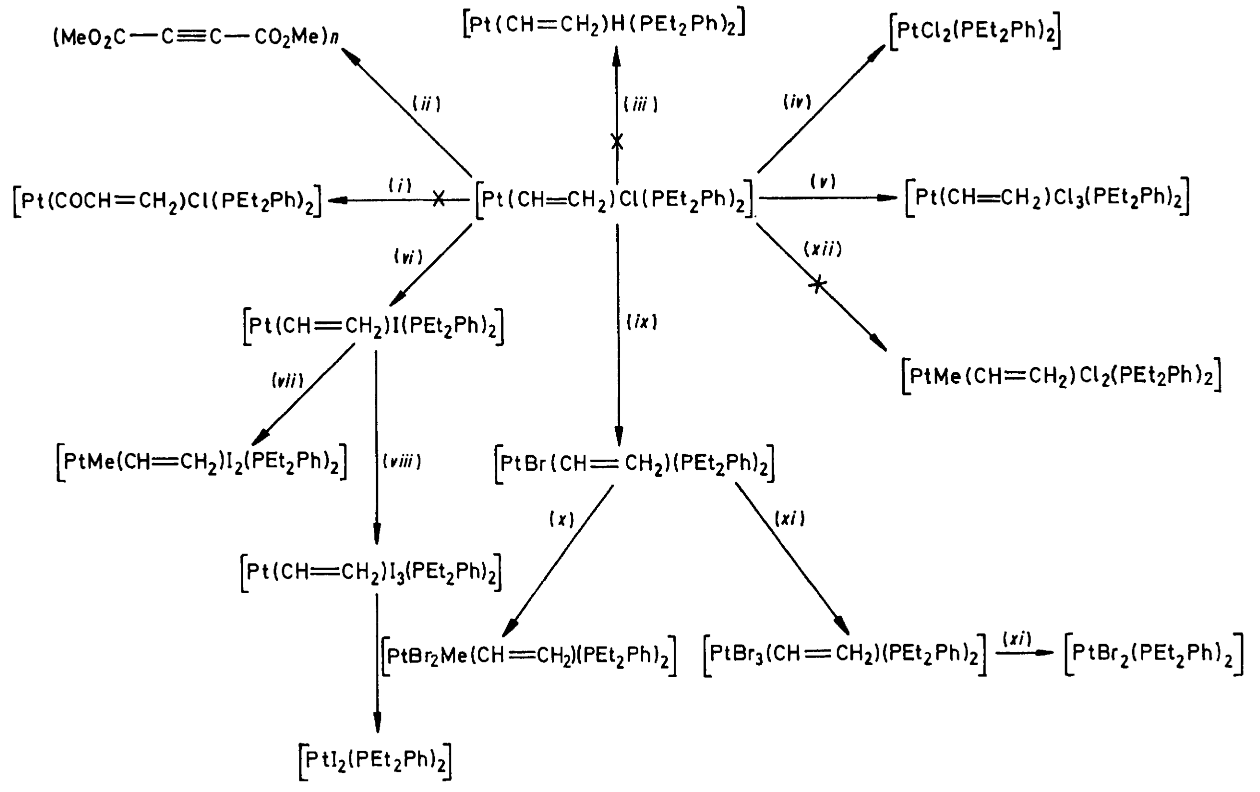


SCHEME 1 Reactions of vinyl compounds. (*i*) CO (1 atm); (*ii*) $\mathrm{MeO_2CC{\equiv}CCO_2Me}$; (*iii*) $\mathrm{SiEt_3H}$, reflux; (*iv*) HCl–$\mathrm{OEt_2}$ (1 equivalent); (*v*) $\mathrm{Cl_2}$ in benzene (1 equivalent); (*vi*) NaI, $\mathrm{Me_2CO}$; (*vii*) MeI (4 weeks); (*viii*) $\mathrm{I_2}$ in benzene (1 equivalent); (*ix*) LiBr, $\mathrm{Me_2CO}$; (*x*) MeBr (7 weeks); (*xi*) $\mathrm{Br_2}$ in benzene (1 equivalent); (*xii*) MeCl (4 weeks)

TABLE 2

Chemical shifts and coupling-constant data (in Hz) for ^{1}H n.m.r. spectra of the vinyl groups in the new platinum complexes

Complex	Oxidation state of Pt	Chemical shifts [a] (p.p.m.) τ_1	τ_2	τ_3	Coupling constants (Hz) $\lvert J(\mathrm{H^1H^2})\rvert$	$\lvert J(\mathrm{H^2H^3})\rvert$	$\lvert J(\mathrm{H^1H^3})\rvert$	$\lvert J(\mathrm{PtH^2})\rvert$	$\lvert J(\mathrm{PtH^3})\rvert$	$\lvert J(\mathrm{PH^1})\rvert$
trans-$[\mathrm{Pt(CH{=}CH_2)Cl(PEt_2Ph)_2}]$	II	3.15	4.37	5.28	10.5	2.2	18.0	156	85	4.3
trans-$[\mathrm{PtBr(CH{=}CH_2)(PEt_2Ph)_2}]$	II	3.18	4.39	5.27	10.5	2.0	17.8	165	88	4.5
trans-$[\mathrm{Pt(CH{=}CH_2)I(PEt_2Ph)_2}]$	II	3.21	4.36	5.27	10.5	2.0	17.7	192	88	4.5
$[\mathrm{Pt(CH{=}CH_2)Cl_3(PEt_2Ph)_2}]$	IV	4.02	5.38	5.12	7.1	1.2	15.0	76	47	*
$[\mathrm{PtBr_3(CH{=}CH_2)(PEt_2Ph)_2}]$	IV	4.28	5.60	5.24	7.1	1.0	15.0	70	41	3.5
$[\mathrm{PtBr_2Me(CH{=}CH_2)(PEt_2Ph)_2}]$	IV	*	4.71	5.25	8.2	*	17.0	132	66	*
$[\mathrm{PtMe(CH{=}CH_2)I_2(PEt_2Ph)_2}]$	IV	*	4.80	5.25	8.0	1.0	16.5	134	70	*
trans-$[\mathrm{Pt(CH{=}CH_2)Cl(PMe_2Ph)_2}]$	II	3.12	4.26	5.15	10.5	2.0	17.5	162	88	*
trans-$[\mathrm{PtBr(CH{=}CH_2)(PMe_2Ph)_2}]$	II	3.24	4.36	5.27	10.3	2.0	17.7	168	90	*
$[\mathrm{PtBrMe(CH{=}CH_2)I(PMe_2Ph)_2}]$	IV	3.15	4.94	5.50	7.8	*	17.0	156	70	*

* Masked by other resonances.

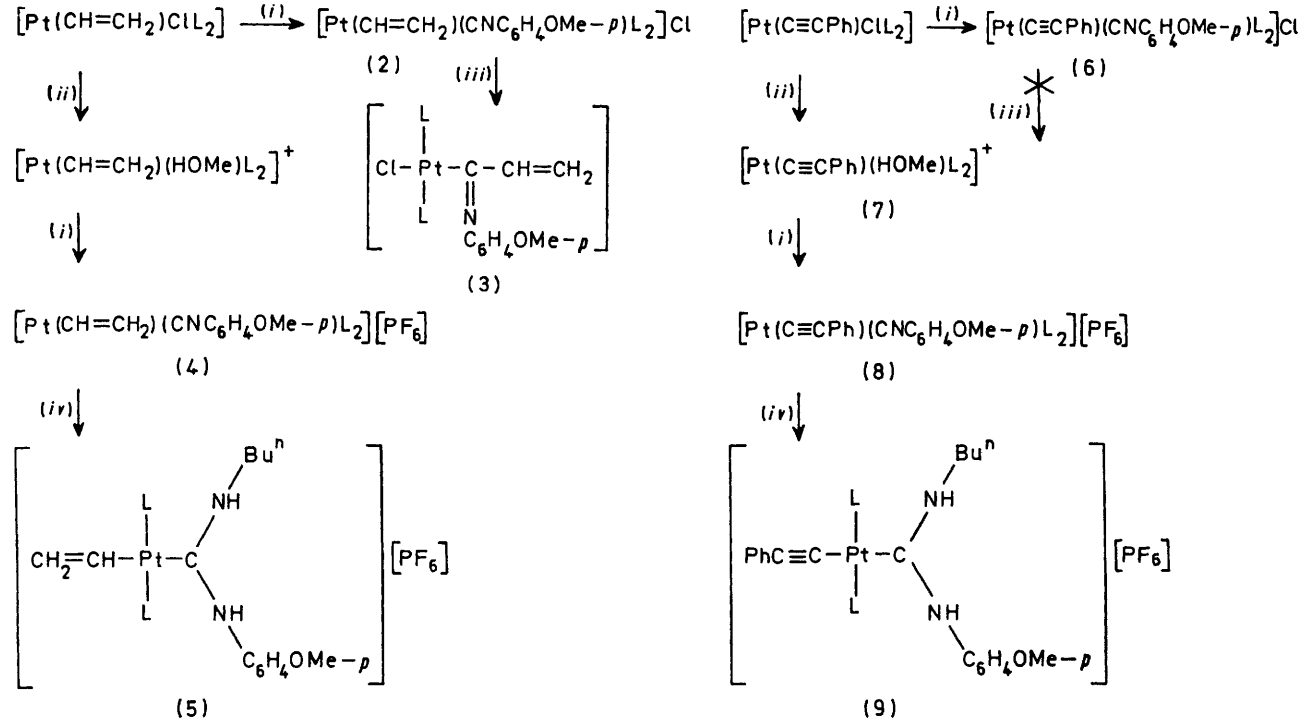
[a] Relative to $\mathrm{SiMe_4}$ in $\mathrm{CDCl_3}$

TABLE 3

Carbon-13 n.m.r. spectroscopic data for the new vinylplatinum complexes

Complex	Chemical shifts (δ/p.p.m.) [a]				Coupling constants (J/Hz) [b,c]			
	Cα	Cβ	C^1	C^2	Cα	Cβ	C^1 [c]	C^2 [c]
trans-$[\mathrm{Pt(CH{=}CH_2)Cl(PMe_2Ph)_2}]$	132	119.5	12.0 [d]		880 [b]	279 [b] 4.5 [c]	19.5 [e]	
trans-$[\mathrm{Pt(CH{=}CH_2)Cl(PEt_2Ph)_2}]$	131	118.7	14.2	7.7	870 [b]	216 [b] 4.0 [c]	17.5	11.5
trans-$[\mathrm{Pt(CH{=}CH_2)I(PEt_2Ph)_2}]$	138.5	118.4	17.2	8.3	872 [b] 10 [c]	*f*	18.3	7.3
$[\mathrm{Pt(CH{=}CH_2)Cl_3(PEt_2Ph)_2}]$	169	116.6	13.6	7.6	11 [c]	*f*	23.2	*f*
$[\mathrm{PtBr_3(CH{=}CH_2)(PEt_2Ph)_2}]$	*f*	119.4	14.7	8.3	*f*	*f*	*ca.* 16	*f*
$[\mathrm{PtMe(CH{=}CH_2)I_2(PEt_2Ph)_2}]$	172	116.0	16.4	9.2 8.5	*f*	*f*	*f*	*f*
trans-$[\mathrm{Pt(CH{=}CH_2)\{C(NHBu^n)NHC_6H_4OMe\text{-}}p\mathrm{\}(PEt_2Ph)_2][PF_6]}$ [g]	156	120.7	15.9	7.9	*f*	*f*	15.3	*f*

[a] Downfield from $\mathrm{SiMe_4}$ in $\mathrm{CDCl_3}$. C^1 and C^2 are the methylene and methyl carbons respectively of the phosphine ligand [b] To ^{195}Pt. [c] To ^{31}P. [d] For phosphine methyl group. [e] $^1J(^{31}\mathrm{P}{-}^{13}\mathrm{C})$ of phosphine methyl group. [f] Not detected, or obscured. [g] Chemical shift of carbene carbon, 202 p.p.m.



SCHEME 2 Isocyanide reactions (L = PEt_2Ph for vinyl, $PMePh_2$ for alkynyl). (*i*) *p*-$MeOC_6H_4NC$; (*ii*) Ag[PF_6], MeOH; (*iii*) C_6H_6, reflux; (*iv*) NBu^nH_2, reflux (50 min)

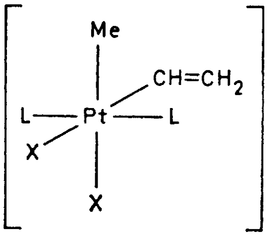
addition to the double bond. Addition of chlorine to platinum(IV) vinyl complexes containing the CCl=CHCl ligand has been reported to give substitution affording the corresponding $CCl=CCl_2$ complex, but the decomposition of [PtBr(CH=CHBr)$(PMe_2Ph)_2$] in chloroform during 30 min to give *cis*-[$PtBr_2(PMe_2Ph)_2$] has also been described.[7] The vinyl group in [$PtBr_3(CH=CH_2)$-$(PEt_2Ph)_2$] may therefore have been lost by a sequence of substitution–elimination reactions at the double bond. The addition of a methyl halide, MeX [equation (3)], using neat halide as solvent in each case showed the

$$MeX + trans\text{-}[PtX(CH=CH_2)(PEt_2Ph)_2] \longrightarrow [PtX_2Me(CH=CH_2)(PEt_2Ph)_2] \quad (3)$$

reactivity order I > Br > Cl. When X = I, the reaction was essentially complete after several weeks at room temperature; heating the reaction mixture gave mainly *trans*-[$PtI_2(PEt_2Ph)_2$]. When X = Br, *ca.* 60% addition had occurred after the same time interval, whereas when X = Cl no adduct was formed even after 8 weeks. {This difficulty has previously been noted for an alkyl analogue; thus, methyl chloride added to *cis*-[$PtMe_2(PMe_2Ph)_2$] but not to *trans*-[$PtMeCl(PMe_2Ph)_2$].[33]} The stereochemistry of the adducts was established to be (1) from n.m.r. data.

The σ-bonded platinum evidently does not activate the double bond with respect to addition by MeX or X_2. The platinum–vinyl bond was rapidly attacked by hydrogen chloride; 1 equivalent in diethyl ether cleaved the vinyl group from *trans*-[$Pt(CH=CH_2)Cl(PEt_2Ph)_2$] in a few minutes at room temperature, giving *trans*-[$PtCl_2(PEt_2Ph)_2$]. The resistance of this bond to HCl cleavage in partially chlorinated vinyl compounds has been shown to be considerably greater and is increased by progressive chlorination of the vinyl ligand.[7]

Insertion reactions of an aryl isocyanide, R'NC, were examined; it was considered likely that these would be thermodynamically favoured because of conjugation and cross-conjugation in the new ligand $CH_2=CH-C(=NR')$ so produced. The results are summarised in Scheme 2, which also shows comparative data on the alkynyl; spectroscopic data for some of the products are in Tables 1, 3, 4, and 5.



(1)

When *trans*-[$Pt(CH=CH_2)Cl(PEt_2Ph)_2$] was stirred with 1 equivalent of *p*-methoxyphenyl isocyanide there was no insertion, but starting material was not recovered and spectroscopic data (i.r., n.m.r.) on the yellow oil obtained were consistent with the formation of the ionic species (2). A new peak appeared at 2 180 cm^{-1} in the i.r. spectrum, compared with 2 124 cm^{-1} in the uncoordinated isocyanide, and no bands were observed in the

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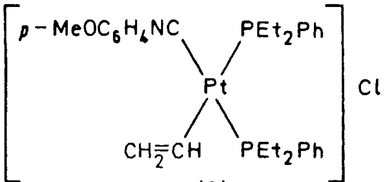
[33] J. D. Ruddick and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 2801.

Pt–Cl region (250—350 cm^{-1}). The n.m.r. spectrum of the oil was similar to that of (4), the cation isolated by initial treatment of the chlorovinyl complex with silver hexafluorophosphate and subsequent isocyanide treatment, as shown in Scheme 2. Insertion of the isocyanide occurred readily in refluxing benzene to give the imidoylplatinum(II) complex (3). The i.r. spectrum of (3) contained no band in the isocyanide region, but a new band appeared at 1 757 cm^{-1}, which is assigned to a coupled vibration of the unsaturated imidoyl group. This is rather higher than the value recently reported by Otsuka and Ataka.[34] These authors described the first series of isocyanide insertions into the platinum–alkenyl bond. The conjugated ligand may have a rather high *trans* influence, as ν(Pt–Cl) has been found in the unsaturated acyl complex *trans*-[Pt(COCH=CHPh)Cl(PPh$_3$)$_2$],[35] and it may be that conjugated systems of this type are often associated with high *trans* influence. It seems unlikely, however, that unsaturation at carbon atoms further removed from the metal would have more than a minor effect, in view of the small differences in *trans* influence associated with changes in the hybridisation of the ligating carbon atom. The ^{1}H n.m.r. spectrum of the imidoyl complex (3) showed marked changes in the vinyl-group resonances. The spectrum was no longer pseudo-first order, and there was no observable Pt–H coupling (Table 4).



(2)

TABLE 4

Proton n.m.r. data [a] for carbene and isocyanide derivatives of platinum

Complex	Vinyl protons	NH protons [b]	Methyl (phosphine) protons
[Pt(CH=CH$_2$)(CNC$_6$H$_4$OMe-*p*)(PEt$_2$Ph)$_2$][PF$_6$]	τ$_2$ 3.95, τ$_3$ 5.00 [*J*(H^{1}H^3) 18, *J*(H^{1}H^2) 12]		8.85 (a)
[Pt(CH=CH$_2$){C(NHBu^n)NHC$_6$H$_4$OMe-*p*}(PEt$_2$Ph)$_2$][PF$_6$]	τ$_2$ 3.88, τ$_3$ 4.94 [*J*(H^{1}H^2) 9]	1.02, 1.28, 1.58, 1.83	9.00 (q)
[Pt{C(CH=CH$_2$)=NC$_6$H$_4$OMe-*p*}Cl(PEt$_2$Ph)$_2$]	τ$_1$ 3.72, τ$_2$ 3.84, τ$_3$ 4.60 [*J*(H^{1}H^2) 9.5, *J*(H^{2}H^3) 2.0, *J*(H^{2}H^3) 16.0]		8.96 (q)
[Pt(C≡CPh)(CNC$_6$H$_4$OMe-*p*)(PMePh$_2$)$_2$][PF$_6$]			7.50 (tt)
[Pt(C≡CPh){C(NHBu^n)NHC$_6$H$_4$OMe-*p*}(PMePh$_2$)$_2$][PF$_6$]		1.36	8.70 (tt)

[a] τ Values; *J* values (in Hz) are given in square brackets. q = quintet; tt = triplet of triplets. Nomenclature for vinyl protons is as in Table 2. [b] Assigned by disappearance on D$_2$O addition.

TABLE 5

Phosphorus n.m.r. data (24.29 MHz) [a]

Complex	Chemical shift (δ/p.p.m.) [b]	|*J*(Pt–P)|/kHz
trans-[Pt(CH=CH$_2$)Cl(PMe$_2$Ph)$_2$]	+96.4	2.90
trans-[Pt(CH=CH$_2$)Cl(PEt$_2$Ph)$_2$]	+97.8	2.92
trans-[PtBr(CH=CH$_2$)(PEt$_2$Ph)$_2$]	+100.6	2.91
trans-[PtMe(CH=CH$_2$)I$_2$(PEt$_2$Ph)$_2$]	+97.9	2.54
trans-[PtBr$_3$(CH=CH$_2$)(PEt$_2$Ph)$_2$]	+121.6	1.64
trans-[Pt(CH=CH$_2$)Cl$_3$(PEt$_2$Ph)$_2$]	+122.2	1.65
[Pt(CH=CH$_2$){C(NHBu^n)NHC$_6$H$_4$OMe-*p*}(PEt$_2$Ph)$_2$][PF$_6$]	+107.0	1.901
cis-[Pt(CF=CF$_2$)(PPh$_3$)$_2$(SnMe$_3$)]	115.0	1.84

[a] Spectra were run as saturated CHCl$_3$ solutions. [b] Measured upfield from external P$_4$O$_6$.

Comparative Reactivity Data on Alkynylplatinum Complexes.—The alkynyl *trans*-[Pt(C≡CPh)Cl(PMePh$_2$)$_2$], prepared by SnMe$_3$Cl elimination outlined in equation (1a), did not undergo insertion of *p*-methoxyphenyl isocyanide even under prolonged heating under reflux (24 h), although the i.r. spectrum suggested that co-ordination of isocyanide to give (6) [ν(C=N) 2 185 cm^{-1}] had occurred. The lack of insertion is surprising and is probably not a consequence of the use of a less basic phosphine, as previous examples of insertions into platinum–alkyl bonds have involved the use of triphenylphosphine. Both alkynyl and alkenyl groups should facilitate isocyanide insertion if conjugation in the product is important, although evidence for conjugation involving C≡C and a double bond is not particularly powerful. However, Cl$^-$ abstraction from the alkynyl complex by Ag[PF$_6$] is observably slower than from the vinyl, so the failure to insert isocyanide may reflect a lack of lability of Cl$^-$ in the former complex rather than the difficulty of the insertion reaction, a relevant feature if the first step in the mechanism is loss of the halide ion. The reactions of cations of the type [PtRL$_2$(solvent)]$^+$ have been extensively explored by Chisholm and Clark,[36] chiefly for the case in which R = Me. Both the cations [Pt(CH=CH$_2$)(HOMe)(PEt$_2$Ph)$_2$]$^+$ and [Pt(C≡CPh)(HOMe)(PEt$_2$Ph)$_2$]$^+$ are readily generated (Scheme 2).

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[34] S. Otsuka and K. Ataka, *J.C.S. Dalton*, 1976, 327.

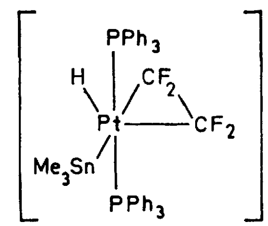
[35] S. P. Dent, C. Eaborn, A. Pidcock, and B. Ratcliff, *J. Organometallic Chem.*, 1972, **46**, C68.

[36] M. H. Chisholm and H. C. Clark, *Accounts Chem. Res.*, 1973, **6**, 202.

The addition of an equivalent quantity of *p*-methoxyphenyl isocyanide to either cation gave the crystalline complex (4) or (8) on removal of solvent. These were sufficiently stable to be recrystallised from methanol in the air without decomposition. They gave mass spectra (Table 1) in which the highest peak generally corresponded to the parent cation. Each cation reacted smoothly when heated under reflux with n-butylamine to give the cationic carbene complex (5) or (9). However, no reaction occurred, even under prolonged heating with *p*-anisidine, aniline, or cyclohexylamine, which, for the first two, is consistent with the failure to obtain methylcarbene complexes using aromatic amines in similar reactions.[37] Predominantly steric barriers to reaction are implied by the lack of reaction with cyclohexylamine. (*p*-Methoxyphenyl isocyanide has been reported to be the most sensitive of a series of aromatic isocyanides to nucleophilic attack, in a kinetic study.[38]) Each of the carbene complexes (5) or (9) formed gave peaks in the mass spectrometer corresponding to the parent cation; the vinyl carbene complex (5) gave low-field N–H resonances in the ^{1}H n.m.r. [assigned by ^{2}H exchange (Table 4)], and bands in the i.r. spectrum assigned to ν(N–H) at 3 440 and 3 550 cm^{-1}. The 2-phenylethynyl carbene complex (9) gave only a single N–H resonance, and ν(N–H) in the i.r. spectrum was at 3 328 and 3 340 cm^{-1}.

Fluorovinylplatinum Complexes.—In contrast to $SnMe_3(CH{=}CH_2)$, oxidative addition of the perfluorovinyl analogue to $[Pt(PPh_3)_3]$, $[Pt(PPh_3)_4]$, or $[Pt(CHPh{=}CHPh)(PPh_3)_2]$ took place during several hours at room temperature, giving *cis*-$[Pt(CF{=}CF_2)(PPh_3)_2(SnMe_3)]$ in good yield. This reaction is analogous to that already reported for $SnMe_3(C{\equiv}CPh)$.[1] The stereochemical assignment was deduced from ^{119}Sn n.m.r. measurements,[39] which gave $|^2J(^{119}Sn\text{–}H)|$ as 43.9 Hz and $\delta(^{119}Sn)$ as 0 ± 2 p.p.m. relative to $SnMe_4$. The ^{31}P n.m.r. spectrum showed the presence of two inequivalent P atoms, also consistent with a *cis* formulation (Table 5). The ^{19}F spectrum of this complex was not obtained due to low solubility, but ^{1}H n.m.r. showed a $SnMe_3$ resonance at τ 10.33 with $|^3J(^{195}Pt\text{–}^1H)|$ 9, $|^1J(^{195}Pt\text{–}^{119}Sn)|$ 44, and $|^1J(^{195}Pt\text{–}^{117}Sn)|$ 41 Hz. The more soluble PMe_2Ph analogue of this complex was obtained in modest yield from $[Pt(PMe_2Ph)_4]$;[40] it was well characterised (Table 1) and has *trans* stereochemistry as judged by the ^{1}H n.m.r. phosphine-methyl resonance patterns.[41]

Several experiments were carried out with *cis*-$[Pt(CF{=}CF_2)(PPh_3)_2(SnMe_3)]$. No reaction was observed between equimolar quantities of hydrogen chloride and the complex in benzene–diethyl ether, and starting material was recovered. By contrast a large excess of HCl immediately gave *cis*-$[PtCl_2(PPh_3)_2]$. Two equivalents of HCl gave a mixture of products, including probably $[PtClH(PPh_3)_2]$ [ν(Pt–H) 2 218 cm^{-1}], but no single product was isolated. Cleavage of $[Pt(C{\equiv}CPh)(PPh_3)_2(SnMe_3)]$ with HCl has been found to give chiefly $[PtClH(PPh_3)_2]$.[1] One equivalent of HF in benzene appeared not to react with the fluorovinyl complex at room temperature, and starting material was recovered. However, on heating the complex under reflux with two equivalents of HF in benzene an orange solution containing a trace amount of precipitate formed. The low affinity of Pt for F was expected to result in $SnMe_3F$ precipitation, but the precipitate gave an i.r. spectrum in which ν(Sn–F) was absent. The bulk of the product after recrystallisation gave C, H, and F analyses consistent with the stoicheiometry $[Pt(CF{=}CF_2)(HF)(PPh_3)_2(SnMe_3)]$ and the i.r. spectrum of the complex showed a peak at 2 045 cm^{-1} assigned to ν(Pt–H) and others assignable to ν(C=C). These data are consistent with structure (10). Attempted hydrogenolysis (80 atm, 80 °C) * of the fluorovinyl complex gave a product, containing a new band in the i.r. at 1 745 cm^{-1}, which was not separated from decomposition products and has not been identified.



(10)

Other Reactions of $SnMe_3(CF{=}CF_2)$.—Reaction of *trans*-$[PtClHL_2]$ ($L = PPh_3$ or PMe_2Ph) and an equivalent quantity of $SnMe_3(CF{=}CF_2)$ led to unidentified products for $L = PPh_3$, but to a small quantity of *trans*-$[Pt(CF{=}CF_2)Cl(PMe_2Ph)_2]$ when $L = PMe_2Ph$. This product must be formed by $SnMe_3H$ elimination from an intermediate addition complex [equation (4)]. The compound

$$SnMe_3(CF{=}CF_2) + trans\text{-}[PtClH(PMe_2Ph)_2] \longrightarrow [Pt(CF{=}CF_2)ClH(PMe_2Ph)_2(SnMe_3)] \longrightarrow [Pt(CF{=}CF_2)Cl(PMe_2Ph)_2] + SnMe_3H \quad (4)$$

$SnMe_3(CF{=}CF_2)$ did not react either with $[RhCl(PPh_3)_3]$ or *trans*-$[Ir(CO)Cl(PPh_3)_2]$ on prolonged heating under reflux, and hence shows the higher reactivity of $SnMe_3(C{\equiv}CPh)$.[1] This is also shown by the greater rate of metathetical reaction of the latter with dichloroplatinum(II) complexes (Table 1). The low reactivity of $SnMe_3(CH{=}CH_2)$ is thus shown by (*a*) its failure to add to platinum(0) species, (*b*) the formation of only monovinyls in platinum(II) metatheses, and (*c*) the failure of $SnMe_3(CH{=}CH_2)$ to add to $[RhCl(PPh_3)_3]$ or *trans*-$[Ir(CO)Cl(PPh_3)_2]$. Thus, in both oxidative addition and metatheses the reactivity order of $SnMe_3R$ is $R = C{\equiv}CPh > CF{=}CF_2 > CH{=}CH_2$. Each reaction, whatever the detailed mechanism, presumably requires rate-controlling fission of the Sn–C bond and the ability of the

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* Throughout this paper: 1 atm = 101 325 Pa.

[37] H. C. Clark and L. E. Manzer, *Inorg. Chem.*, 1972, **11**, 503.

[38] B. Crociani, T. Boschi, M. Nicolini, and U. Belluco, *Inorg. Chem.*, 1972, **11**, 1292.

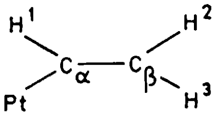
[39] D. H. Harris, M. F. Lappert, J. S. Poland, and W. McFarlane, *J.C.S. Dalton*, 1975, 311.

[40] H. C. Clark and K. Itoh, *Inorg. Chem.*, 1971, **10**, 1707.

[41] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1407.

ligand to co-ordinate to the transition metal in an intermediate or transition state *via* π interactions [*cf.* the unreactivity of $SnMe_3(CH_2SiMe_3)$]. The reactivity order is also the same as the observable stability of the series of compounds to air and moisture.[42]

Spectra of New Vinylplatinum Complexes.—N.m.r. data are presented in Tables 2—5, using the nomenclature below for the vinyl group. I.r. and mass spectral data are included in Table 1.



^1H *N.m.r. spectra.* Apparent first-order spectra were obtained for the vinyl protons for all the complexes containing the vinyl group directly bonded to platinum. They have been assigned following the order of chemical shifts determined for *trans*-$[PtBr(CH=CH_2)(PPh_3)_2]$,[8] and the values for the new complexes are reported in Tables 2 and 4. This assignment results in all cases in apparent coupling constants with the relative order of magnitude $|J_{trans}| > |J_{cis}| > |J_{gem}|$. The observed chemical shift values correlate well with the expected electron density on the metal, particularly for τ_2 (the proton *trans* to platinum). Thus we found shifts at highest fields for the platinum(IV) complexes. Within this group the trihalogeno(vinyl) complexes had higher chemical shifts for τ_1 and τ_2 than the dihalogenomethyl-(vinyl) complexes, perhaps related to greater electron withdrawal from platinum by three halogen atoms.

Changes in the platinum oxidation state did not affect all the couplings equally. Thus, $|^3J(H-H)_{trans}|$, $|^3J(H-H)_{cis}|$, and $|^2J(H-H)_{gem}|$ were little affected by changing oxidation state, and are similar in magnitude to those previously observed for *trans*-$[PtBr(CH=CH_2)(PPh_3)_2]$.[8] However, the $^{195}Pt-^1H$ couplings $J(Pt-H^2)$ and $J(Pt-H^3)$ (that is, the couplings through the vinyl double bond) were almost halved in $[PtX_3(CH=CH_2)(PEt_2Ph)_2]$ compared with the corresponding platinum(II) complex *trans*-$[PtX(CH=CH_2)(PEt_2Ph)_2]$, although the decrease was again less marked in $[PtX_3(CH=CH_2)(PEt_2Ph)_2]$. The magnitude of proton–metal coupling constants in a series of main-group vinyl complexes has been correlated with the electronegativity of the central metal atom,[43] lower values being associated with strong electron withdrawal by the metal. The changes we observe are in the same direction, and parallel the decrease in ν(C=C) observed on increasing oxidation state (Table 1). This parameter is, however, a less sensitive indicator of changes in electron availability.

^{13}C *N.m.r.* Data for several of the new complexes are presented in Table 4, and include vinyl complexes in which there are changes in *trans* ligand, oxidation state, and charge. Carbon-13 data on (chlorovinyl)-platinum complexes have previously been published[7] without discussion of the assignment, and are a valuable comparison with our own data. Assignment of the vinyl-carbon resonances was complicated by the appearance of the aromatic carbons of the phosphine in the same region of the spectrum, but both were identified by the appearance of ^{195}Pt satellites with coupling constants in the expected ranges.[7] For the α-carbon $|^1J(Pt-C)|$ was in the range 870—880 Hz in three neutral platinum(II) vinyl complexes, a value intermediate between that for *trans*-$[Pt(AsMe_3)_2PhCl]$ (858 Hz)[44] and for *trans*-$[Pt(CH=CHCl)Cl(PMePh_2)_2]$ (900 Hz).[7] The chemical shift of C_α in all three complexes is then in the 131—138.5 p.p.m. region (with reference to $SiMe_4$) and in the same region as the phenyl carbons of the phosphine. For the β-carbon of the vinyl group more assignments can be made, as this resonance was in all cases at a higher field than the phenyl-carbon resonance, in the range 116—121 p.p.m., and in two cases the coupling to Pt was clearly observed, *ca.* 270 Hz. The central resonance of the triplet was itself a triplet, and is unambiguously assigned to coupling with the phosphorus atoms by its collapse to a singlet in the ^{31}P-decoupled spectrum. As expected, this is a small coupling, 4 Hz. In spectra for which Pt satellites were not visible, the resonance due to C_β was always within the above range, making it relatively insensitive to variations in electron density at Pt.

In the spectrum of $[Pt(CH=CH_2)Cl_3(PEt_2Ph)_2]$, a new peak was observed at 169 p.p.m., as a 1 : 2 : 1 triplet. This signal is presumably due to the α-carbon of the vinyl group, which as expected for a platinum(IV) complex is downfield with respect to the related platinum(II) species. There was no corresponding change in the β-carbon shift. The appearance of the α-carbon resonance as a triplet may be assigned to *cis*-phosphorus coupling, with $|^2J(C-P)|$ *ca.* 11 Hz. The assignments of C_α in the final two complexes of Table 4 must remain tentative because of the lack of coupling-constant data. The spectra were insufficiently resolved for these to be observed.

^{31}P *N.m.r.* Chemical-shift and coupling-constant data for a series of complexes are presented in Table 5. The coupling constants for the platinum(II) complexes are all in the range expected for *trans*-phosphorus ligands.[45]

EXPERIMENTAL

General Procedures.—Solvents were dried over and distilled from potassium–benzophenone or P_4O_{10} as appropriate, and were rigorously degassed *in vacuo* before use. All the reactions were performed in an atmosphere of dry oxygen-free nitrogen. Melting points were determined using a Kofler hot-stage apparatus and are uncorrected. Analyses were by Mrs. A. G. Olney of this department and by Alfred Bernhardt, Mülheim, West Germany. Infrared spectra

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[42] D. E. Palmer and C. J. Cardin, unpublished work.

[43] H. D. Visser and J. P. Oliver, *J. Organometallic Chem.*, 1972, **40**, 7.

[44] H. C. Clark and J. E. H. Ward, *J. Amer. Chem. Soc.*, 1974, **96**, 1741.

[45] J. F. Nixon and A. Pidcock, *Ann. Rep. N.M.R. Spectroscopy*, 1969, **2**, 345.

were recorded on a Perkin-Elmer 457, ^{1}H n.m.r. spectra were recorded on Varian T60, A60, or HA100, ^{31}P spectra on a Perkin-Elmer R10, and ^{13}C spectra on a Bruker HFX13 and a Jeol FT machine. Mass spectra were obtained on an A.E.I. MS9 instrument.

Starting Materials.—Published procedures were used for the preparation of *cis*-$[PtCl_2L_2]$ (L = PPh_3, $PMePh_2$, PMe_2Ph, PEt_2Ph, or PEt_3),[46] $[Pt(PPh_3)_4]$,[47] $[Pt(PPh_3)_3]$,[48] $[Pt(PhCH{=}CHPh)(PPh_3)_2]$,[48] $[Pt(PMe_2Ph)_4]$,[40] $[PtClH(PPh_3)_2]$,[49] and $[PtClH(PMe_2Ph)_2]$.[49] Gifts of trifluorovinyl bromide from Dr. M. Green (Bristol), $[RhCl(PPh_3)_3]$ and $[Ir(CO)Cl(PPh_3)_2]$ from Dr. B. ¸etinkaya, and $SnMe_3(C{\equiv}CPh)$ from Dr. D. E. Jessup are gratefully acknowledged. The compounds $SnMe_3(CH{=}CH_2)$,[50] $Sn(CH{=}CH_2)_4$,[50,51] and *p*-$MeOC_6H_4NC$ [52,53] were prepared by literature methods, whereas $SnMe_3(CF{=}CF_2)$ was prepared by a modified version of the literature method.[54,55]

The Preparation of Vinyl-, Fluorovinyl-, and Alkynyl-compounds.—*(A) By halogen replacement.* *(i)* trans-*Bis(dimethylphenylphosphine)halogeno(vinyl)platinum*(II). (*a*) Magnesium turnings (0.24 g, 0.1 mol) were covered with thf (25 cm^3) and activated with ethylene dibromide (a few drops). Vinyl bromide (70 cm^3, 0.11 mol) in thf (7 cm^3) was added over 20 min at 40—50 °C to give a brown solution of vinylmagnesium bromide. *cis*-Dichlorobis(dimethylphenylphosphine)platinum(II) (4.2 g, 0.077 mol) was added as a fine suspension in thf (100 cm^3) and dissolved instantaneously giving a yellow solution. The solution was stirred for 3 h, then hydrolysed with saturated aqueous ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted several times with diethyl ether. The combined inorganic fractions were dried by extraction with saturated brine, and then evaporated to dryness, giving a yellow solid. Chromatography on Florisil in chloroform gave a yellow solid (0.34 g) which was recrystallised from ethanol to give trans-*bromobis(dimethylphenylphosphine)vinylplatinum*(II) as long white needles. Elution of the column with acetone–chloroform (1 : 1) gave a second fraction (2.20 g, 45%), recrystallised from ethanol as yellow needles, which was identified by m.p. and analytical data as dibromobis(dimethylphenylphosphine)platinum(II) (Found: C, 31.2; H, 3.85. Calc. for $C_{16}H_{22}Br_2P_2Pt$: C, 30.5; H, 3.55%), m.p. 192 °C (lit.,[41] 201—204 °C). An i.r. band at 2 160 cm^{-1} for the crude product suggested that one of the hydrido-complexes $[PtXH(PMe_2Ph)_2]$ (X = Cl or Br) was also present, although neither was isolated as a separate fraction from chromatography.

(*b*) Phenyl-lithium (65 mmol, 35 cm^3 of a 1.88 mol dm^{-3} solution) was treated with tetravinyltin (2.3 g, 16 mmol) and, after stirring for 2 h, the very insoluble tetraphenyltin was filtered off.[55] The solution of vinyl-lithium was added to suspended *cis*-$[PtCl_2(PMe_2Ph)_2]$ (1.47 g, 2.2 mmol) in thf (30 cm^3) and the resulting orange solution was stirred for 3 h. Hydrolysis with saturated $[NH_4]Cl$ gave an orange organic layer which was separated, combined with ether washings of the aqueous layer, dried by extraction with saturated brine, and evaporated to dryness. The resulting brown oil was stirred with hexane and gave a small amount of buff powder with much brown oily substance. The i.r. spectrum of the buff powder suggested the formation of some vinylic product, but none could be isolated.

(*c*) Dibromobis(dimethylphenylphosphine)platinum(II) was covered with benzene (50 cm^3) and tetravinyltin (0.33 cm^3, 1.72 mmol) was added. The solution was warmed at 40 °C for 0.5 h to give an orange solution, and, after cooling, evaporation of solvent *in vacuo* gave a brown solid. Extraction with hexane left an orange-brown residue which was shown by i.r. and n.m.r. to contain vinylic products. Attempted recrystallisation from ethanol gave a brown oil and a yellow solution, and concentration of the solution gave a few colourless needles contaminated with large quantities of intractable brown material. The needles were characterised as trans-*bromobis(dimethylphenylphosphine)vinylplatinum*(II) (Found: C, 36.2; H, 4.45%), m.p. 112 °C.

(*d*) A suspension of *cis*-$[PtCl_2(PMe_2Ph)_2]$ (3.4 g, 6.27 mmol) was heated in refluxing thf (60 cm^3) with trimethyl(vinyl)tin (2.7 cm^3, 14.2 mmol) for 7 h, when the yellow solution began to darken. After cooling, the solution was evaporated to small volume and precipitated starting material was filtered off. Evaporation of the filtrate gave a sticky yellow solid which was washed with hexane and recrystallised from ethanol, giving colourless needles of trans-*chlorobis(dimethylphenylphosphine)vinylplatinum*(II) (1.08 g). A later experiment using xylene–chloroform (2 : 1) as solvent gave 35% conversion into product after heating under reflux for 12 h, but did not show the darkening in colour observed when thf was used as solvent.

(*ii*) trans-*Chlorobis(diethylphenylphosphine)vinylplatinum*(II). *cis*-Dichlorobis(diethylphenylphosphine)platinum(II) (2.9 g, 4.85 mmol) was heated in refluxing thf (100 cm^3) with trimethyl(vinyl)tin (1.8 g, 9.42 mmol) for 72 h. After 48 h all the starting halide had dissolved giving a clear yellow solution which did not darken. Volatiles were removed *in vacuo* and the product was washed twice with hexane to remove trimethyltin chloride. The remaining crude solid (2.81 g) was recrystallised from acetone (30 cm^3). Starting material (0.57 g) was deposited at room temperature, and on cooling the filtrate to -20 °C colourless prisms of *trans*-chlorobis(diethylphenylphosphine)vinylplatinum(II) (1.4 g, 50%), m.p. 108 °C, were deposited. From some preparations, a small proportion of *trans*-$[PtCl_2(PEt_2Ph)_2]$ was also isolated.

(*iii*) trans-*Chlorobis(diethylphenylphosphine)(trifluorovinyl)platinum*(II). *cis*-Dichlorobis(diethylphenylphosphine)platinum(II) (0.388 g, 0.65 mmol) was heated in refluxing thf (25 cm^3) with trimethyl(trifluorovinyl)tin (0.159 g, 0.65 mmol) for 18 h. The resulting solution was cooled to -15 °C, and a few colourless needles were deposited. These were filtered off and identified by their m.p. (195 °C) as the starting complex. The filtrate was evaporated to give a yellow oily solid, which was washed twice with pentane (20 cm^3) to remove $SnMe_3Cl$. The residue, after drying, was recrystallised from methanol (10 cm^3) to give white needles of trans-*chlorobis(diethylphenylphosphine)(trifluorovinyl)platinum*(II) (0.307 g).

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(*iv*) trans-*Bis*(*diethylphenylphosphine*)*bis*(*trifluorovinyl*)-*platinum*(II). *cis*-Dichlorobis(diethylphenylphosphine)-platinum(II) (0.39 g, 0.65 mmol) was heated in refluxing thf (25 cm^3) with trimethyl(trifluorovinyl)tin (0.32 g, 1.8 mmol) for 18 h. The solution was cooled to −15 °C depositing only a trace amount of white solid, which was filtered off. The solution was evaporated and the remaining yellow oil was washed with two portions of cold pentane (10 cm^3), when it solidified to a pale yellow solid. Recrystallisation by evaporation of an acetone solution (5 cm^3) gave small colourless prisms of *bis*(*diethylphenylphosphine*)*bis*(*trifluorovinyl*)*platinum*(II) (0.30 g).

(*v*) trans-*Chlorobis*(*diethylphenylphosphine*)(*phenylethynyl*)-*platinum*(II). *cis*-Dichlorobis(diethylphenylphosphine)-platinum(II) (0.35 g, 0.58 mmol) was heated in refluxing thf (15 cm^3) with trimethyl(phenylethynyl)tin (0.15 g, 0.57 mmol) for 24 h to give a clear yellow solution. Volatiles were removed *in vacuo* leaving a buff oily solid. This was briefly heated in refluxing hexane (50 cm^3), leaving a trace amount of white solid, assumed to be the starting platinum complex. From the hexane filtrate large needles of trans-*chlorobis*(*diethylphenylphosphine*)(*phenylethynyl*)*platinum*(II) (0.37 g) were deposited. Recrystallisation from acetone gave the product as small colourless prisms suitable for crystallographic work.

(*vi*) trans-*Chlorobis*(*methyldiphenylphosphine*)(*phenylethynyl*)*platinum*(II). A suspension of *cis*-dichlorobis(methyldiphenylphosphine)platinum(II) (1.41 g, 0.211 mmol) was heated under reflux in thf (30 cm^3) with trimethyl(phenylethynyl)tin (0.6 g, 0.22 mol). After 1 h, all suspended solid had dissolved, the solution was cooled and volatiles removed *in vacuo*. The buff oily residue was treated with diethyl ether (30 cm^3) and gave a buff powder (1.2 g). Recrystallisation from acetone gave trans-*chlorobis*(*methyldiphenylphosphine*)(*phenylethynyl*)*platinum*(II) (0.46 g), as small colourless prisms.

(*vii*) trans-*Chlorobis*(*methyldiphenylphosphine*)*vinylplatinum*(II). A suspension of *cis*-$[PtCl_2(PMePh_2)_2]$ (2.7 g, 0.40 mmol) was heated under reflux in thf (60 cm^3) with trimethyl(vinyl)tin (1.0 g, 0.53 mmol) for 20 h giving a clear brown solution. Volatiles were removed *in vacuo* and the resulting solid, after washing with hexane (30 cm^3), was recrystallised twice from ethanol–acetone giving a mixture of large colourless plates and small yellow needles. The crystals were separated by hand and the plates characterised as trans-*chlorobis*(*methyldiphenylphosphine*)*vinylplatinum*(II) (0.06 g). The needles were identified as *cis*-$[PtCl_2(PMePh_2)_2]$ m.p. 259—261 °C [lit.,[56] 253—268 °C (decomp.)].

(*viii*) *Attempted preparation of* trans-*chlorobis*(*triethylphosphine*)*vinylplatinum*(II). *cis*-Dichlorobis(triethylphosphine)-platinum(II) (0.6 g, 1.07 mmol) was dissolved in warm thf (25 cm^3) and heated under reflux with trimethyl(vinyl)tin (1.0 cm^3, 5.23 mmol) for 4 h, giving a brown solution. Volatiles were removed *in vacuo* giving a brown oil. Addition of hexane (30 cm^3) gave a buff solid and yellow solution. The buff solid was recrystallised from ethanol and characterised as *cis*-$[PtCl_2(PEt_3)_2]$, m.p. 190 °C (lit.,[45] 191—192 °C) (Found: C, 29.0; H, 5.90. Calc. for $C_{12}H_{30}Cl_2P_2Pt$: C, 28.7; H, 6.00%). The hexane-soluble fraction was evaporated to dryness and recrystallised from acetone to give yellow needles of *trans*-$[PtCl_2(PEt_3)_2]$ (Found: C, 29.5; H, 6.30%), m.p. 138 °C (lit.,[45] 142 °C). An i.r. spectrum of the crude hexane-soluble fraction showed the presence of a vinyl-containing complex.

(*ix*) *Other attempted metatheses*. Using the procedure described above, no reaction was found to take place between trimethyl(vinyl)tin and *cis*-dichlorobis(triphenylarsine)-platinum(II) or *cis*-$[PtCl_2(PMe_2Ph)_2]$ on heating under reflux in thf or dimethylformamide (dmf). Neither stilbene-bis(triphenylphosphine)platinum(0) nor tris(triphenylphosphine)platinum(0) reacted with trimethyl(vinyl)tin under a variety of reaction conditions. *cis*-Dichlorobis(dimethylphenylphosphine)platinum(II) (1.0 g, 1.8 mmol) in thf (30 cm^3) was heated under reflux with trimethyl(trimethylsilylmethyl)tin (1.5 cm^3, 6 mmol) for 48 h. Volatiles were removed; the remaining solid was the platinum starting material (analysis and i.r.). Even under prolonged heating under reflux in benzene, no reaction was observed between trimethyl(trifluorovinyl)tin and chlorotris(triphenylphosphine)rhodium(I) or *trans*-carbonylchlorobis(triphenylphosphine)iridium(I).

(*x*) *Reaction of* trans-*chlorohydridoplatinum*(II) *complexes with trimethyl*(*trifluorovinyl*)*tin*. *trans*-Chlorohydridobis-(triphenylphosphine)platinum(II) (0.718 g, 0.95 mmol) was heated under reflux in benzene (30 cm^3) with trimethyl-(trifluorovinyl)tin (0.5 g, 2.04 mmol) for 90 min. The colour of the orange solution gradually deepened. Volatiles were removed *in vacuo*, and the remaining orange oily solid was washed with hexane (25 cm^3) to give a buff solid. Recrystallisation from acetone gave unidentified products. *trans*-Chlorobis(dimethylphenylphosphine)hydridoplatinum-(II) (0.4 g, 0.7 mmol) was heated under reflux in benzene with trimethyl(trifluorovinyl)tin (0.5 cm^3, 2 mmol) for 1 h, and stirred at room temperature overnight. Removal of volatiles and recrystallisation from acetone gave pale yellow plates of trans-*chlorobis*(*dimethylphenylphosphine*)(*trifluorovinyl*)*platinum*(II) (Found: C, 36.2; H, 4.25. $C_{18}H_{22}ClF_3P_2Pt$ requires C, 36.5; H, 4.4%), m.p. 155—158 °C.

(*B*) *By oxidative addition*. (*i*) cis-(*Trifluorovinyl*)(*trimethylstannio*)*bis*(*triphenylphosphine*)*platinum*(II). (*a*) Tris-(triphenylphosphine)platinum(0) (3.3 g, 3.36 mmol) was dissolved in benzene (40 cm^3), giving an orange solution, and trimethyl(trifluorovinyl)tin (0.8 g, 3.26 mmol) was added. After stirring for 15 h at room temperature the colour of the solution had lightened to yellow. Volatiles were removed, and the remaining yellow solid (2.8 g) was washed with diethyl ether (2 × 25 cm^3 portions) and recrystallised from benzene, giving small colourless prisms of cis-(*trifluorovinyl*)-(*trimethylstannio*)*bis*(*triphenylphosphine*)*platinum*(II) (Found: C, 51.4; H, 4.10. $C_{41}H_{39}F_3P_2PtSn$ requires C, 51.1; H, 4.10%) (2.4 g, 75%), m.p. 171—174 °C (decomp.).

(*b*) Stilbenebis(triphenylphosphine)platinum(0) (1.32 g, 0.36 mmol) was dissolved in benzene (25 cm^3) giving an orange solution. Trimethyl(trifluorovinyl)tin (0.1 g, 0.41 mmol) was added and the colour of the solution became pale yellow. After stirring for 1 h, the solution was concentrated *in vacuo* to 5 cm^3, and addition of hexane (40 cm^3) precipitated the product as a pale yellow powder (0.35 g). It was washed with hexane, dried, and recrystallised from ethanol–benzene to give small colourless prisms of cis-(*trifluorovinyl*)(*trimethylstannio*)*bis*(*triphenylphosphine*)*platinum*(II) (0.26 g).

(*ii*) *Bis*(*dimethylphenylphosphine*)(*trifluorovinyl*)(*trimethylstannio*)*platinum*(II). A crude sample of tetrakis(dimethylphenylphosphine)platinum(II) [39] (from 2.8 of $K_2[PtCl_4]$) was dissolved in benzene (30 cm^3) and trimethyl(trifluorovinyl)-tin (0.5 g, 2.1 mmol) was added. The brown solution was

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[56] D. Seyferth and M. A. Weiner, *J. Amer. Chem. Soc.*, **1961**, **83**, 3583.

stirred at room temperature for 15 h without colour change, but darkened on gentle warming. A small amount of platinum metal was filtered off, and volatiles were removed giving a brown oil. Stirring with hexane (30 cm^3) failed to yield any solid. The oil was chromatographed in benzene on a Florisil column (100—200 mesh), eluting with benzene, benzene–chloroform (1 : 1), chloroform, and finally acetone. The first two fractions, eluted with benzene, gave colourless oils on evaporation. These solidified on washing with hexane and both appeared (from i.r. spectra) to be the desired product. They were combined and, after several recrystallisations from methanol, white needles of cis-*bis(dimethylphenylphosphine)(trifluorovinyl)(trimethylstannio)-platinum*(II) (0.085 g) were obtained.

Reactions of Vinyl and Related Derivatives of Platinum(II).—(*a*) *Metatheses. trans*-Chlorobis(diethylphenylphosphine)vinylplatinum(II) (0.5 g) was stirred in acetone (10 cm^3) with lithium bromide (1 g) for 15 h. Solvent was removed and the residue was washed with water leaving a white powder (0.5 g). Recrystallisation from acetone gave colourless prisms of trans-*bromobis(diethylphenylphosphine)vinylplatinum*(II). *trans*-Chlorobis(diethylphenylphosphine)vinylplatinum(II) (0.4 g) was dissolved in acetone (8 cm^3) and sodium iodide (1 g) was added. After stirring for 15 h, evaporation of solvent *in vacuo* left a yellow solid, which was thoroughly washed with water and dried (0.4 g). Recrystallisation from acetone gave pale yellow prisms of *trans*-bis(diethylphenylphosphine)iodo(vinyl)platinum(II).

(*b*) *Halogen addition. trans*-Chlorobis(diethylphenylphosphine)vinylplatinum(II) (0.204 g, 0.339 mmol) was treated with a benzene solution of chlorine (28 cm^3, 0.013 mol dm^{-3}). After stirring the yellow solution for 30 min, volatiles were removed *in vacuo*, leaving a yellow residue (0.220 g). Recrystallisation from acetone gave large yellow needles of *trichlorobis(diethylphenylphosphine)vinylplatinum*(IV).

trans-Bromobis(diethylphenylphosphine)vinylplatinum(II) (0.30 g, 0.473 mmol) was dissolved in benzene (5 cm^3) and treated with a benzene solution of bromine (7.25 cm^3, 0.065 mol dm^{-3}). After stirring the orange solution for 20 min, volatiles were removed *in vacuo* to give a deep yellow solid (0.32 g). Recrystallisation from acetone gave fine dark yellow needles of *tribromobis(diethylphenylphosphine)vinylplatinum*(IV). Similarly, *dibromochlorobis(diethylphenylphosphine)vinylplatinum*(IV) (8%), m.p. 170 °C, was obtained from [Pt(CH=CH$_2$)Cl(PEt$_2$Ph)$_2$].

trans-Bis(diethylphenylphosphine)iodo(vinyl)platinum(II) (0.21 g, 0.31 mmol) was treated with iodine (0.08 g, 0.31 mmol) in benzene (20 cm^3) to give a dark red solution. After stirring for 3 h, volatiles were removed *in vacuo* to give a brown solid (0.26 g). Recrystallisation from ethanol gave a mixture of dark red needles (m.p. 120 °C) and yellow prisms (m.p. 138 °C). It was suspected that the former were the desired product, but in an attempt to purify them by further recrystallisation nearly all the crystals obtained were the yellow prismatic species. These were shown to be *trans*-[PtI$_2$(PEt$_2$Ph)$_2$] by n.m.r. and analysis (lit.,[46] m.p. 137—138 °C).

(*c*) *Methyl halide addition. trans*-Chlorobis(dimethylphenylphosphine)vinylplatinum(II) (0.10 g, 0.19 mmol) was dissolved in methyl iodide (5 cm^3) and the solution was set aside for 4 weeks in the dark at room temperature. Unchanged halide was removed *in vacuo*, leaving a yellow residue. Recrystallisation from methanol gave yellow plates of *chlorobis(dimethylphenylphosphine)iodo(methyl)-vinylplatinum*(IV) (0.06 g). Similarly from *trans*-[PtBr(CH=CH$_2$)(PMe$_2$Ph)$_2$] (0.17 g, 0.294 mmol), yellow prisms of *bromobis(dimethylphenylphosphine)iodo(methyl)vinylplatinum*(IV) (0.12 g) were obtained.

trans-Bromobis(diethylphenylphosphine)vinylplatinum(II) (0.2 g, 0.32 mmol) was introduced into a large thick-walled ampoule and methyl bromide (2 cm^3) was condensed in on the vacuum line. The ampoule was sealed and allowed to stand in the dark for 6 weeks. Volatiles were removed *in vacuo*, and the residue (0.23 g) was recrystallised from acetone to give colourless prisms of *dibromobis(diethylphenylphosphine)methyl(vinyl)platinum*(IV) (0.09 g). Evaporation of the filtrate gave pale yellow prisms of *trans*-[PtBr(CH=CH$_2$)(PEt$_2$Ph)$_2$] (Found: C, 41.4; H, 5.35. C$_{22}$H$_{33}$BrP$_2$Pt requires C, 41.6; H, 5.25%), m.p. 140.5 °C.

trans-Bis(diethylphenylphosphine)iodo(vinyl)platinum(II) (0.19 g, 0.28 mmol) was dissolved in methyl iodide (5 cm^3) and the solution was put aside for 4 weeks in the dark. Volatiles were removed *in vacuo* and the yellow oily residue was washed with hexane to give a yellow powder (0.195 g, 0.24 mmol). Recrystallisation from chloroform–methanol gave thin colourless prisms of *bis(diethylphenylphosphine)-di-iodo(methyl)vinylplatinum*(IV) (0.12 g). Evaporation of the filtrate gave a small quantity of yellow prisms of trans-*bis(diethylphenylphosphine)iodo(vinyl)platinum*(II) (Found: C, 38.3; H, 5.10. C$_{22}$H$_{33}$IP$_2$Pt requires C, 38.7; H, 4.90%), m.p. 99 °C.

trans-Chlorobis(diethylphenylphosphine)vinylplatinum(II) (0.4 g) was introduced into a Carius tube and methyl chloride (2 cm^3) was condensed in under vacuum. The sealed tube was set aside for 7 weeks in the dark. Removal of volatiles and recrystallisation from acetone gave colourless prisms (0.33 g) of trans-*chlorobis(diethylphenylphosphine)vinylplatinum*(II) (Found: C, 44.6; H, 5.90. C$_{22}$H$_{33}$ClP$_2$Pt requires C, 44.8; H, 5.65%), m.p. 107—108 °C.

(*d*) *Insertion reactions. trans*-Chlorobis(diethylphenylphosphine)vinylplatinum(II) (0.250 g, 0.424 mmol) was heated under reflux in benzene (30 cm^3) with *p*-methoxyphenyl isocyanide (0.060 g, 0.45 mmol) for 1 h, giving a yellow solution. Removal of volatiles gave an orange oily solid, which was washed with hexane (10 cm^3) giving a powder. Extraction with diethyl ether (20 cm^3) gave a yellow solution and a small amount of insoluble residue. The ether solution was evaporated to dryness and the yellow powder (0.210 g) was recrystallised from benzene–diethyl ether to give canary-yellow needles of trans-[N-p-*methoxyphenylacrylimidoyl)*]*chlorobis(diethylphenylphosphine)platinum*(II). *trans*-Chlorobis(dimethylphenylphospine)vinylplatinum(II) (0.105 g, 0.178 mmol) was dissolved in benzene (25 cm^3) and a slow stream of carbon monoxide gas was passed through the solution for 16 h. Removal of volatiles gave a white solid characterised by m.p. and analysis as the starting complex. *trans*-Chlorobis(diethylphenylphosphine)vinylplatinum(II) (0.200 g, 0.339 mmol) was dissolved in benzene (12 cm^3) and dimethyl acetylenedicarboxylate (5 cm^3) was added. The solution was set aside for 5 d, then concentrated *in vacuo*. Addition of diethyl ether (10 cm^3) precipitated a buff solid which was dried, reprecipitated, and identified as an oligomer of the organic reagent (0.27 g) (Found: C, 49.3; H, 3.85. Calc. for C$_6$H$_4$O$_4$: C, 50.7; H, 4.25%), m.p. 94 °C.

trans-Chlorobis(methyldiphenylphosphine)phenylethynylplatinum(II) (0.09 g, 0.13 mmol) was heated under reflux in benzene (50 cm^3) for 24 h with *p*-methoxyphenyl isocyanide (0.015 g, 0.13 mmol). Removal of volatiles *in* *vacuo* gave a yellow solid containing (i.r.) co-ordinated isocyanide, but no insertion product.

(*e*) *Attempted reduction.* *trans*-Chlorobis(diethylphenylphosphine)vinylplatinum(II) (0.27 g, 0.475 mmol) was dissolved in benzene (30 cm^3) and refluxed with triethylsilane (1 cm^3) for 3 h, giving a pale yellow solution. Removal of volatiles left a pale yellow oily solid, which yielded the white platinum(II) starting material (m.p., analysis) (0.25 g) after stirring with hexane (20 cm^3) for 4 h.

(*f*) *Reactions of cationic complexes formed by chloride abstraction.* *trans*-Chlorobis(diethylphenylphosphine)vinylplatinum(II) (0.384 g, 0.652 mmol) was dissolved in methanol (10 cm^3) and silver(I) hexafluorophosphate (0.165 g, 0.562 mmol) was added. A white precipitate formed immediately and was filtered off after stirring for 10 min. The silver chloride precipitate discoloured rapidly once formed, due to formation of metallic silver. To the resulting very pale yellow solution was added *p*-methoxyphenyl isocyanide (0.088 g, 0.652 mol) in methanol (10 cm^3), and the solution began to darken. After stirring for 5 min, removal of volatiles *in vacuo* gave a white oily solid contaminated with some particles of black material. The oil was washed with hexane (20 cm^3) and was recrystallised from hot methanol to give white needles of trans-*bis*(*diethylphenylphosphine*)(p-*methoxyphenyl isocyanide*)*vinylplatinum*(II) *hexafluorophosphate* (0.27 g, 60%), m.p. 98—100 °C.

This product (0.30 g, 0.36 mmol) was dissolved in n-butylamine (7 cm^3) and the solution was heated under reflux for 50 min. Removal of volatiles *in vacuo* gave a buff oil, which on washing with hexane (20 cm^3) gave a buff oily solid. After thorough drying *in vacuo*, the product was dissolved in the minimum volume of acetone at room temperature and diethyl ether was added until the solution became opalescent. Fine colourless needles of trans-(*butylamino*-p-*methoxyphenylaminocarbene*)*bis*(*diethylphosphine*)-*vinylplatinum*(II) *hexafluorophosphate* (0.28 g) were deposited when the solution was left at −15 °C.

trans-Bis(diethylphenylphosphine)(*p*-methoxyphenyl isocyanide)vinylplatinum(II) hexafluorophosphate failed to react on prolonged (12—20 h) heating under reflux with *p*-anisidine (1 g in benzene, 10 cm^3), aniline (2 cm^3 in benzene, 6 cm^3), or cyclohexylamine (10 cm^3). In the two latter cases there was extensive decomposition.

trans-Chlorobis(methyldiphenylphosphine)(phenylethynyl)platinum(II) (0.300 g, 0.410 mmol) was dissolved in thf (60 cm^3) and Ag[PF$_6$] (0.103 g, 0.410 mmol) in thf (5 cm^3) was added. A white solid was precipitated. After stirring for 10 min, the solution was filtered, and *p*-methoxyphenyl isocyanide (0.055 g, 0.41 mmol) in thf (10 cm^3) was added. After stirring for 5 min, the brown solution was evaporated giving a brown oil. Washing with diethyl ether (20 cm^3) gave a brown solid. Recrystallisation from hot methanol (filtering off some insoluble dark solid through Celite) gave small buff prisms of trans-*bis*(*methyldiphenylphosphine*)(p-*methoxyphenyl isocyanide*)(*phenylethynyl*)*platinum*(II) *hexafluorophosphate* (0.22 g), which were recrystallised (CHCl$_3$–MeOH) to yield colourless prisms. This hexafluorophosphate (0.25 g, 0.25 mmol) was heated under reflux in n-butylamine (10 cm^3) and benzene (10 cm^3) for 4 h, giving a buff solution. Volatiles were removed *in vacuo* and the resulting solid was dissolved in hot methanol (10 cm^3) and filtered, removing a small quantity of black solid; the filtrate was evaporated to dryness, washed with hexane (10 cm^3) and diethyl ether (10 cm^3), and the resulting white solid (0.12 g) was recrystallised from methanol (6 cm^3) at −15 °C to give small colourless needles of trans-(*butylamino*-p-*methoxyphenylaminocarbene*)*bis*(*methyldiphenylphosphine*)(*phenylethynyl*)*platinum*(II) *hexafluorophosphate*.

(*g*) *Miscellaneous reactions.* *trans*-Chlorobis(diethylphenylphosphine)vinylplatinum(II) (0.100 g, 0.169 mmol) was dissolved in benzene (4 cm^3) and a benzene solution (0.86 cm^3) of hydrogen chloride (0.196 mol dm^{-3}, 0.169 mmol) was added, giving an immediate yellow colour. After 10 min, volatiles were removed *in vacuo*, and the yellow solid residue was recrystallised from ethanol (5 cm^3) giving fine yellow crystals. These were shown by i.r. and analysis to be a mixture of *cis*- and *trans*-[PtCl$_2$(PEt$_2$Ph)$_2$] with the *trans* isomer predominant.

Tribromobis(diethylphenylphosphine)vinylplatinum(IV) (0.055 g, 0.069 mmol) was dissolved in benzene (4 cm^3) and a benzene solution (1.1 cm^3) of bromine (0.342 g in 25 cm^3, 0.081 mmol) was added. The orange solution was stirred for 10 h with little lightening of the colour. Removal of volatiles gave an orange solid which was recrystallised from acetone to give pale yellow needles of *trans*-dibromobis(diethylphenylphosphine)platinum(II) (Found: C, 35.1; H, 4.45. Calc. for $C_{20}H_{30}Br_2P_2Pt$: C, 34.9; H, 4.40%) (0.02 g, 42%), m.p. 194—196 °C.

trans-Chlorobis(diethylphenylphosphine)vinylplatinum(II) (0.20 g, 0.34 mmol) was dissolved in methanol (3 cm^3) and *p*-methoxyphenyl isocyanide (0.045 g, 0.34 mmol) was added. A yellow solution was rapidly formed which, on evaporation *in vacuo*, gave a yellow oil. Its spectral properties suggested that the bis(diethylphenylphosphine)-(*p*-methoxyphenyl isocyanide)vinylplatinum(II) cation had formed, but the complex could not be crystallised from various solvents or solvent mixtures. (In a related reaction,[37] a similar difficulty has been reported.)

Reactions of cis-(*Trifluorovinyl*)(*trimethylstannio*)*bis*(*triphenylphosphine*)*platinum*(II).—(*a*) *With hydrogen chloride.* The complex (0.100 g, 0.104 mmol) was dissolved in benzene (5 cm^3), and a solution of hydrogen chloride in diethyl ether–benzene (0.887 cm^3, 0.118 mol dm^{-3}) was added. After stirring for 2 d, the solution was evaporated *in vacuo*. The residue was shown by m.p. and analysis to be the starting complex. In a further experiment, the complex (0.14 g) was dissolved in benzene (10 cm^3) and treated with a large excess of a solution of hydrogen chloride in diethyl ether. After stirring for 2 h, volatiles were removed *in vacuo* leaving a white residue. On recrystallisation from methanol–benzene, white crystals of dichlorobis(triphenylphosphine)platinum(II) (analysis and spectra) were obtained.

(*b*) *With hydrogen.* Several experiments were performed: (*i*) at atmospheric pressure by passage of gas through a benzene solution (no reaction), (*ii*) at 60 atm at 40—80 °C for 1—3 h in C_6H_6 (7—25 cm^3) using complex (0.20 g). An unidentified product with a $\nu_{max.}$ at 1 720—1 745 cm^{-1} was formed in small quantity.

(*c*) *With hydrofluoric acid.* The complex (0.150 g, 0.155 mmol) was dissolved in benzene (10 cm^3) and a solution of HF (0.081 g, 0.31 mmol) in diethyl ether (3.8 cm^3) was added. The solution was heated under reflux for 2 h, turning yellow after a few minutes and then orange. A slight cloudiness was observed, and a small amount of unidentified precipitate was filtered off. Evaporation of the filtrate *in vacuo* gave an orange oil which on thorough washing with hexane (20 cm^3) gave an orange powder (0.08 g). This was recrystallised (EtOH and then Me$_2$CO) to give fine white needles (55%) of

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[37] S. O. Grim, R. L. Keiter, and W. McFarlane, *Inorg. Chem.*, 1967, **6**, 1133.

complex (11) (Found: C, 50.1; H, 3.80; F, 7.55. $C_{41}H_{40}F_4P_2PtSn$ requires C, 50.0; H, 4.05; F, 7.70%), m.p. 192—193 °C (decomp.).

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