Carbon–Chlorine Bond Activation in 2-Chloromethylallyl Complexes of Platinum(II)

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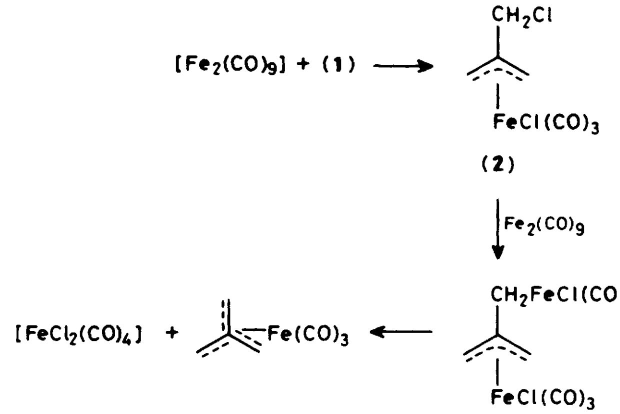
Treatment of $[Pt(C_2H_4)(PPh_3)_2]$ or $[Pt(PPh_3)_4]$ with 3-chloro-2-chloromethylprop-1-ene (**1**) and KPF_6 at room temperature affords $[Pt\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}(PPh_3)_2][PF_6]$ (**3a**). The carbon–chlorine bond in (**3a**) is reactive and treatment of (**3a**) with the Lewis bases L (L = PPh_3, NEt_3, or pyridine) in the presence of KPF_6 affords the dicationic salts $[Pt\{\eta^3\text{-}CH_2C(CH_2L)CH_2\}(PPh_3)_2][PF_6]_2$. Reaction of (**3a**) with lithium bromide gives $[Pt\{\eta^3\text{-}CH_2C(CH_2Br)CH_2\}(PPh_3)_2][PF_6]$. A phosphonium salt $[Pt\{\sigma\text{-}CH_2C(CH_2PPh_3)CH_2\}\{P(OMe)_3\}_3][PF_6]_2$ is formed on addition of trimethyl phosphite and KPF_6 to (**3a**). Evidence for the activation of the carbon–chlorine bond in (**3a**) is provided by the much slower reaction of (**1**) with PPh_3 and KPF_6 to give $[CH_2{=}C(CH_2Cl)(CH_2PPh_3)][PF_6]$ and triethylamine and KPF_6 with $[Pt\{\sigma\text{-}CH_2C({=}CH_2)CH_2Cl\}(S_2CNMe_2)(PPh_3)]$ to give $[Pt\{\sigma\text{-}CH_2C({=}CH_2)CH_2NEt_3\}(S_2CNMe_2)(PPh_3)][PF_6]$. A bridging trimethylenemethane complex $[Pt\{\eta^3\text{-}CH_2C[CH_2PtCl(PPh_3)_2]CH_2\}(PPh_3)_2][PF_6]$ is formed in the reaction of (**3a**) with $[Pt(C_2H_4)(PPh_3)_2]$ and KPF_6. N.m.r. data for the complexes are reported, the assignments of the *syn* and *anti* protons in $[Pt\{\eta^3\text{-}CH_2C(CH_2PPh_3)CH_2\}(PPh_3)_2][PF_6]_2$ being confirmed by a proton–proton nuclear Overhauser enhancement difference experiment.

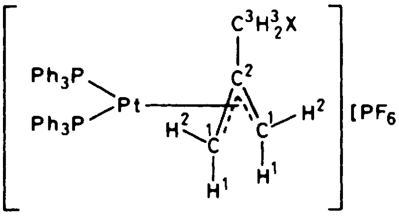
Although the first trimethylenemethane [tmm, $C(CH_2)_3$] complex $[Fe(CO)_3(\eta^4\text{-tmm})]$ was obtained by the reaction of $CH_2{=}C(CH_2Cl)_2$ (**1**) with $[Fe_2(CO)_9]$,[1,2] subsequent attempts to obtain trimethylenemethane complexes of other metals using the organic substrate (**1**) have in general not proved successful. Thus whilst the reactions of $[FeCl_2L_2]$ (L = PMe_2Ph or PMe_3) with (**1**) in the presence of excess magnesium have produced 40—47% yields of the complexes $[FeL_3(\eta^4\text{-tmm})]$,[3] the reaction of (**1**) with $[Cr(CO)_6]$ produced a 1% yield of $[Cr(CO)_4(\eta^4\text{-tmm})]$ and treatment of (**1**) with $Na_2[Mo(CO)_5]$ gave a similar low yield of $[Mo(CO)_4(\eta^4\text{-tmm})]$.[4] The mechanism of formation of $[Fe(CO)_3(\eta^4\text{-tmm})]$ is considered to involve initial formation of a (2-chloromethylallyl)iron tricarbonyl chloride complex $[FeCl(CO)_3\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}]$ (**2**) followed by oxidative addition of the C–Cl bond of (**2**) to the co-ordinatively unsaturated species $Fe(CO)_4$ and elimination of $[FeCl_2(CO)_4]$ as outlined in the Scheme.[2] The involvement of a 2-halogenomethylallyl complex in this reaction and the report that treatment of $[Pd_2Cl_2\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}_2]$ with SbF_5 afforded a trimethylenemethane palladium complex[5] suggested that an investigation of the synthesis and chemistry of 2-halogenomethylallyl complexes might lead to a better understanding of the reactions of (**1**) with metal complexes. In this paper we report our studies on 2-chloromethylallyl complexes of platinum(II).

Results and Discussion

Allyl halides readily oxidatively add to zerovalent platinum complexes to afford either σ- or η^3-allyl complexes,[6–8] and we find that reaction of 3-chloro-2-chloromethylprop-1-ene with either $[Pt(C_2H_4)(PPh_3)_2]$ or $[Pt(PPh_3)_4]$ at room temperature followed by addition of KPF_6 afforded the cationic 2-chloromethylallyl complex (**3a**). Complex (**3a**) was fully identified spectroscopically (Table), the n.m.r. data indicating that the η^3-allyl is non-fluxional at room temperature as observed in related cationic 2-methylallyl complexes.[9–12] In refluxing toluene, the reaction of (**1**) with $[Pt(PPh_3)_4]$ did not give (**3a**) and a different complex (**4**) was isolated as its bis(hexafluorophosphate) salt. The structure of this complex followed from an examination of its n.m.r. spectra (Table). Comparison of the



Scheme.



(**3a**), X = Cl

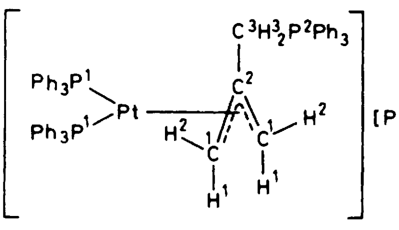
(**3b**), X = Br

$^{13}C\text{-}\{^1H\}$ n.m.r. spectra of (**4**) and (**3a**) allowed assignments to be made for the allylic carbon atoms. Moreover, the carbon atom C^3 exhibits ^{13}C–^{31}P coupling in agreement with the presence of the CH_2PPh_3 group. In the ^{31}P n.m.r. spectrum of (**4**) this quaternised phosphorus atom exhibits a small coupling to ^{195}Pt [δ 22.8, $J(^{31}P\text{–}^{195}Pt)$ = 225 Hz] as compared to the triphenylphosphine ligands bound to platinum [δ 14.7, $J(^{31}P\text{–}^{195}Pt)$ = 3 926 Hz]. The formation of (**4**) presumably proceeds *via* the 2-chloromethylallyl complex (**3a**) followed by sub-

Table. Selected n.m.r. spectroscopic data (*J* values in Hz)

Complex	
(3a)	$\delta_H{}^a$ 3.16 [2 H, dt, $\lvert {}^3J(P_{cis}H) + {}^3J(P_{trans}H)\rvert 6.6$, ${}^2J$(PtH) 37.8, H^1], 3.61 (2 H, br s, H^2), 4.08 [2 H, s, ${}^3J$(PtH) 52.8, H^3]; $\delta_C{}^b$ 45.4 [s, *J*(PtC) 34, C^3], 67.3 [m (A part of AXX′ system), $\lvert {}^2J(P_{cis}C) + {}^2J(P_{trans}C)\rvert 29.1$, C^1], C^2 not observed; $\delta_P{}^c$ 15.9 [s, *J*(PPt) 3 906]
(3b)	$\delta_H{}^a$ 3.14 [2 H, dt, $\lvert {}^3J(P_{cis}H) + {}^3J(P_{trans}H)\rvert 7.4$, ${}^2J$(PtH) 37.6, H^1], 3.57 (2 H, br s, H^2), 3.89 [2 H, s, ${}^3J$(PtH) 45.6, H^3]; $\delta_C{}^b$ 32.0 [s, *J*(PtC) 35.5, C^3], 67.9 [m (A part of AXX′ system), $\lvert {}^2J(P_{cis}C) + {}^2J(P_{trans}C)\rvert 29.0$, *J*(CPt) 72.1, C^1], C^2 not observed
(4)	$\delta_H{}^a$ 2.95 (2 H, br s, H^2), 3.28 [2 H, m, $\lvert {}^3J(P_{cis}H) + {}^3J(P_{trans}H)\rvert 5.6$, ${}^2J$(PtH) 20.0, H^1], 3.78 [2 H, d, ${}^2J$(P^{2}H) 14.3, ${}^4J$(PtH) 28.3, H^3]; $\delta_C{}^b$ 32.4 [d, *J*(CP^2) 49.2, ${}^3J$(CPt) 20.1, C^3], 70.3 [m, $\lvert {}^2J(P_{cis}C) + {}^2J(P_{trans}C)\rvert 31.9$, C^1], 125.1 [s, *J*(CPt) 37.2]; $\delta_P{}^c$ 14.7 [s, *J*(PPt) 3 926, P^1], 22.8 [s, ${}^4J$(PPt) 225, P^2]
(5a)	$\delta_H{}^d$ 1.05 [9 H, br m, N(CH$_2$C*H*$_3$)$_3$], 3.1—3.4 [10 H, overlapping signals due to H^2, H^3, and N(C*H*$_2$CH$_3$)$_3$], 3.53 [2 H, d, $\lvert {}^3J(P_{cis}H) + {}^3J(P_{trans}H)\rvert 6.6$, ${}^2J$(PtH) 36]; $\delta_P{}^d$ 15.1 [s, *J*(PtP) 3 931]
(5b)	$\delta_H{}^e$ 3.58 [2 H, m, $\lvert {}^3J(P_{cis}H) + {}^3J(P_{trans}H)\rvert 9.0$, ${}^2J$(PtH) 36.9, H^1], 3.77 (2 H, br s, H^2), 5.57 [2 H, s, ${}^3J$(PtH) 40.4, H^3]; $\delta_P{}^c$ 14.7 [s, *J*(PPt) 3 936]
(6)	$\delta_H{}^f$ 2.26 [2 H, d, ${}^3J$(PH) 5.38, *J*(PtH) 92.29, PtC*H*$_2$], 3.23 (3 H, s, NMe), 3.29 (3 H, s, NMe), 3.92 [2 H, s, *J*(PtH) 6.0, CH$_2$Cl], 4.43 [1 H, br s, *J*(PtH) 26.01, C=C*H*], 4.80 [1 H, br s, *J*(PtH) 29.01, C=C*H*]; $\delta_P{}^c$ 19.0 [s, *J*(PPt) 4 092]
(7)	$\delta_H{}^d$ 1.18 [9 H, t, *J*(HH) 6.8, N(CH$_2$C*H*$_3$)$_3$], 2.19 [2 H, d, *J*(PH) 4.7, *J*(PtH) 99, PtCH$_2$], 3.05 [6 H, q, *J*(HH) 6.8, N(C*H*$_2$CH$_3$)$_3$], 3.18 (3 H, s, NMe), 3.35 (3 H, s, NMe), 3.43 (2 H, s, CH$_2$N), 4.83 [1 H, br s, *J*(PtH) 28.5, C=C*H*], 4.90 [1 H, br s, *J* (PtH) 30, C=C*H*]
(8)	$\delta_H{}^d$ 3.3 [4 H, d, *J*(P^{1}H) 1.5, *J*(PtH) 42, CH$_2$CCH$_2$], 3.6 (27 H, s, MeO), 3.8 [2 H, d, *J*(P^{1}H) 15, *J*(PtH) not observed, C*H*$_2$P^1]; $\delta_P{}^c$ 20.2 [s, *J*(PtP^1) 17.1, CH$_2$*P*^{1}Ph$_3$], 111.3 {br s, Pt[*P*(OMe)$_3$]$_3$}
(9)	$\delta_H{}^g$ 2.46 [2 H, s, *J*(Pt^{1}H) 35.9, *J*(Pt^{2}H) 75.0, H^3], 2.49 [2 H, s, *J*(Pt^{1}H) 46.4, H^1], 3.46 (2 H, br s, H^2); $\delta_C{}^b$ 34.2 [d, *J*(CP) 83.8, *J*(CPt) 442.8, C^3], 65.4 [m, $\lvert {}^2J(P_{cis}C) + {}^2J(P_{trans}C)\rvert 33.4$, C^1], 148.3 [dt, ${}^3J$(CP^3) 12.3, ${}^3J$(CP^2) or ${}^3J$(CP^1) 3.1, C^2]; $\delta_P{}^h$ 17.1 [d, *J*(P^{1}P^2) 16, *J*(P^{2}Pt^2) 4 286, *J*(P^{2}Pt^1) 2.1, P^2], 18.7 [d, *J*(P^{1}P^3) 2.6, *J*(P^{3}Pt^1) 3 697, *J*(P^{3}Pt^2) 21], 21.2 [dt, *J*(P^{1}P^2) 16, *J*(P^{1}P^3) 2.6, *J*(P^{1}Pt^2) 1 997, *J*(P^{1}Pt^1) 160]; $\delta_{Pt}{}^i$ −728 [dt, *J*(Pt^{1}P^3) 3 697, *J*(Pt^{1}P^1) 160, *J*(Pt^{1}Pt^2) 1 040, Pt^1], −40 [ddt, *J*(Pt^{2}P^1) 1 997, *J*(Pt^{2}P^2) 4 286, *J*(Pt^{2}P^3) 21, *J*(Pt^{1}Pt^2) 1 040]

[a] 400 MHz, CD$_2$Cl$_2$. [b] 100 MHz, CD$_2$Cl$_2$. [c] 24.3 MHz, CD$_2$Cl$_2$. [d] 90 MHz, CD$_2$Cl$_2$. [e] 90 MHz, (CD$_3$)$_2$CO. [f] 400 MHz, CDCl$_3$. [g] 360 MHz, CD$_2$Cl$_2$; ^{31}P broad-band decoupled. [h] 36.3 MHz, CD$_2$Cl$_2$; relative to H$_3$PO$_4$. [i] 19.1 MHz, CH$_2$Cl$_2$, CD$_2$Cl$_2$.



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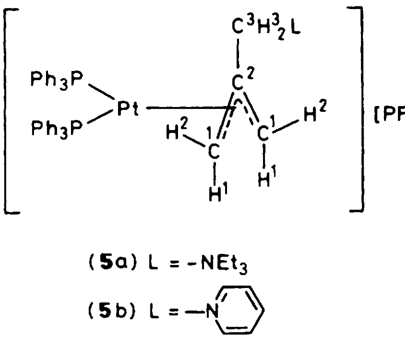
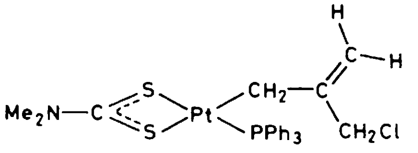


(**5a**) L = -NEt$_3$

(**5b**) L =



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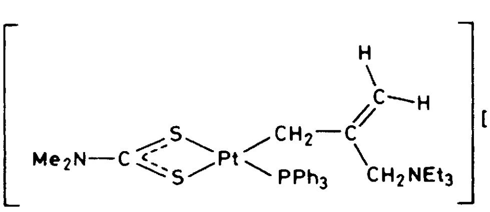
sequent quaternisation of free triphenylphosphine which would be present in solution. In agreement with this we find that (**4**) results from the reaction of (**3a**) with triphenylphosphine in refluxing toluene followed by treatment of the product with KPF$_6$.

The ease of formation of the phosphonium salt (**4**) indicates an enhanced reactivity of the C–Cl bond in the complex (**3a**) over that in 3-chloro-2-chloromethylprop-1-ene as demonstrated by reactions with triphenylphosphine. Thus the 2-chloromethylallyl complex (**3a**) reacted rapidly in refluxing toluene or as a suspension in light petroleum (b.p. 60—80 °C) with PPh$_3$ to give the phosphonium derivative (**4**) whereas the dichloride (**1**) required prolonged refluxing with PPh$_3$ in methyl cyanide containing KPF$_6$ to give the salt [CH$_2$=C(CH$_2$Cl)(CH$_2$PPh$_3$)][PF$_6$]. Further indication of the activation of the C–Cl bond in (**3a**) is provided by its reactions with triethylamine, pyridine, and lithium bromide which occurred at room temperature to afford respectively the quaternary ammonium salt (**5a**), the alkylpyridinium salt (**5b**), and the bromo derivative (**3b**).

Treatment of the chloromethylallyl complex (**3a**) with sodium dimethyldithiocarbamate afforded the σ-chloromethylallyl derivative (**6**) characterised by its analytical data and spectroscopic properties, the i.r. spectrum showing characteristic bands of bidentate dithiocarbamate with a singlet at 973 cm^{-1} (ν_{CS}), an intense absorption at 1 545 cm^{-1} ($\nu_{C=N}$), and a Pt–S stretch at 370 cm^{-1}.[13–15] Analogous σ-allyl complexes of palladium(II) have previously been obtained by addition of tertiary phosphines to [Pd(η^3-allyl)(S$_2$CNMe$_2$)].[16] The formation of the σ-allyl species (**6**) was of interest since it afforded the opportunity to compare the reactivity of η^3- and σ-chloromethylallyl complexes. Studies with triethylamine showed that treatment of the σ-allyl (**6**) with NEt$_3$ in the presence of KPF$_6$ in a refluxing mixture of methyl cyanide and trichloromethane afforded the quaternary ammonium salt (**7**). In contrast the η^3-allyl (**3a**) reacts with triethylamine at room temperature to form (**5a**). Interestingly the reaction of excess trimethyl phosphite with (**3a**) also resulted in the formation of a σ-allyl species (**8**) which contains quaternised triphenylphosphine. Quaternisation of the displaced triphenylphosphine rather than trimethyl phosphite, which was in excess, is consistent with the greater nucleophilicity of triphenylphosphine as compared to trimethyl phosphite.

The ^{31}P n.m.r. spectrum of (**8**) indicated a rapid interchange of the phosphite ligands bound to platinum, a broad resonance being observed at room temperature. This shifted to lower field



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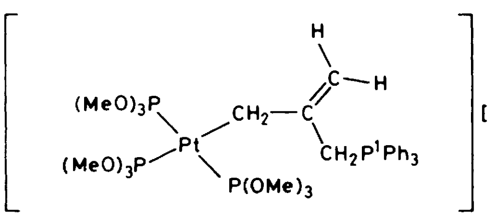

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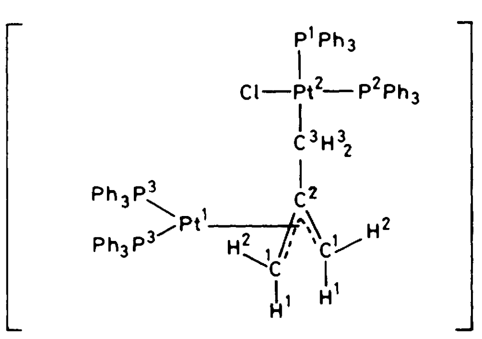

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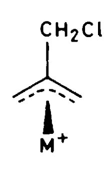
on addition of free ligand showing that the averaging is due to a dissociative process. At −100 °C, in acetone as solvent, the signal due to co-ordinated $P(OMe)_3$ had sharpened considerably but no $^{31}P-^{195}Pt$ coupling indicative of a static structure could be detected. Phosphite dissociation coupled with a $\sigma-\eta^3$-allyl exchange process would cause each end of the allyl group to appear equivalent. The ^1H n.m.r. spectrum of complex (**8**) confirmed this equivalence, only a single resonance being observed for the terminal allyl protons. Similar behaviour has been observed in related systems.[11]

The ready cleavage of the carbon chlorine in (**3a**) suggested that oxidative addition reactions between complex (**3a**) and low-valent metal substrates should lead to dinuclear metal complexes in which a trimethylenemethane moiety bridged two metal atoms. Accordingly the reaction between (**3a**) and $[Pt(C_2H_4)(PPh_3)_2]$ was investigated. The product isolated from this reaction was characterised by a combination of microanalytical and spectroscopic data and was formulated as the bridged trimethylenemethane complex (**9**). The value of $J(Pt^1Pt^2)$ for this complex was found to be 1 040 Hz (Table). However, since the magnitude of J(PtPt) determined for a series of Pt–Pt bonded complexes gives little information on the extent of metal–metal bonding[17] it is not clear whether a Pt · · · Pt interaction occurs in the dinuclear complex (**9**).

Nuclear Overhauser Enhancement (*N.O.E.*) *Studies*.—The assignments to the *syn* and *anti* protons in the η^3-allyl complexes (**3**)—(**5**) have relied on the observation that *anti* protons generally give signals to higher frequency and exhibit larger coupling to the phosphorus ligands.[18,19] For the complex (**4**) this has been confirmed by an n.O.e. difference experiment. A simple model indicates that the shortest H^2–H^3 distance is *ca.* 3 Å whilst the corresponding H^1–H^3 distance is *ca.* 4 Å. In the n.O.e. difference spectrum irradiation at H^3 gave a clear enhancement at the resonance assigned to the *syn* hydrogens H^2 with no significant effect at H^1, confirming the assignment.



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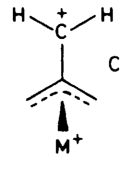

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Conclusions

These studies indicate that the platinum atom in $[Pt\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}(PPh_3)_2][PF_6]$ (**3a**) activates the C–Cl bond to further oxidative addition. Some evidence for a weakening of this C–Cl bond is provided by the i.r. spectrum of (**3a**) which shows a medium to weak absorption at 637 cm^{-1} which is absent in the corresponding bromo derivative (**3b**) and the derivatives (**4**) and (**6**) and can be assigned to ν_{C-Cl}. The carbon–chlorine stretching frequencies of monochlorinated acyclic compounds commonly occur in the range 750—700 cm^{-1}.[20] Recently it has been suggested that the activation of C–X bonds (X = halide) in derivatives MCH_2X, MCH_2CH_2X, and $M(CH_2)_3X$ may occur by lowering the energy of the transition state by contributions from the resonance forms $[M{=}CH_2]^+X^-$, $[MC_2H_4]^+X^-$, and $[M(\overline{CH_2CH_2CH_2})]^+X^-$ respectively.[21] The activation now established in the η^3-allyl (**3a**) may be due to the resonance forms (**10**) and (**11**) which would result in activation of the C–Cl bond. Loss of chloride from (**10**) would produce the η^3-tmm species (**11**), which on the basis of theoretical[22] and experimental[5] studies would not be expected to collapse to the corresponding η^4-tmm analogue. Similar activation has been observed in chloromethylallyl palladium(II) systems.[23,24] We also note that the formation of the trimethylenemethane-bridged platinum complex (**9**) provides some evidence for the involvement of similar di-iron species in the formation of $[Fe(CO)_3(\eta^4\text{-tmm})]$, Scheme.

Experimental

Infrared spectra were recorded as CsCl discs on a Perkin-Elmer 580 spectrophotometer. High-field n.m.r. spectra (^1H and ^{13}C) were obtained using the S.E.R.C. service facilities at the Universities of Warwick and Edinburgh. Other n.m.r. measurements were obtained using Varian EM 390 (^1H, 90 MHz), JEOL-PS-100 (^1H, 100 MHz), and JEOL JNM-FX 60 (^{31}P, 24.3 MHz) instruments. The ^{195}Pt spectrum was obtained using the S.E.R.C. low-field service at the City of London Polytechnic. Hydrogen-1 and ^{13}C chemical shifts are quoted relative to $SiMe_4$ (0.0 p.p.m.). Phosphorus-31 chemical shifts were measured relative to $[P(OH)_4]^+$ in D_2O at 0 °C and ^{195}Pt chemical shifts are quoted with respect to $\Xi(^{195}Pt)$ = 21.4 MHz.

Experiments were carried out under a dry, oxygen-free, nitrogen atmosphere unless otherwise stated, using solvents which were dried and distilled under nitrogen prior to use. All the complexes isolated were stable in air. The compounds $[Pt(C_2H_4)(PPh_3)_2]$[25] and $[Pt(PPh_3)_4]$[26] were prepared as described in the literature.

Preparation of $[Pt\{\eta^3\text{-}CH_2C(CH_2Cl)CH_2\}(PPh_3)_2][PF_6]$ **(3a)**.—(*a*) *From* $[Pt(C_2H_4)(PPh_3)_2]$. The compound $[Pt(C_2H_4)(PPh_3)_2]$ (0.63 g, 0.8 mmol) was added to a solution of 3-chloro-2-chloromethylprop-1-ene (0.11 g, 0.8 mmol) in toluene (30 cm^3). A green solution was instantly formed and on slowly warming to 80 °C the solution became pale yellow. After 1 h the solvent was removed *in vacuo* and the white residue was dissolved in methyl cyanide (30 cm^3). Potassium hexafluorophosphate (0.5 g) in methyl cyanide (10 cm^3) was added to the solution and the solvent was removed from the white suspension *in vacuo*. The residue was extracted with dichloromethane and the resulting suspension was filtered. The solvent was removed *in vacuo* and recrystallisation of the white residue from dichloromethane–diethyl ether gave white *microcrystals* of **(3a)** (0.65 g, 80%) (Found: C, 50.3; H, 3.8. $C_{40}H_{36}ClF_6P_3Pt$ requires C, 50.8; H, 4.1%); ν_{C-Cl} 637mw cm^{-1}.

(*b*) *From* $[Pt(PPh_3)_4]$. The compound $[Pt(PPh_3)_4]$ (1.0 g, 0.8 mmol) was dissolved in toluene (50 cm^3) containing 3-chloro-2-chloromethylprop-1-ene (0.2 cm^3). On stirring for 2 min the yellow colour of the solution was discharged and the solution was evaporated to dryness *in vacuo* at 0 °C. The white residue was dissolved in methyl cyanide (30 cm^3), filtered if necessary to remove any of the phosphonium salt $[Pt\{\eta^3\text{-}CH_2C(CH_2PPh_3)CH_2\}(PPh_3)_2]Cl_2$, and the solution treated as above with a solution of KPF_6 to afford **(3a)** (0.56 g, 73%).

Preparation of $[Pt\{\eta^3\text{-}CH_2C(CH_2PPh_3)CH_2\}(PPh_3)_2][PF_6]_2$ **(4)**.—$[Pt(PPh_3)_4]$ (1.0 g, 0.8 mmol) and 3-chloro-2-chloromethylprop-1-ene (0.15 cm^3) were stirred in toluene (50 cm^3) for 2 min after which time the yellow colour had faded. The solution was then refluxed for 30 min and then evaporated to dryness *in vacuo*. The residue was then suspended in methyl cyanide and refluxed with an excess of KPF_6 for 1 h. The mixture was evaporated to dryness *in vacuo* and the residue was stirred with dichloromethane and filtered. Evaporation of the filtrate to dryness and recrystallisation of the residue from dichloromethane–diethyl ether gave white microcrystals of **(4)** (0.91 g, 85%) (Found: C, 52.5; H, 3.9. $C_{58}H_{51}F_{12}P_5Pt$ requires C, 52.2; H, 3.9%).

Reactions of **(3a)**.—(*a*) *With lithium bromide.* An excess of lithium bromide and **(3a)** (0.25 g, 0.26 mmol) in methyl cyanide (30 cm^3) were stirred for 15 h at room temperature and then evaporated to dryness *in vacuo*. The residue was extracted with dichloromethane and the filtered solution was evaporated to dryness. Recrystallisation of the residue from dichloromethane–diethyl ether gave white *microcrystals* of $[Pt\{\eta^3\text{-}CH_2C(CH_2Br)CH_2\}(PPh_3)_2][PF_6]$ **(3b)** (0.11 g, 42%) (Found: C, 48.1; H, 3.6. $C_{36}H_{30}BrF_6P_3Pt$ requires C, 48.0; H, 3.7%).

(*b*) *With* $[Pt(C_2H_4)(PPh_3)_2]$. The complex **(3a)** (0.31 g, 0.32 mmol) was dissolved in warm toluene (30 cm^3) and $[Pt(C_2H_4)(PPh_3)_2]$ (0.24 g, 0.32 mmol) was added. The solution was refluxed for 1 h and stirred at room temperature for 15 h. The resultant white precipitate was filtered off, washed with toluene and light petroleum (b.p. 40—60 °C) and dried *in vacuo* to afford white *microcrystals* of $[Pt\{\eta^3\text{-}CH_2C[CH_2PtCl(PPh_3)_2]CH_2\}(PPh_3)_2][PF_6]$ **(9)** (0.37 g, 64%) (Found: C, 53.7; H, 4.0. $C_{76}H_{66}ClF_6P_5Pt$ requires C, 54.5; H, 4.0%).

(*c*) *With triethylamine plus* KPF_6. An excess of triethylamine was added to a solution of **(3a)** (0.4 g, 0.42 mmol) in methyl cyanide (50 cm^3) containing KPF_6 (1.5 g, 8.2 mmol). After stirring for 1 min the solution became cloudy due to the formation of potassium chloride and after a further 15 min the suspension was evaporated to dryness *in vacuo*. The residue was extracted with dichloromethane and the filtered solution was evaporated to dryness. The residue was recrystallised from dichloromethane–diethyl ether and dried *in vacuo* at 40 °C to give white *microcrystals* of $[Pt\{\eta^3\text{-}CH_2C(CH_2NEt_3)CH_2\}(PPh_3)_2][PF_6]_2$ **(5a)** (0.43 g, 88%) (Found: C, 47.7; H, 4.5; N, 1.2. $C_{46}H_{51}F_{12}NP_4Pt$ requires C, 47.4; H, 4.4; N, 1.2%).

(*d*) *With pyridine plus* KPF_6. The complex **(3a)** (0.42 g, 0.44 mmol) and KPF_6 (1.5 g, 8.2 mmol) were dissolved in methyl cyanide (50 cm^3) and a few drops of pyridine were added to the stirred solution. After 1 h the cloudy solution was evaporated to dryness. The residue was extracted with dichloromethane and the filtered solution was concentrated to a small volume. Addition of diethyl ether at 0 °C gave white *microcrystals* of $[Pt\{\eta^3\text{-}CH_2C(CH_2NC_5H_5)CH_2\}(PPh_3)_2][PF_6]_2$ **(5b)** (0.36 g, 72%) (Found: C, 47.8; H, 3.7; N, 1.1. $C_{45}H_{41}F_{12}NP_4Pt$ requires C, 47.3; H, 3.6; N, 1.2%).

(*e*) *With sodium dimethyldithiocarbamate.* The complex **(3a)** (0.3 g, 0.31 mmol) and $Na[S_2CNMe_2]$ (0.1 g, 0.7 mmol) were stirred in methyl cyanide (25 cm^3) and slowly heated to 50 °C. The white precipitate was filtered off, washed with methyl cyanide and dried *in vacuo* to give $[Pt\{\sigma\text{-}CH_2C(=CH_2)CH_2Cl\}(S_2CNMe_2)(PPh_3)]$ **(6)** (0.12 g, 58%) (Found: C, 44.2; H, 4.1; N, 2.0. $C_{25}H_{27}ClNPPtS_2$ requires C, 45.0; H, 4.1; N, 2.1%).

(*f*) *With trimethyl phosphite plus* KPF_6. The complex **(3a)** (0.5 g, 0.52 mmol) and KPF_6 (2 g, 10.9 mmol) were dissolved in methyl cyanide (30 cm^3) and a few drops of trimethyl phosphite were added. The turbid solution was stirred for 5 min, evaporated to dryness, and the residue was extracted with dichloromethane and filtered. Evaporation of the filtrate gave an oil which on treatment with dichloromethane and ethanol gave $[Pt\{\sigma\text{-}CH_2C(CH_2PPh_3)CH_2\}\{P(OMe)_3\}_3][PF_6]_2$ **(8)** as a white solid (0.58 g, 87%) (Found: C, 31.7; H, 4.1. $C_{31}H_{48}F_{12}O_9P_6$ requires C, 31.7; H, 4.1%).

Reaction of **(6)** *with Triethylamine plus* KPF_6.—The complex **(6)** and excess KPF_6 were stirred under reflux in a 1 : 1 chloroform–methyl cyanide mixture with excess triethylamine for 24 h. The suspension was evaporated to dryness and the residue was extracted with dichloromethane and filtered. Evaporation of the filtrate and recrystallisation of the residue from dichloromethane–ethanol gave $[Pt\{\sigma\text{-}CH_2C(=CH_2)CH_2NEt_3\}(S_2CNMe_2)(PPh_3)][PF_6]$ **(7)** as a white solid (0.035 g, 18%) (Found: C, 41.9; H, 4.7; N, 3.0. $C_{31}H_{42}F_6N_2P_2PtS_2$ requires C, 42.4; H, 4.8; N, 3.2%).

Reaction of $CH_2=C(CH_2Cl)_2$ *with Triphenylphosphine plus* KPF_6.—Triphenylphosphine (2 g, 7.6 mmol) was added to $CH_2=C(CH_2Cl)_2$ (1.5 g, 12.0 mmol) in methyl cyanide. KPF_6 (2 g, 10.9 mmol) was added to the green solution which was refluxed for 3 d to give a colourless solution and a white precipitate. The mixture was evaporated to dryness and the residue was extracted with dichloromethane. Filtration of the extract and evaporation of the filtrate gave a sticky solid which was stirred with diethyl ether to give a white powder. This was washed with diethyl ether and dried *in vacuo* at 40 °C to give $[CH_2=C(CH_2Cl)(CH_2PPh_3)][PF_6]$ (3.2 g, 85%) (Found: C, 53.5; H, 4.4. $C_{22}H_{21}ClF_6P_2$ requires C, 53.1, H, 4.2%).

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References

1 G. F. Emerson, K. Ehrlich, W. P. Giering, and P. C. Lauterbur, *J. Am. Chem. Soc.*, 1966, **88**, 3172.

2 K. Ehrlich and G. F. Emerson, *J. Am. Chem. Soc.*, 1972, **94**, 2464.

3 J. M. Grosselin, H. Le Bozec, C. Moinet, L. Toupet, and P. H. Dixneuf, *J. Am. Chem. Soc.*, 1985, **107**, 2809.

4 J. S. Ward and R. Pettit, *Chem. Commun.*, 1970, 1419.

5 J. Lukas and P. A. Kramer, *J. Organomet. Chem.*, 1971, **31**, 111.

6 F. R. Hartley, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, vol. 6, p. 471.

7 H. C. Volger and K. Vreize, *J. Organomet. Chem.*, 1967, **9**, 537.

8 M. C. Baird and G. Wilkinson, *J. Chem. Soc. A*, 1967, 865.

9 B. E. Mann, B. L. Shaw, and G. Shaw, *J. Chem. Soc. A*, 1971, 3536.

10 H. C. Clark and C. R. Jablonski, *Inorg. Chem.*, 1975, **14**, 1518.

11 N. M. Boag, M. Green, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1208.

12 D. J. Mabbott, B. E. Mann, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1977, 294.

13 F. Bonati and R. Ugo, *J. Organomet. Chem.*, 1967, **10**, 257.

14 C. O'Connor, J. D. Gilbert, and G. Wilkinson, *J. Chem. Soc. A*, 1969, 84.

15 D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc. A*, 1969, 1152.

16 J. Powell and A. W. L. Chan, *J. Organomet. Chem.*, 1972, **35**, 203.

17 N. M. Boag, J. Browning, C. Crocker, P. L. Goggin, R. J. Goodfellow, M. Murray, and J. L. Spencer, *J. Chem. Res. (S)*, 1978, 228.

18 D. A. Clarke, R. D. W. Kemmitt, M. A. Mazid, P. McKenna, D. R. Russell, M. D. Schilling, and L. J. S. Sherry, *J. Chem. Soc., Dalton Trans.*, 1984, 1993.

19 C. Conway, R. D. W. Kemmitt, A. W. G. Platt, D. R. Russell, and L. J. S. Sherry, *J. Organomet. Chem.*, 1985, **292**, 419.

20 S. F. Dyke, A. J. Floyd, M. Sainsbury, and R. S. Theobald, 'Organic Spectroscopy,' 2nd edn., Longman, London and New York, 1978, p. 89.

21 P. K. Monaghan and R. J. Puddephatt, *Inorg. Chim. Acta*, 1983, **76**, L237.

22 T. A. Albright, *J. Organomet. Chem.*, 1980, **198**, 159.

23 T. A. Albright, P. R. Clemens, R. P. Hughes, D. E. Hunton, and L. D. Margerum, *J. Am. Chem. Soc.*, 1982, **104**, 5369.

24 B. K. Dallas, R. P. Hughes, and K. Schumann, *J. Am. Chem. Soc.*, 1982, **104**, 5380.

25 D. M. Blake and D. M. Roundhill, *Inorg. Synth.*, 1978, **18**, 120.

26 L. Malatesta and C. Cariello, *J. Chem. Soc.*, 1958, 2323.

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