η-Allylmetal Chemistry. Part 7.[1] Allylic Alkylation catalysed by Platinum Complexes. Isolation of Rigid (σ-Allyl)(pentane-2,4-dionato)platinum(II) Complexes

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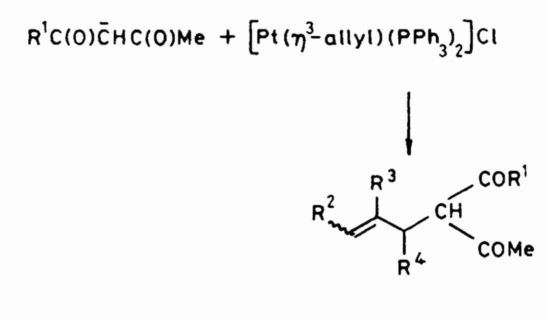
Reactions of β-diketo-anions with η^3-allylbis(triphenylphosphine)platinum(II) complexes or allyl acetates in the presence of triphenylphosphineplatinum complexes afford high yields of allylic alkylation products. Alkylation of the corresponding η^3-but-2-enylplatinum(II) complex gives a larger amount of the product of coupling at the secondary carbon than of that at the primary carbon, while the reversed selectivity is found in the reaction of the η^3-but-2-enylpalladium(II) complex. Reactions of η^3-allylmono(triphenylphosphine)platinum(II) complexes with thallium(I) pentane-2,4-dionate give stereochemically rigid, thermally stable, (σ-allyl)(pentane-2,4-dionato)platinum(II) complexes.

ALLYLIC alkylation by means of reactions between η^3-allylpalladium(II) complexes and carbanions derived from β-diketo-compounds has received much attention in recent years,[2] but there is no report on the corresponding reaction of analogous η^3-allylplatinum(II) complexes. In continuation of work on η-allylplatinum(II) chemistry,[1] I have undertaken a comparative study of allylic alkylation using η^3-allyl-platinum(II) and -palladium(II) complexes. The study on the platinum complexes appeared to be of particular interest in that organoplatinum intermediates involved in the reaction are expected to be more stable than the analogous organopalladium intermediates, and this would shed some light on the mechanistic aspects of the reaction. The present paper describes the isolation and/or spectroscopic identification of reaction intermediates in the allylic alkylation with η^3-allylplatinum(II) complexes, including (σ-allyl)(pentane-2,4-dionato)platinum(II), a class of the most rigid σ-allylplatinum(II) complexes.

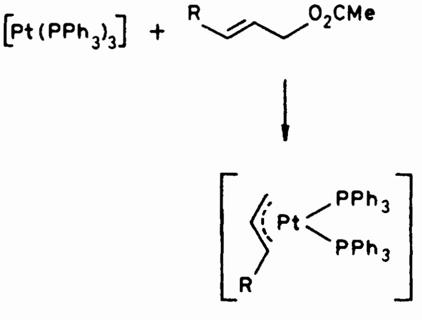
RESULTS AND DISCUSSION

Although it is generally accepted that organoplatinum(II) complexes are much more reluctant to undergo oxidative cleavage of metal–carbon bonds than the analogous organopalladium(II) complexes, I have found a very rapid quantitative reaction between η^3-allylplatinum(II) complexes and β-diketo-anions [equation (1)]. The initial product in this alkylation reaction may well be $[\mathrm{Pt(olefin)(PPh_3)_2}]$ (see later), which might be capable of undergoing oxidative-addition reactions. Moreover, since I have separately confirmed that the η^3-allylplatinum(II) complexes can be prepared easily by the reaction between $[\mathrm{Pt(PPh_3)_3}]$ and allyl acetates [equation (2)], it may also be expected that the reaction between allyl acetates and the β-diketo-anions occurs in the presence of a catalytic amount of phosphineplatinum complexes to give the same products as in equation (1). This was indeed found to be the case with $[\mathrm{Pt(PPh_3)_3}]$, $[\mathrm{Pt(\eta^3\text{-}allyl)(PPh_3)_2}]\mathrm{Cl}$ (allyl = $\mathrm{CH_2CH{=}CH_2}$, $\mathrm{CH_2CH{=}CHMe}$, or $\mathrm{CH_2CMe{=}CH_2}$), or $[\mathrm{PtH(Cl)(PPh_3)_2}]$ as the effective catalyst [equation (3)]. A similar catalytic function of $[\mathrm{Pd(PPh_3)_4}]$ was reported in the alkylation of allyl acetates.[2] In this reaction, as well as in the related palladium-catalysed exchange of allyl groups between esters, ethers, and amines,[3] the formation of η^3-allylpalladium(II) intermediates from palladium(0) complexes and allyl carboxylates has been postulated,



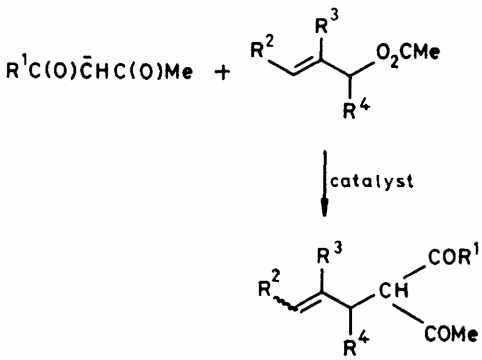
(1)

R¹= Me or OMe ; R², R³, R⁴= H or Me



(2)

R = H or Me



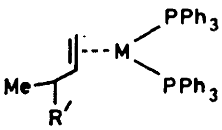
(3)

R¹= Me or OMe ; R², R³, R⁴= H or Me

but never confirmed. In any case, reaction (2) as well as its palladium analogue must be, more or less, reversible, and the irreversibility in the C–C bond-formation step may be important in driving the palladium- and platinum-catalysed alkylation of allyl acetates to completion.

Of further interest in equations (1) and (3) is the fact that the alkylation of $[Pt(\eta^3\text{-}CH_2CH{=}CHMe)Cl(PPh_3)_2]$ or $MeCH{=}CHCH_2O_2CMe$ and $CH_2{=}CHCH(Me)O_2CMe$ in the presence of the platinum catalysts gave a larger amount of $CH_2{=}CHCH(Me)R'$ [$R' = CH(COR)(COMe)$], a product of coupling at the secondary carbon, than $MeCH{=}CHCH_2R'$ (see Table 1). This result may be contrasted with the observation that the alkylation of $[Pd(\eta^3\text{-}CH_2CH{=}CHMe)Cl(PPh_3)_2]$ or both $MeCH{=}CHCH_2O_2CMe$ and $CH_2{=}CHCH(Me)O_2CMe$ in the presence of the palladium catalyst gave a larger amount of the product of coupling at the primary carbon (Table 1). In addition, it was reported previously [4] that treatment of $[Pd(\eta^3\text{-}CH_2CH{=}CHMe)(acac)]$ (acac = MeCOCHCOMe) with carbon monoxide in benzene affords $MeCH{=}CHCH_2CH(COMe)_2$ and $CH_2{=}CHCH(Me)CH(COMe)_2$ in a 6 : 1 ratio. However, the alkylation of $PhCH{=}CHCH_2O_2CMe$ using both the platinum and palladium catalysts resulted in almost preferential formation of $PhCH{=}CHCH_2R'$.

Factors which affect the regioselectivity in the allylic alkylation are difficult to explain satisfactorily,[5] but it is relevant to consider the stability of the initial products, $[M(olefin)(PPh_3)_2]$ (1) and (2), of which (1; M = Pt) was actually detected by ^1H n.m.r. spectroscopy (see Experimental section). For both the platinum and palladium complexes, steric repulsions may destabilise the metal–olefin interaction in (2) relative to that in (1). With regard to electronic effects, it was proposed previously that the order of π backbonding from the metal to the olefin in $[M(CH_2{=}CH_2)(PPh_3)_2]$ is Pt > Pd.[6a] Since less alkyl substitution at the olefinic carbon is expected to favour metal to olefin π donation,[6b] the combined effect of the electronic and steric factors should result in a greater difference between the stabilities of (1) and (2) for M = Pt than for M = Pd. The energy of the transition state [5] on the way to (1; M = Pt) may well be sufficiently lower than that to (2; M = Pt) to yield a larger amount of $CH_2{=}CHCH(Me)R'$.[*] The difference in the energy of the transition state is possibly less important in the reaction of the palladium complex, and the alkylation in this case could be controlled by the ease of approach of the nucleophile to the opposite side of the η^3-but-2-enyl plane with respect to the palladium atom,[2] affording the primary coupling product in higher yield.



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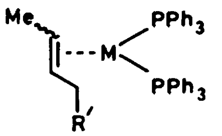


(2)

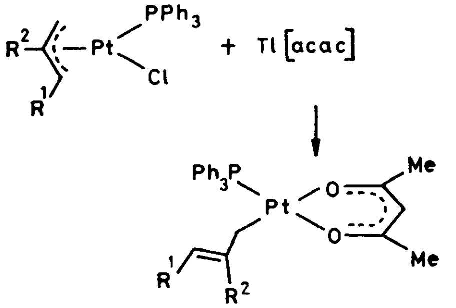
TABLE 1

Alkylation of η^3-but-2-enylmetal complexes or but-2-enyl acetate

Nucleophile	Reagent [a]	Catalyst [a]	$[MeCH{=}CHCH_2CH(COR)(COMe)]$: $[CH_2{=}CHCH(Me)CH(COR)(COMe)]$
$Tl[CH(COMe)_2]$	Pt		0.59
	$R'O_2CMe$	Pt	0.67
	Pd		2.23
	$R'O_2CMe$	Pd	2.03
$Tl[CH(CO_2Me)(COMe)]$	Pt		0.59
	$R'O_2CMe$ [b]	Pt	0.54
	Pd		2.04
	$R'O_2CMe$ [b]	Pd	1.50

[a] Pt ≡ $[Pt(\eta^3\text{-}CH_2CH{=}CHMe)Cl(PPh_3)_2]$, Pd ≡ $[Pd(\eta^3\text{-}CH_2CH{=}CHMe)Cl(PPh_3)_2]$, $R' = MeCH{=}CHCH_2$. [b] An almost identical result was obtained with $CH_2{=}CHCH(Me)O_2CMe$.

Isolation of (*σ-Allyl*)(*pentane-*2,4-*dionato*)*platinum*(II) *Complexes*.—It was pointed out previously [2,7] that 2 mol of tertiary phosphine ligand per Pd atom are preferable for a clean alkylation reaction to occur between $[Pd(\eta^3\text{-allyl})Cl]$ and the β-diketo-nucleophiles. In view of this fact, it seems particularly interesting that (σ-allyl)(pentane-2,4-dionato)platinum(II) complexes, (3), can be isolated from reaction (4) by employing a 1 : 1 ratio of PPh_3 to Pt. Complexes (3) are stable in the solid state, and in hot benzene or tetrahydrofuran solution. Addition of 1 mol of PPh_3 to a chloroform solution of (3)



(4)

(3a) $R^1 = R^2 = H$
(3b) $R^1 = Me, R^2 = H$
(3c) $R^1 = H, R^2 = Me$

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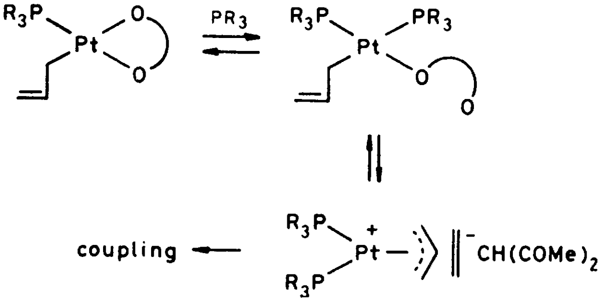
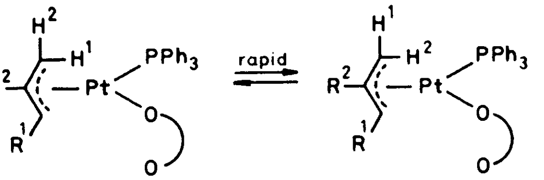
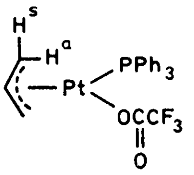
[*] In view of the greater tendency of η^3-allylplatinum(II) complexes to form σ-allyl species compared to the palladium(II) analogues,[1] a greater degree of bond distortion in the η^3-but-2-enylplatinum(II) than in the corresponding palladium(II) complex is an attractive alternative explanation [5] for the different regioselectivity in the two metal systems, although we could not confirm such a difference in bond distortion spectroscopically.

caused an immediate coupling to occur to give the alkylation products. However, only a small amount of these products could be obtained from slow decomposition of (3) in the same solution at higher temperature, in the absence of the phosphine, although the major products in this case remain to be identified. Complexes of the type [M(η^3-allyl)(acac)] (M = Pd or Pt) having a chelated pentane-2,4-dionate ligand are also stable in solution.[8] These facts suggest that the role of the two molecules of phosphine in the allylic alkylation can be attributed, in part, to their ability to inhibit the chelation of the β-diketo-anions to the metal, thereby promoting ionic dissociation of these anions.[9] Nucleophilic attack of the anions at the η^3-allyl plane in cationic complexes has been suggested to be a ready process.[10]



The synthesis, ^{1}H n.m.r. spectra, and crystal structure of σ-allyl-palladium(II) and -platinum(II) complexes have received much attention in the last few years,[1,11,12] in view of the role of these species as intermediates in reactions of η^3-allylmetal complexes. I believe that complexes (3) represent one of the most rigid types of σ-allyl complex of these metals in solution, as will be described below. The chelate co-ordination of the acac ligand appears so tight that the ^{1}H n.m.r. spectra of (3) at room temperature can be satisfactorily interpreted in terms of rigid σ-allyl–platinum bonding (see Table 2). An alternative form of bonding might involve a non-rigid η^3-allyl structure, *e.g.* as shown below. However, this possibility can be readily eliminated since the ^2J(Pt–CH$_2$) values of (3) are much larger than the average of J(Pt–H) for the *syn* (41.5 Hz) and *anti* protons (92 Hz) of [Pt(η^3-CH$_2$CH=CH$_2$)(acac)] [8] as well as the average of those (≤20, 82 Hz) of [Pt(η^3-CH$_2$CH=CH$_2$)(O$_2$CCF$_3$)(PPh$_3$)] (see Experimental section).





Most aspects of the ^{1}H n.m.r. spectra of (3) in benzene or 1,2-dichlorobenzene did not change significantly on heating except that two non-equivalent acac methyl resonances coalesced into singlets [coalescence temperatures: 90 (3a), 85 (3b), and 65 °C (3c)]. At these temperatures the coupling between ^{31}P and the CH$_2$ protons is still observable and the chemical shifts of the allylic as well as the ligand proton resonances are almost the same as those at room temperature, indicating that the predominant species at the higher temperatures is still the σ-allyl form without dissociation of the phosphine. The order of the coalescence temperatures above is the reverse of that of the tendency for the σ-allyl-platinum(II) form to be converted into the η^3-allyl form,[1] CH$_2$CH=CH$_2$ $\simeq$ CH$_2$CH=CHMe < CH$_2$CMe=CH$_2$. These results may suggest that the coalescence of the methyl-proton resonances in the acac ligand in (3) proceeds *via* η^3-allyl complex as an intermediate or the transition state. The existence of (3) predominantly as the σ-allyl form, even at high temperature, is in marked contrast to the ready dissociation of PPh$_3$ from *trans*-[Pt-(σ-CH$_2$CH=CHR)(C$_6$HCl$_4$)(PPh$_3$)$_2$] (R = H or Me) at 90 °C to form the η^3-allyl complexes.[1]

TABLE 2

Hydrogen-1 n.m.r. data [a] for [Pt(σ-allyl)(acac)(PPh$_3$)] complexes (3)

	Allyl				acac	
Complex	–CH$_2$–	–CH=		Me	Me	–CH=
(3a) [b]	2.33 (dd) J(H) 8.0 J(P) 4.0 J(Pt) 89	5.91 (ddt) J(H) 8.0 J(H') 16.5 J(H'') 9.8	4.7—4.2 (m)		1.55 (s) 1.92 (s)	5.28 (s)
(3b) [c]	2.43 (dd) J(H) 8.0 J(P) 4.0 J(Pt) 90	5.7 (m)	4.79 (dq) J(H) 6 J(H') 15	1.41 (d) J(H) 6 J(Pt) 20	1.52 (s) 1.91 (s)	5.20 (s)
(3c) [d]	2.92 (d) J(P) 4.0 J(Pt) 94		4.56 (br) 4.75 (br)	2.14 (s)	1.47 (s) 1.85 (s)	5.20 (s)

[a] Chemical shifts (δ) in p.p.m., J in Hz. [b] In CDCl$_3$. [c] In C$_6$H$_4$Cl$_2$-1,2. [d] In C$_6$H$_6$.

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded on a Japan Electron Optics JNM-PS-100 spectrometer with SiMe$_4$ as internal standard. The complexes [Pt(η^3-allyl)Cl(PPh$_3$)$_2$] [12,13] and [Pt(η^3-allyl)Cl(PPh$_3$)] [12] (allyl = CH$_2$CH=

CH_2, $CH_2CH{=}CHMe$, or $CH_2CMe{=}CH_2$) were prepared according to the reported methods. The complex $[Pd(\eta^3\text{-}CH_2CH{=}CHMe)Cl(PPh_3)_2]$ was prepared *in situ* by mixing a dichloromethane solution of $[\{Pd(\eta^3\text{-}CH_2CH{=}CHMe)Cl\}_2]$ with 2 equivalents of PPh_3, and this solution was used, without isolating the complex, for catalytic as well as stoicheiometric alkylation reactions. The salts $Tl[CH(COR)(COMe)]$ (R = Me or OMe) were prepared by treating thallium(I) ethoxide with the appropriate β-diketone in ethanol.

Allylic Alkylation.—Identification of the alkylation products was based on comparison of g.l.c., and of ^1H n.m.r. spectra, with those of authentic samples prepared by the reaction of sodium salts of the β-diketo-compounds with the appropriate allyl chlorides. Total yields of the alkylation products always exceeded 90%. The isomer ratio, $[MeCH{=}CHCH_2CH(COMe)_2]:[CH_2{=}CHCH(Me)CH(COMe)_2]$ was determined by ^1H n.m.r. spectroscopy on the basis of the peak areas due to $-CH{=}CH-$ (δ 5.2—5.8), $CH_2{=}C\lt$ (4.9—5.1), as well as $MeCH{=}C-$ [1.61, J(H) 6.0] and $-MeCH-$ [0.98 p.p.m., J(H) 6.7 Hz]. The ratio $[MeCH{=}CHCH_2CH(CO_2Me)(COMe)]:[CH_2{=}CHCH(Me)CH(CO_2Me)(COMe)]$ was determined similarly. The compound $MeCH{=}CHCH_2R'$ [$R' = CH(COR)(COMe)$] always contained a small amount of the *Z* isomer, but its exact amount was not determined.

Stoicheiometric alkylation. In a typical experiment, $Tl[CH(COMe)_2]$ (91 mg, 0.30 mmol) was added to a stirred solution of $[Pt(\eta^3\text{-}CH_2CH{=}CHMe)Cl(PPh_3)_2]$ (243 mg, 0.30 mmol) in dichloromethane (2 cm^3) under nitrogen at room temperature. Precipitation of TlCl occurred immediately, and the solution became reddish brown. After 30 min $CCl_2{=}CCl_2$ (50 mg, 0.30 mmol) was added, and the solution was filtered. The solvents were removed *in vacuo*, and the residual mixture was subjected to g.l.c. and ^1H n.m.r. analyses. The ^1H n.m.r. spectrum of the reaction mixture before adding $CCl_2{=}CCl_2$ showed that the amount of $MeCH{=}CHCH_2CH(COMe)_2$[14] present was almost identical with that in Table 1, but the resonances due to $CH_2{=}CHCH(Me)CH(COMe)_2$[14] were very weak. Instead, a slightly broadened doublet [0.51 p.p.m., J(H) 6.4 Hz] and two singlets (1.90, 2.03 p.p.m.) were observed, all of which disappeared completely on adding $CCl_2{=}CCl_2$ or PPh_3, and were replaced by the resonances due to $CH_2{=}CHCH(Me)CH(COMe)_2$.

Similarly, the spectrum of the reaction mixture from $[Pt(\eta^3\text{-}CH_2CH{=}CHMe)Cl(PPh_3)_2]$ and $Tl[CH(CO_2Me)(COMe)]$ before adding $CCl_2{=}CCl_2$ showed, besides the resonances of $MeCH{=}CHCH_2CH(CO_2Me)(COMe)$ [1.62 (d), J(H) 5.9 Hz, 3 H; 2.19 (s), 3 H; 2.52 (br), 2 H; 3.68 (s) p.p.m., 3 H], a pair of doublets [0.50, J(H) 6.5; 0.62 p.p.m., J(H) 6.5 Hz] and two pairs of singlets (1.96, 1.99; 3.55, 3.61 p.p.m.), all of equal intensity, which again disappeared completely on adding $CCl_2{=}CCl_2$. In this case the two doublets were replaced by those [1.02, J(H) 6.7; 1.06 p.p.m., J(H) 6.7 Hz] of $CH_2{=}CHCH(Me)CH(CO_2Me)(COMe)$. The sets of resonances which disappear on treatment with $CCl_2{=}CCl_2$ or PPh_3 are assigned to those of [1; M = Pt, $R' = CH(COMe)_2$ or $CH(CO_2Me)(COMe)$], although the olefinic proton resonances of these complexes could not be detected, possibly owing to their broadness and superimposition with more intense absorptions. In these experiments, the addition of more than a five-fold excess of PPh_3 to the reaction mixture caused precipitation of yellow crystalline $[Pt(PPh_3)_4]$. No ^1H n.m.r. evidence for the palladium analogues (1) or (2) (M = Pd) could be obtained in the analogous reaction mixture from $[Pd(\eta^3\text{-}CH_2CH{=}CHMe)Cl(PPh_3)_2]$.

Catalytic alkylation. In a typical experiment, to a stirred dichloromethane solution (5 cm^3) containing allyl acetate (100 mg, 1.00 mmol) and 0.05 mmol of the catalyst $\{[Pt(\eta^3\text{-}allyl)Cl(PPh_3)_2]$, $[PtH(Cl)(PPh_3)_2]$, or $[Pt(PPh_3)_3]\}$ was added $Tl[CH(COMe)_2]$ (303 mg, 1.00 mmol) under nitrogen. The solution was stirred vigorously for 30 min. After filtration, the solvent was evaporated *in vacuo*, and the residue when examined by g.l.c. and by ^1H n.m.r. spectroscopy showed almost quantitative formation of $CH_2{=}CHCH_2CH(COMe)_2$.

Reaction of Allyl Acetate with $[Pt(PPh_3)_3]$.—To a dichloromethane solution (10 cm^3) of $[Pt(PPh_3)_3]$ (196 mg, 0.20 mmol) was added allyl acetate (50 mg, 0.50 mmol) under nitrogen. The initial yellow colour of the solution paled gradually. A slight excess of $Na[ClO_4]$ was then added and the solvent was removed *in vacuo*. The resulting solid was recrystallised from CH_2Cl_2–n-hexane to give 103 mg (60%) of $[Pt(\eta^3\text{-}allyl)(PPh_3)_2][ClO_4]$.[15] The complex $[Pt(\eta^3\text{-}CH_2CH{=}CHMe)(PPh_3)_2][ClO_4]$[15] was obtained similarly.

Preparation of (σ-*Allyl*)(*pentane*-2,4-*dionato*)(*triphenylphosphine*)*platinum*(II).—A benzene solution (10 cm^3) containing $[Pt(\eta^3\text{-}allyl)Cl(PPh_3)]$ (160 mg, 0.30 mmol) and $Tl[CH(COMe)_2]$ (91 mg, 0.30 mmol) was stirred vigorously for 2 h. The precipitate of TlCl was filtered off, and the volume of the solution reduced to *ca.* 3 cm^3 *in vacuo*. n-Hexane (*ca.* 5 cm^3) was added and the solution was kept in a refrigerator overnight, to give 80 mg (45%) of fine crystalline $[Pt(\sigma\text{-}CH_2CH{=}CH_2)(acac)(PPh_3)]$ (3a), m.p. 145—146 °C (decomp.) (Found: C, 52.4; H, 4.6. Calc. for $C_{26}H_{27}O_2PPt$: C, 52.2; H, 4.5%); i.r. spectrum in Nujol 1 615 [ν(C=C)], 1 580 and 1 517 cm^{-1} (acac). Complexes (3b), m.p. 155 °C (decomp.) (Found: C, 52.5; H, 4.7. Calc. for $C_{27}H_{29}O_2PPt$: C, 53.0; H, 4.8%) and (3c), m.p. 118—120 °C (decomp.) (Found: C, 53.0; H, 4.8. Calc.: C, 53.0; H, 4.8%) were obtained similarly. Infrared spectrum in Nujol: (3c), 1 625 cm^{-1} [ν(C=C)].

Preparation of (1—3-η-*Allyl*)(*trifluoroacetato*)(*triphenylphosphine*)*platinum*(II).—To a dichloromethane solution (5 cm^3) of $[Pt(\eta^3\text{-}CH_2CH{=}CH_2)Cl(PPh_3)]$ (220 mg, 0.41 mmol) was added $Ag[O_2CCF_3]$ (90 mg, 0.41 mmol) in methanol (2 cm^3). The solution was stirred for 3 h at room temperature, filtered, the filtrate evaporated to dryness, and the residue recrystallised from acetone–n-hexane to give 150 mg (60%) of a colourless crystalline solid, m.p. 155—160 °C (decomp.) (Found: C, 45.0; H, 3.3. Calc. for $C_{23}H_{20}F_3O_2PPt$: C, 45.2; H, 3.3%); i.r. spectrum in Nujol 1 680 cm^{-1} [ν(CO)]. Hydrogen-1 n.m.r. spectrum in $CDCl_3$: 2.20 (br d), J(H) 12, J(Pt) 82 Hz; 2.94 (vbr), width at half-height *ca.* 15 Hz; 3.39 (dd), J(H) 13.5, J(P) 9, J(Pt) 30 Hz; and 4.6—5.2 (m) p.p.m.

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