The Oxidative Addition of Allylic Halides to Bis(cyclo-octa-1,5-diene)platinum; Dynamic Behaviour of σ- and 1—3-η-Allyl(cyclo-octa-1,5-diene)platinum Complexes

By **Neil M. Boag, Michael Green, John L. Spencer, and F. Gordon A. Stone,** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Addition of [Pt(cod)$_2$] (cod = cyclo-octa-1,5-diene) to an excess of an allylic halide affords crystalline compounds [PtX(σ-allyl)(cod)] (X = Cl or Br; allyl = C_3H_5, 2-MeC_3H_4, 3-MeC_3H_4, or 3-PhC_3H_4). Halide-anion abstraction with silver tetrafluoroborate yields the cationic complexes [Pt(η^3-allyl)(cod)][BF_4]. The variable-temperature ^{1}H and ^{13}C n.m.r. spectra are reported, and discussed in terms of a dynamic process involving reversible co-ordination of a donor solvent molecule.

In recent years there has been considerable interest in the synthesis and dynamic behaviour [1,2] of allylic metal complexes. By comparison with nickel [3] and palladium,[4] there have been relatively few studies of the platinum systems,[1,5-10] probably because of a lack of suitable synthetic pathways. The development of a practical synthesis of bis(cyclo-octa-1,5-diene)platinum [11] provided an opportunity to study the reaction of this platinum(0) complex with allylic halides, the corresponding reactions with bis(cyclo-octa-1,5-diene)nickel [3] having been shown to afford the halogen-bridged species [{Ni(μ-X)(η^3-allyl)}$_2$] (X = Cl or Br).

RESULTS AND DISCUSSION

Addition of [Pt(cod)$_2$] (cod = cyclo-octa-1,5-diene) to an allyl halide in light petroleum at room temperature gave in good yield the crystalline compounds (1)—(8) characterised by elemental analysis (Table 1), and by i.r. and n.m.r. spectroscopy (Tables 2 and 3) as monomeric σ-allyl complexes [PtX(σ-$CH_2CR^1{=}CHR^2$)(cod)]. If the reactants are mixed in the reverse order then red-brown powders of indeterminate composition are obtained. Although the i.r. spectra of (1)—(3) and (6)—(8) showed bands characteristic of an unco-ordinated C=C group and a Pt–Cl system at *ca.* 1 620 and 320 cm^{-1}, respectively, the crotyl species (4) and (5) did not show a band in the 1 620 cm^{-1} region, although the presence of a σ-crotyl group was firmly established by ^{1}H and ^{13}C n.m.r. spectroscopy. A rather low Pt–Cl stretching frequency was also observed for (4) (Table 1), although this may be coincidental. The absence of a ν(C=C) stretch in the i.r. spectrum of *trans*-[Pt(σ-crotyl)(σ-C_6HCl_4)(PPh_3)$_2$] has been previously noted but not discussed.[12]

Examination of the ^{1}H and ^{13}C n.m.r. spectra of (1)—(3) and (8), *i.e.* those complexes without a substituent in the 3-position, indicated that these compounds exhibited dynamic behaviour in solution. The terminally substituted analogues (4)—(7) were rigid on the n.m.r. time scale. Since the observation of limiting spectra for (1)—(3) required a temperature range in excess of 160 °C it was only possible to study completely the dynamic behaviour of the 2-chloro-substituted derivative (8).

The ^{13}C spectra of the rigid molecules (4)—(7) showed a resonance at *ca.* 28 p.p.m. with a coupling ^1J(PtC) *ca.* 540 Hz, characteristic [13] of a carbon atom [C^1] σ-bonded to platinum (Table 2). As expected from the ^{1}H spectra (Table 3), the protons H^1 and H^2 were equivalent showing a distinctive resonance at τ *ca.* 7 [^2J(PtH) *ca.* 95 Hz]. In the dynamic compounds (1)—(3), all of which contain symmetrical σ-allyl groups (R^2 = H), the carbon environments C^1 and C^3 are time-averaged, and occur near 70 p.p.m. [J(PtC) *ca.* 300 Hz]. This allowed identification

TABLE 1

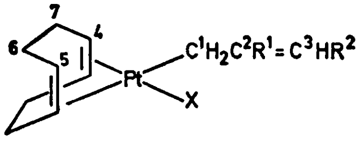
Allylplatinum compounds [PtX(σ-$CH_2CR^1{=}CHR^2$)(cod)] (1)—(8) and [Pt(η^3-$CH_2CR^1CHR^2$)(cod)][BF_4] (9)—(12)

	Complex [a]	M.p. (θ_c/°C)	Yield (%)	Analysis (%) [b]		I.r.[c] (cm^{-1})	
				C	H	ν(C=C)	ν(PtCl)
(1)	$R^1 = R^2 = H$, X = Cl [d]	92—94 (decomp.)	95	34.5 (34.8)	4.5 (4.5)	1 615	327
(2)	$R^1 = R^2 = H$, X = Br	92—93	84	31.0 (31.1)	4.1 (4.0)	1 614	
(3)	R^1 = Me, R^2 = H, X = Cl [e]	45—46	72	36.7 (36.6)	5.1 (4.9)	1 617	323
(4)	R^1 = H, R^2 = Me, X = Cl	108—109	98	36.6 (36.6)	5.0 (4.9)		304
(5)	R^1 = H, R^2 = Me, X = Br	107—110	90	32.7 (32.9)	4.4 (4.4)		
(6)	R^1 = H, R^2 = Ph, X = Cl	137—138 (decomp.)	97	44.8 (44.8)	4.8 (4.4)	1 616	323
(7)	R^1 = H, R^2 = Ph, X = Br	133—134	90	40.6 (40.8)	4.0 (4.2)	1 615	
(8)	R^1 = Cl, R^2 = H, X = Cl [f]	79—80	78	31.8 (31.9)	3.8 (3.9)	1 616	325
(9)	R^1 = H, R^2 = H	191—196 (decomp.)	84	30.6 (30.6)	4.0 (4.0)		
(10)	R^1 = Me, R^2 = H	>250	89	32.4 (32.4)	4.3 (4.3)		
(11)	R^1 = H, R^2 = Me	184 (decomp.)	72	32.2 (32.4)	4.3 (4.3)		
(12)	R^1 = H, R^2 = Ph	108—109	79	40.4 (40.3)	4.4 (4.2)		

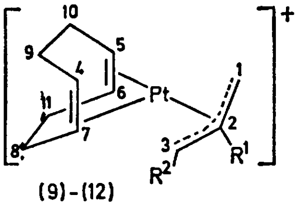
[a] All the complexes are white, except (6) which is yellow, (8) which is orange, and (7) which is burnt orange. [b] Calculated values are given in parentheses. [c] Nujol mull. [d] Cl, 9.8 (9.3%). [e] Cl, 8.9 (9.0%). [f] Cl, 16.8 (17.1%).

TABLE 2

Carbon-13 n.m.r. data [a]



(1)-(8)



(9)-(12)

Complex	R^1	R^2	X	C^1	C^2	C^3	C^4	C^5	C^6	C^7
(1)	H	H	Cl	69.9 (300)	140.9 (48)	69.9 (300)	99.4 (131)	99.4 (131)	29.9	29.9
(2)	H	H	Br	69.1 (284)	140.3 (41)	69.1 (284)	99.7 (127)	99.7 (127)	30.0	30.0
(3)	Me [b]	H	Cl	70.2 (295)	148.3 (30)	70.2 (295)	100.0 (131)	100.0 (131)	29.9	29.9
(4)	H	Me [c]	Cl	27.0 (554)	133.2 (46)	121.6 (38)	84.9 (234)	113.5 (27)	31.8 (24)	28.1 (24)
(5)	H	Me [c]	Br	26.5 (535)	133.0 (44)	120.8 (37)	86.6 (236)	112.4 (29)	31.7 (23)	28.3 (23)
(6)	H	Ph [d]	Cl	28.8 (547)	133.7 (53)	126.1 (38)	85.4 (225)	113.4 (30)	32.0 (24)	28.0 (23)
(7)	H	Ph [d]	Br	28.0 (533)	134.0 (51)	126.1 (37)	87.1 (223)	112.7 (31)	31.7 (23)	28.3 (21)
(8) [e]	Cl	H	Cl	29.8 (616)	146.2 (55)	110.9 (71)	89.0 (214)	113.0 (39)	31.9 (18)	28.5 (16)
(8) [f]	Cl	H	Cl		146.6		100.1 (115)	100.1 (115)	29.9	29.9
(9) [e,g]	H	H		68.0 (144)	122.0 (45)	68.0 (144)	104.5 (128)	104.5 (128)	102.5 (104)	102.5 (104)
(9) [h,i]	H	H		68.1 (145)	122.0 (46)	68.1 (145)	103.8 (116)	103.8 (116)	103.8 (116)	103.8 (116)
(10) [e,i]	Me [j]	H		67.2 (153)	140.1 (44)	67.2 (153)	103.4 (125)	103.4 (125)	102.0 (101)	102.0 (101)
(10) [h,k]	Me [l]	H		67.5 (153)	140.4	67.5 (153)	103.1 (114)	103.1 (114)	103.1 (114)	103.1 (114)
(11) [e,m]	H	Me [c]		62.5 (172)	121.1 (51)	87.2 (117)	103.7 (128)	109.5 (134)	103.2 (104)	102.5 (106)
(11) [h,k]	H	Me [n]		62.5 (175)	121.3 (51)	87.8 (118)	103.7	103.7	103.7	103.7
(12) [e,o]	H	Ph [p]		62.9 (171)	115.5 (49)	89.3 (106)	103.7 (132)	112.4 (139)	104.3 (110)	102.4 (106)
(12) [h,q]	H	Ph [r]		63.0 (176)	115.5 (48)	90.3 (107)	103.4	103.4	103.4	103.4

[a] Measured at 26 °C in $CDCl_3$ unless otherwise indicated. Chemical shifts (δ) in p.p.m. relative to $SiMe_4$, positive values to high frequency; $^{195}Pt-^{13}C$ coupling constants (Hz) given in parentheses throughout Table. [b] Resonance for Me group at 25.1. [c] Resonance for Me group at 17.3. [d] Resonances for Ph group at 138.7(12), 125.7, 128.4, and 126.0 p.p.m. [e] In $CH_2Cl_2-CD_2Cl_2$ at −90 °C. [f] In $CD_3C_6D_5$ at 70 °C, resonances for C^1 and C^3 not observed. [g] Resonances for C^8 and C^9 at 30.3(17), and for C^{10} and C^{11} at 30.2(7) p.p.m. [h] In $CH_2Cl_2-CD_2Cl_2$ at 26 °C. [i] Resonances for C^8-C^{11} at 30.3(10) p.p.m. [j] Resonance for Me group at 25.3(42) p.p.m. [k] Resonances for C^8-C^{11} at 30.5 p.p.m. [l] Resonance for Me group at 25.0(44) p.p.m. [m] Resonances for C^8 at 31.0, C^9 30.8(15), C^{10} 29.8(17), and C^{11} 29.1 p.p.m. [n] Resonance for Me group at 17.1 p.p.m. [o] Resonances for C^8 at 31.0, C^9 30.5, C^{10} 30.0, and C^{11} 29.0 p.p.m. [p] Resonances for Ph group at 127.5, 129.6, and 134.6 p.p.m. [q] Resonances for C^8 and C^9 at 30.8(11), and for C^{10} and C^{11} 29.6 p.p.m. [r] Resonances for Ph group at 127.0, 130.1, 129.9, and 134.9 p.p.m.

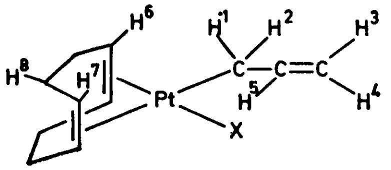
of the resonance for C^3 in the non-dynamic molecules, since the mean of the C^1 and C^3 resonances measured for (4)—(7) should correspond to the time-averaged signal observed for (1)—(3). Thus the resonances at 121 p.p.m. for the crotyl derivatives (4) and (5), and at 126 p.p.m. for the cinnamyl compounds (6) and (7), are due to C^3 in these species. The remaining ^{13}C-allyl resonance is then assignable to C^2, occurring at *ca.* 134 p.p.m. in the rigid complexes and at 140—148 p.p.m. in the dynamic molecules.

Whereas the ^1H n.m.r. spectra of the dynamic molecules are readily assigned (Table 3), the corresponding spectra of the rigid compounds (4)—(7) present a problem in interpretation in that the central proton (R^1 = H) and the terminal proton H^3 have absorptions in the same region, resulting in an AB pattern, which on coupling to the equivalent methylene protons H^1 and H^2 gives rise to an ABX_2 spectrum. This multiplet was better resolved in the cinnamyl derivatives (6) and (7) with *J*(BX) *ca.* 0, thus allowing the spectra to be analysed; the presence of a large $J(H^3H^5)$ coupling of 15 Hz suggested a *trans* configuration for the $PtCH_2C=CPh$ system. In the crotyl compounds (4) and (5) the signal due to H^3 and R^1 ($=H^5$) couples to the methyl group resonance affording ABM_2X_3 spectra. Although *J*(AX) and *J*(BM) ≃ 0 Hz, analysis proved impossible for (5), because the multiplet overlaps a methine resonance of the co-ordinated cyclo-octa-1,5-diene. However, partial decoupling experiments on (4) enabled the chemical shifts and coupling constants to be determined, indicating a *trans* configuration for the crotyl ligand.

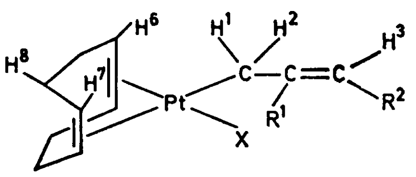
The square-planar geometry of the platinum(II) species results in inequivalence of the methine carbons and protons of the cyclo-octa-1,5-diene because of the presence of different *trans* ligands. In the dynamic molecules averaging occurs of the ^{13}C and ^{1}H resonances. In the case of the rigid compounds the large *trans* influence of the σ-allyl ligand results in the *trans*-olefinic resonances having the smaller ^{195}Pt–^{13}C and ^{195}Pt–^{1}H coupling constant, compared to those for the olefin *trans* to chlorine.

TABLE 3

Hydrogen-1 n.m.r. data for the σ-allylplatinum compounds [a]



(1) and (2)



(3)-(8)

Complex	R^1	R^2	X	
(1)	H	H	Cl	7.6 (m br, 8 H, H^8), 6.26 [d, 4 H, H^{1-4}, $J(H^{1-4}H^5)$ 11, J(PtH) 54], 4.99 [s, 4 H, $H^{6,7}$, J(PtH) 56], 3.91 [qt, 1 H, H^5, $J(H^5H^{1-4})$ 11]
(2)	H	H	Br	7.6 (m br, 8 H, H^8), 6.26 [d, 4 H, H^{1-4}, $J(H^{1-4}H^5)$ 11, J(PtH) 54], 4.95 [s, 4 H, $H^{6,7}$, J(PtH) 58], 3.88 [qt, 1 H, H^5, $J(H^5H^{1-4})$ 11]
(3)	Me	H	Cl	8.12 (s, 3 H, Me), 7.6 (m br, 8 H, H^8), 6.35 [s, 4 H, H^{1-4}, J(PtH) 54], 4.98 [s, 4 H, $H^{6,7}$, J(PtH) 55]
(4)	H	Me	Cl	8.42 [d, 3 H, Me, $J(MeH^3)$ 7, J(PtMe) 14], 7.6 (m br, 8 H, H^8), 7.53 [d, 2 H, $H^{1,2}$, $J(H^{1,2}H^5)$ 8, J(PtH) 95], 5.64 [s, 2 H, H^6, J(PtH) 77], 4.65 [d of q, 1 H, H^3, $J(H^3H^5)$ 13, $J(H^3Me)$ 7], 4.48 [s, 2 H, H^7, J(PtH) 36], 4.35 [d of t, 1 H, H^5, $J(H^5H^3)$ 13, $J(H^5H^{1,2})$ 8]
(5)	H	Me	Br	8.39 [d, 3 H, Me, $J(MeH^3)$ 7, J(PtMe) 12], 7.65 (m br, 8 H, H^8), 7.40 [d, 2 H, $H^{1,2}$, $J(H^{1,2}H^5)$ 7, J(PtH) 92], 5.54 [s, 2 H, H^6, J(PtH) 78], *ca.* 4.60 (m, 2 H, $H^{3,5}$), 4.42 [s, 2 H, H^7, J(PtH) 34]
(6)	H	Ph	Cl	7.7 (m, br, 8 H, H^8), 7.28 [d, 2 H, $H^{1,2}$, $J(H^{1,2}H^5)$ 7, J(PtH) 94], 5.56 [s, 2 H, H^6, J(PtH) 76], 4.42 [s, 2 H, H^7, J(PtH) 36], 3.66 [d, 1 H, H^3, $J(H^3H^5)$ 15, J(PtH) 7], 3.46 [d of t, 1 H, H^5, $J(H^5H^3)$ 15, $J(H^5H^{1,2})$ 7], 2.8 (m, 5 H, Ph)
(7)	H	Ph	Br	7.7 (m br, 8 H, H^8), 7.18 [d, 2 H, $H^{1,2}$, $J(H^{1,2}H^5)$ 8, J(PtH) 96], 5.50 [s, 2 H, H^6, J(PtH) 77], 4.42 [s, 2 H, H^7, J(PtH) 40], 3.69 [d, 1 H, H^3, $J(H^3H^5)$, 15, J(PtH) 8], 3.42 [d of t, 1 H, H^5, $J(H^5H^3)$ 15, $J(H^5H^{1,2})$ 8], 2.8 (m, 5 H, Ph)
(8) [b]	Cl	H	Cl	7.56 (s, 8 H, H^8), 6.12 [s, 4 H, H^{1-4}, J(PtH) 60], 4.85 [s, 4 H, $H^{6,7}$, J(PtH) 57]
(8) [c]	Cl	H	Cl	7.54 (s, 8 H, H^8), 7.29 [s, 2 H, $H^{1,2}$, J(PtH) 103], 5.28 [s, 2 H, H^6, J(PtH) 72], [d] 5.14 [s, 1 H, H^4, J(PtH) 15], [d] 4.98 [s, 1 H, H^3, J(PtH) 18], 4.53 [s, 2 H, H^7, J(PtH) 40]

[a] Measured in $CDCl_3$ solutions at 26 °C unless otherwise stated. Chemical shifts in τ, coupling constants in Hz. [b] Measured in $(CD_3)_2CO$ at 55 °C. [c] Measured in $(CD_3)_2CO$ at −90 °C. [d] Assignments for H^3 and H^4 might be reversed (see text).

The temperature-dependent ^{1}H spectrum of the dynamic system [PtCl{σ-$CH_2C(Cl)=CH_2$}(cod)] (8) is illustrated in Figure 1. At 55 °C the allyl group is dynamic and H^1, H^2, H^3, and H^4 are equivalent and appear at τ 6.12 [J(PtH) 60 Hz]. The positions H^6 and H^7 are also equivalent and absorb at τ 4.85 [^{2}J(PtH) 57 Hz]. At 26 °C the allyl signals have nearly collapsed, and the cyclo-octa-1,5-diene methine resonances are showing evidence of broadening. On cooling to 0 °C the ^{1}H spectrum shows no allyl signals and the H^6,H^7 resonance appears as a broad hump. At −30 °C ill defined resonances are visible at τ *ca.* 5, and under the methylene signals of the cyclo-octa-1,5-diene at τ 7.5. At −90 °C the resonances are completely resolved. The two equivalent allyl protons H^1 and H^2 resonate at τ 7.29 [^{2}J(PtH) 103 Hz], consistent with those established for the rigid complexes (4)—(7). The signals at τ 4.98 [^{4}J(PtH) 18] and 5.14 [^{4}J(PtH) 15 Hz] are assignable to H^3 and H^4, but more specific identification is not possible. The average ^{195}Pt–^{1}H coupling exhibited by H^1–H^4 (59.75 Hz) is in good agreement with the values of 60 Hz observed in the time-averaged spectra. At −90 °C the methine resonance of the co-ordinated cyclo-octa-1,5-diene shows splitting. The resonance at τ 5.28 [^{2}J(PtH) 72 Hz] is assigned to H^6, whilst that at τ 4.53 is attributable to H^7, because of the smaller ^{195}Pt–^{1}H coupling constant (40 Hz).

The equivalence of the cyclo-octa-1,5-diene ligand signals at high temperature suggests that exchange of the ends of the allyl moieties occurs *via* initial formation of a symmetrical five-co-ordinate η^3-allyl species, which may be in equilibrium with a cationic η^3-allyl system (Scheme 1). As illustrated, the five-co-ordinate square-pyramidal species can undergo a synchronous twisting and η^3- to σ-transformation of the bonding mode of the allyl system thus affording the σ-allyl species. It can be seen that if the allyl system carried a terminal substituent then thermodynamic control would favour the formation of the σ-allyl system where the carbon directly bonded to the platinum is least substituted. Thus the end-substituted σ-allyl systems would not be expected to be dynamic, as is observed.

Treatment of the compounds [PtX(σ-$CH_2CR^1=CHR^2$)-(cod)] with silver tetrafluoroborate in methylene chloride leads to rapid (room temperature) precipitation of silver halide and the formation of the η^3-allyl cationic complexes (9)—(12) (Tables 1, 2, and 4). Palladium [14] and platinum [15] cations of this type have been previously obtained by reaction of the halogen-bridged dimers

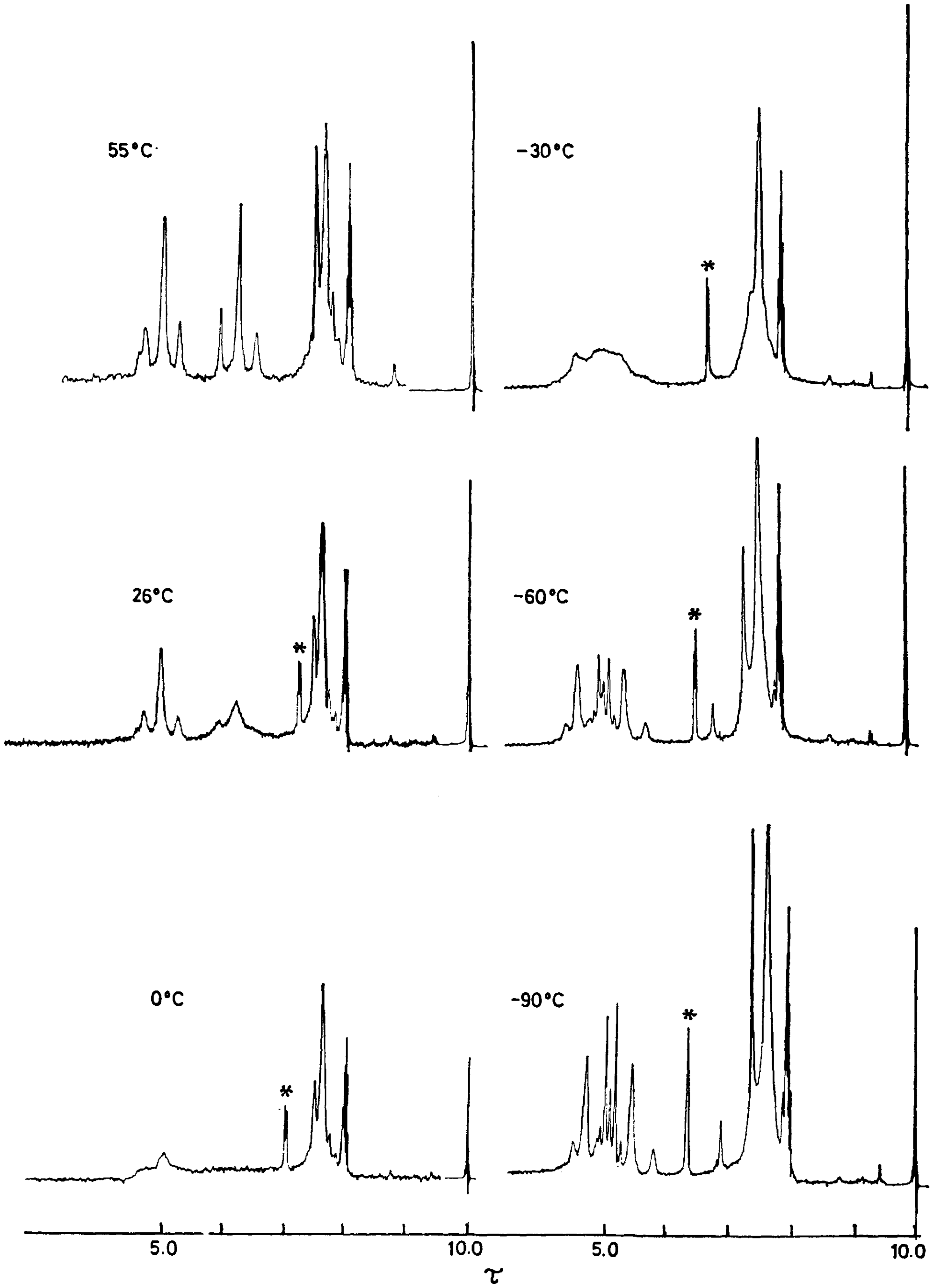


FIGURE 1 Hydrogen-1 n.m.r. spectra for [PtCl{σ-$CH_2C(Cl)=CH_2$}(cod)] (8) at various temperatures in [$^2H_6$]acetone. Water impurity indicated by an asterisk

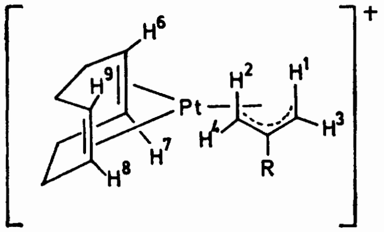
[{MCl(η^3-allyl)}$_2$] with silver salts in the presence of olefinic ligands.

Examination of the ^{13}C and ^1H n.m.r. spectra (Tables 2 and 4) showed that somewhat unexpectedly the allyl group exhibited dynamic behaviour in solution, the protons undergoing *syn–anti* exchange at room temperature. Exchange occurs at the unsubstituted carbon for the terminally substituted complexes (11) and (12), and is solvent dependent, being enhanced by co-ordinating solvents such as acetonitrile. Indeed, it was only possible to observe the fully dynamic spectra of the cations in [$^2H_6$]acetone by adding [$^2H_3$]acetonitrile. This behaviour contrasts with that observed for the species [Pt(η^3-allyl)L_2]X (L = PR_3 or pdma) [pdma = $(CH_3)_2AsC_6H_4As(CH_3)_2$], which are rigid when X = BF_4^-, ClO_4^-, or PF_6^-, but undergo *syn–anti* exchange when X is a halide.[16]

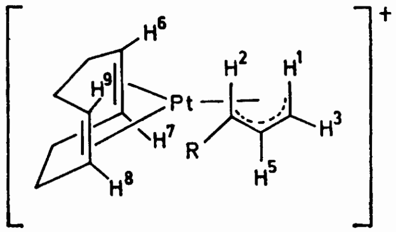
Examination of the ^1H spectra of (11) and (12) (Table

Table 4

Hydrogen-1 n.m.r. data for cationic complexes [a]



(9) and (10)

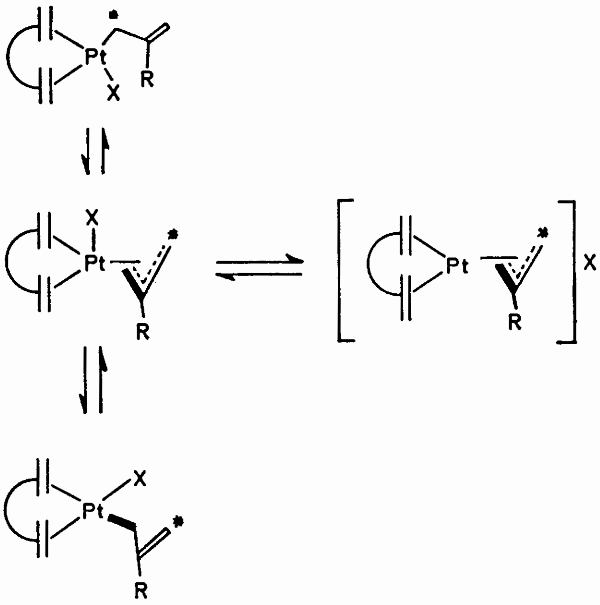


(11) and (12)

Complex	R	
(9) [b]	H	3.76 [s, 4 H, $H^{6,9}$, J(PtH) 76], 4.03 [qt, 1 H, H^5, $J(H^5H^{1-4})$ 11, J(PtH) 76], 5.81 [d, 4 H, H^{1-4}, $J(H^{1-4}H^5)$ 11, J(PtH) 20], 7.6 (m br, 8 H, CH_2)
(9) [c]	H	3.76 [s, 4 H, H^{6-9}, J(PtH) 70], 4.01 [t of t, 1 H, H^5, $J(H^5H^{1,2})$ 14, $J(H^5H^{3,4})$ 7, J(PtH) 74], 4.99 [d, 2 H, $H^{3,4}$, $J(H^{3,4}H^5)$ 7], 6.58 [d, 2 H, $H^{1,2}$, $J(H^{1,2}H^5)$ 14, J(PtH) 33], 7.45 (m br, 8 H, CH_2)
(10) [d]	Me	3.98 [s, 4 H, H^{6-9}, J(PtH) 70], 6.17 [s, 4 H, H^{1-4}, J(PtH) 19], 7.65 (m br, 8 H, CH_2), 8.06 [s, 3 H, Me, J(PtH) 87]
(10) [c,e]	Me	3.69 [s, 2 H, $H^{7,8}$, J(PtH) 78], 3.76 [s, 2 H, $H^{6,9}$, J(PtH) 60], 5.14 (s, 2 H, $H^{3,4}$), 6.76 [s, 2 H, $H^{1,2}$, J(PtH) 32], 7.5 (m br, 8 H, CH_2), 7.96 [s, 3 H, Me, J(PtH) 92]
(11) [b,f]	Me	3.80 [s, 2 H, CH(cod), J(PtH) 76], 4.18 [s, 2 H, CH(cod), J(PtH) 72], 4.20 [d of t, 1 H, H^5, $J(H^5H^2)$ 12, $J(H^5H^{1,3})$ 10, J(PtH) 79], 5.60 [d of q, 1 H, H^2, $J(H^2H^5)$ 12, $J(H^2Me)$ 6.5, J(PtH) 52], 6.12 [d, 2 H, $H^{1,3}$, $J(H^{1,3}H^5)$ 5, J(PtH) 19], 7.5 (m br, 8 H, CH_2), 7.91 [d, 3 H, Me, $J(MeH^2)$, 6.5 J(PtH) 4]
(11) [c,f]	Me	3.72 [s, 1 H, CH(cod), J(PtH) 68], 3.91 [s, 2 H, CH(cod), J(PtH) 72], 4.14 [d of d of d, 1 H, H^5, $J(H^5H^1)$ 15, $J(H^5H^2)$ 13, $J(H^5H^3)$ 5, J(PtH) 53], 4.50 [s, 1 H, CH(cod), J(PtH) 72], 5.33 [d, 1 H, H^3, $J(H^3H^5)$ 5, J(PtH) 13], 5.72 [d of q, 1 H, H^2, $J(H^2H^5)$ 13, $J(H^2Me)$ 6, J(PtH) 53], 6.88 [d, 1 H, H^1, $J(H^1H^5)$ 15, J(PtH) 27], 7.5 (m br, 8 H, CH_2), 7.87 [d, 3 H, Me, $J(MeH^2)$ 6]
(12) [f,g]	Ph [h]	3.39 [d of t, 1 H, H^5, $J(H^5H^2)$ 13, $J(H^5H^{1,3})$ 10, J(PtH) 77], 3.74 [s, 2 H, CH(cod), J(PtH) 74], 4.68 [d, 1 H, H^2, $J(H^2H^5)$ 13, J(PtH) 33], 4.90 [s, 2 H, CH(cod), J(PtH) 70], 5.89 [d, 2 H, $H^{1,3}$, $J(H^{1,3}H^5)$ 10, J(PtH) 18], 7.55 (m br, 8 H, CH_2)
(12) [f,i]	Ph [h]	3.35 (m, 1 H, H^5), 3.80 [s, 2 H, CH(cod), J(PtH) 82], 4.38 [s, 1 H, CH(cod)], 4.73 [d, 1 H, H^2, $J(H^2H^5)$ 12], 5.16 (m, 1 H, H^3), 5.75 [s, 1 H, CH(cod), J(PtH) 75], 6.68 (m, 1 H, H^1), 7.5 (m br, 8 H, CH_2)

[a] Chemical shifts in τ, coupling constants in Hz. [b] Measured at 55 °C in $(CD_3)_2CO$–CD_3CN (4 : 1). [c] Measured at −90 °C in $(CD_3)_2CO$. [d] Measured at 55 °C in CD_3CN. [e] Assignments for $H^{6,9}$ and $H^{7,8}$ may be reversed. [f] For discussion of cod signals see text. [g] Measured at 26 °C in $(CD_3)_2CO$–CD_3CN (4 : 1). [h] Ph resonance at τ 2.5 (m). [i] Measured at −130 °C in $(CD_3)_2CO$–CCl_2F_2 (1 : 1).

4), in particular the value for $J(H^2H^5)$, suggests that in these complexes the methyl and phenyl substituents occupy a *syn* position as illustrated. This provides further support for the conclusion that in the σ-crotyl and cinnamyl complexes a *trans* configuration is adopted by the allyl chain.



Scheme 1

The dynamic processes occurring in the platinum cations (9)—(12) are best exemplified by consideration of the variable-temperature ^1H spectra. The spectra for complex (10) are illustrated in Figure 2. At −70 °C in $[^2H_6]$acetone, the H^1,H^2 signal is observed at τ 6.76 [J(PtH) 32 Hz], H^3,H^4 at 5.14, and the methyl resonance at 7.96 [J(PtH) 92 Hz]. The co-ordinated cod methine resonances are observed as an overlapping pair of singlets at τ 3.76 [J(PtH) 60] and 3.69 [J(PtH) 78 Hz]. This arises since $H^7 \equiv H^8$ and $H^6 \equiv H^9$. A broad signal at τ *ca.* 7.5 is attributable to the cod CH_2 protons. On raising the temperature, broadening and ultimate collapse of the *syn* and *anti* resonances is observed, and is accompanied by simultaneous coalescence of the cod methine signals. By 50 °C, these protons are effectively equivalent, but the allyl protons are only visible as two broad signals. However, addition of *one* drop of $[^2H_3]$-acetonitrile causes the appearance of H^1–H^4 as a broad resonance at τ 5.93. Further dilution to a 25% solution of $[^2H_3]$acetonitrile sharpened this resonance with the appearance of platinum satellites. Unfortunately, solvent effects are evident, the signal shifting to τ 6.31. The fully dynamic spectrum (Figure 2) was obtained in neat $[^2H_3]$acetonitrile at 50 °C.

These observations are consistent with a π–σ–π trans-

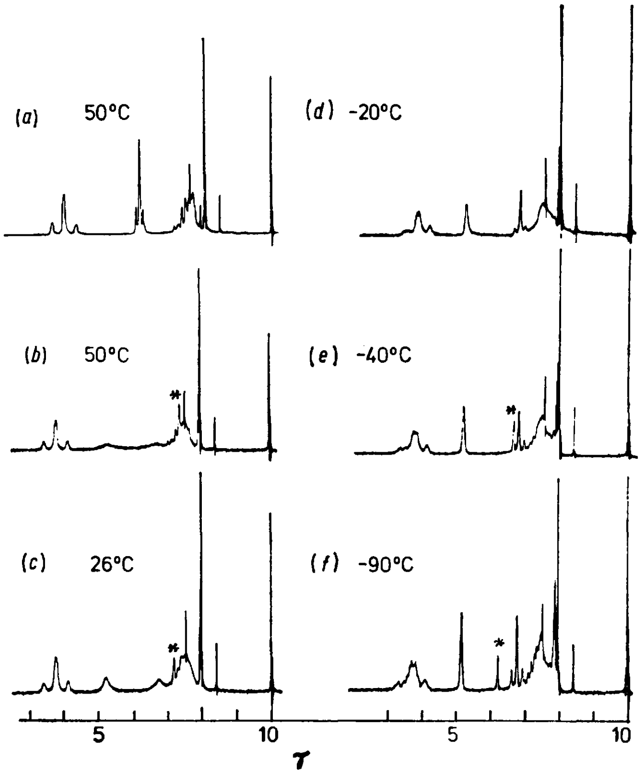
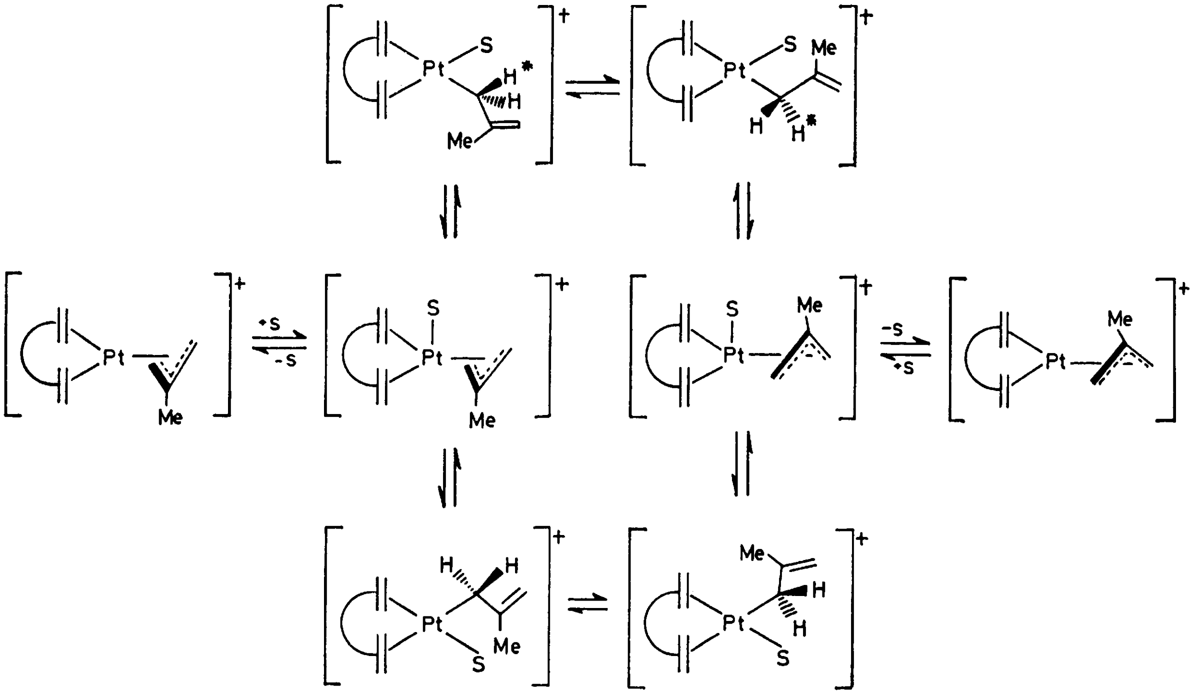


FIGURE 2 Hydrogen-1 n.m.r. spectra for [Pt(η^3-CH_2CMeCH_2)(cod)][BF_4] (10) recorded at various temperatures in [$^2H_6$]-acetone, except for (*a*) in [$^2H_3$]acetonitrile. Water impurity indicated by an asterisk

formation of the type discussed by van Leeuwen and Praat,[17] in which a co-ordinating solvent leads to the formation of a σ-bonded allyl group (Scheme 2). Rotation about the Pt–C bond, followed by loss of the co-ordinating solvent, gives the η^3-bonded allyl. In this process the allyl group undergoes a change equivalent to reflection in a mirror plane, resulting in the equivalence of the cod methine protons. In the case of a symmetrically substituted η^3-allyl system, η^3 to σ conversion can occur with equal probability to either of the two ends of the three-carbon chain, as illustrated. However, this would not be the case with an end-substituted allylic system. The η^3 to σ conversion would occur selectively to form the Pt–C σ bond carrying the least-substituted carbon atom. Examination of the variable-temperature ^1H spectrum of (11) was therefore of interest.

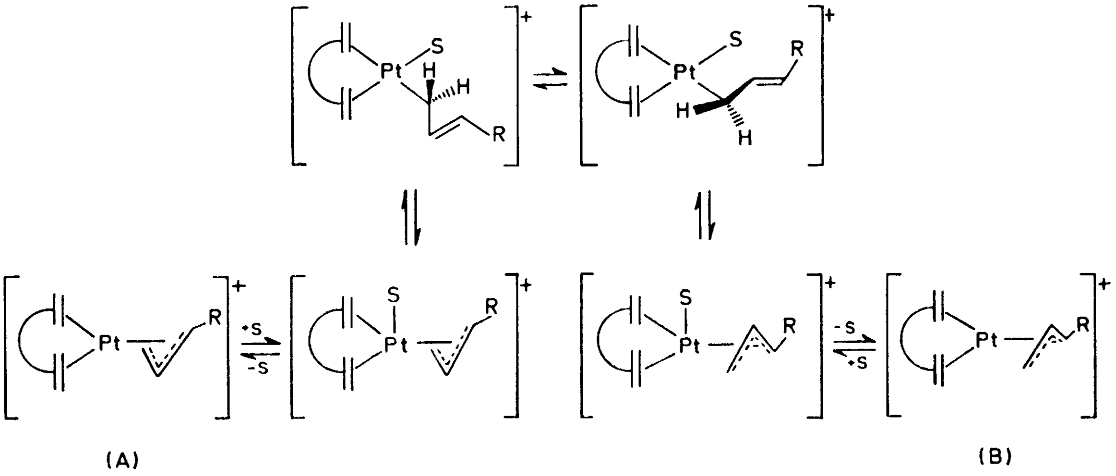
It has been previously mentioned that (11) exists in solution as the *syn* isomer, *syn–anti* exchange, however, occurring with the protons at the unsubstituted end of the allyl chain. At −90 °C, in [$^2H_6$]acetone as solvent, the dynamic process was frozen out allowing analysis of the ^1H spectrum (Table 4). At −60 °C, all the proton resonances are broadening and collapsing, except those due to H^2 and the methyl group. On warming to −30 °C the resonances due to the *syn*- and *anti*-protons H^1 and H^3 are only just visible. The H^2 resonance is still sharp, but the absorption due to H^5 has changed its form. This arises from a conversion of this signal from a doublet of doublets of doublets [coupling to H^1, H^2, and H^3] to a doublet of triplets. Exchange of H^1 and H^3 results in equivalence of those protons with respect to the central proton H^5. At 0 °C, however, the H^1 and H^3 resonances have collapsed completely. By 55 °C, two cod methine resonances are observable at τ 3.82 and 4.23, with H^1 and H^3 being visible as a broad resonance centred at τ 6.08. The signal due to H^2 is unchanged.



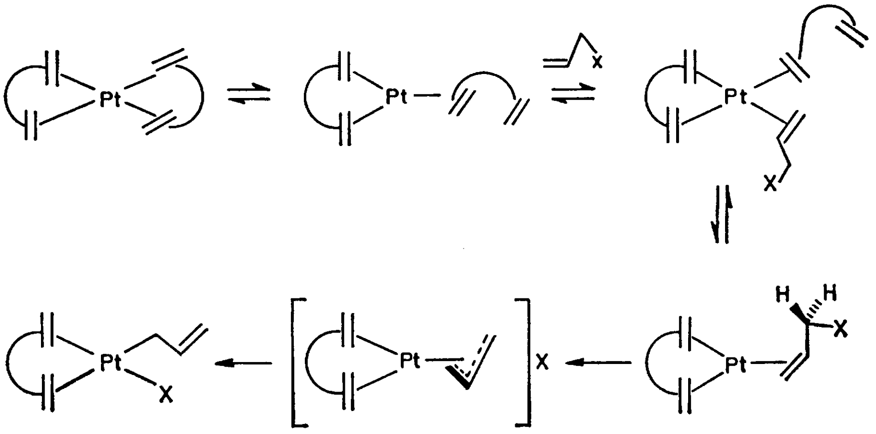
SCHEME 2

Addition of up to 20% [$^2H_3$]acetonitrile sharpened the resonances, but again results in solvent shifts; the signal due to the exchanging H^1 and H^3 protons is now a sharp doublet (coupling to H^5) at τ 6.12.

These observations are explicable in terms of the equilibria depicted in Scheme 3, where compared with the symmetrical η^3-allyl system, selective η^3 to σ conversion leads to a formal exchange between the forms (A) and (B). This fast exchange affords an effective plane of symmetry, which since it lies in the co-ordination plane results in the observed equivalence of H^8 with H^9, and H^6 with H^7.



Scheme 3



Scheme 4

As was discussed earlier, the σ-allylic complexes (1)—(8) are only obtained on addition of the zerovalent platinum complex to an excess of the allylic halide. It was also observed that under similar conditions no reaction occurred between alkyl halides and bis(cyclo-octa-1,5-diene)platinum. This suggests that in the initial reaction the allylic halide functions as an olefin forming a 16-electron η^2-bonded allylic halide, which then *via* internal attack by platinum on the allylic carbon leads to the complexes (1)—(8) (Scheme 4). This suggestion derives further support from the observation that ethylene[11] and electronegatively substituted olefins[18] will readily displace cyclo-octa-1,5-diene from [Pt(cod)$_2$].

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were measured either on a Varian Associates HA100 or JEOL JNM-PS-100 spectrometer. Carbon-13 spectra were obtained on a JEOL PFT-100 FT spectrometer operating on an internal ^{2}H-lock. Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer. All reactions were carried out in an atmosphere of dry oxygen-free nitrogen, using freshly distilled solvents. The allyl halides were purified prior to use by passage through a short column of alumina. Bis(cyclo-octa-1,5-diene)platinum was prepared by the published method.[11] Light petroleum refers to that fraction having b.p. 30—40 °C. Analytical and other data for new compounds are given in Table 1.

*Reaction of Bis(cyclo-octa-*1,5-*diene)platinum with Allyl Chloride.*—Bis(cyclo-octa-1,5-diene)platinum (0.41 g, 1 mmol) was added with stirring at room temperature to a solution of allyl chloride (0.2 cm^3, an excess) in light petroleum (10 cm^3). After 15 min the supernatant liquid was removed, and the off-white precipitate washed with light petroleum (3×5 cm^3) and dried *in vacuo* to give white *crystals* of (1) [PtCl(σ-CH$_2$CH=CH$_2$)(cod)] (0.36 g, 95%).

A similar procedure afforded the compounds (2) [PtBr(σ-CH$_2$CH=CH$_2$)(cod)], (3) [PtCl{σ-CH$_2$C(Me)=CH$_2$}(cod)], (4) [PtCl(σ-CH$_2$CH=CHMe)(cod)], (5) [PtBr(σ-CH$_2$CH=CHMe)(cod)], (6) [PtCl(σ-CH$_2$CH=CHPh)(cod)], (7) [PtBr(σ-CH$_2$CH=CHPh)(cod)], and (8) [PtCl{σ-CH$_2$C(Cl)=CH$_2$}(cod)].

Preparation of the Salt [Pt(η^3-C$_3$H$_5$)(cod)][BF$_4$].—To a suspension of silver tetrafluoroborate (0.194 g, 1 mmol) in dichloromethane (10 cm^3) was added compound (1) (0.38 g, 1 mmol). The reaction mixture was stirred (room temperature) in the absence of light for 2 h, and then filtered through Celite. Reduction of the volume of the solvent (5 cm^3) *in vacuo* followed by the addition of diethyl ether afforded white *crystals* of (9) [Pt(η^3-C$_3$H$_5$)(cod)][BF$_4$] (0.36 g, 84%).

In a like manner were prepared (10) [Pt(η^3-2-MeC$_3$H$_4$)(cod)][BF$_4$], (11) [Pt(η^3-3-MeC$_3$H$_4$)(cod)][BF$_4$], and (12) [Pt(η^3-3-PhC$_3$H$_4$)(cod)][BF$_4$].

We thank the S.R.C. for support.

[9/602 *Received*, 18*th April*, 1979]

REFERENCES

[1] H. Kurosawa and G. Yoshida, *J. Organometallic Chem.*, 1976, **120**, 297.

[2] K. Vrieze, in 'Dynamic Nuclear Magnetic Resonance Spectroscopy,' eds. L. M. Jackman and F. A. Cotton, Academic Press, New York, 1975, ch. 11, and refs. therein.

[3] P. W. Jolly and G. Wilke, 'The Organic Chemistry of Nickel,' Academic Press, New York, 1974, vol. 1.

[4] P. M. Maitlis, 'The Organic Chemistry of Palladium,' Academic Press, New York, 1971, vol. 1.

[5] B. E. Mann, B. L. Shaw, and G. Shaw, *J. Chem. Soc.* (*A*), 1971, 3536.

[6] N. M. Boag, M. Green, J. L. Spencer, and F. G. A. Stone, *J. Organometallic Chem.*, 1977, **127**, C51.

[7] G. Carturan, A. Scrivanti, U. Belluco, and F. Morandini, *Inorg. Chim. Acta*, 1978, **27**, 37.

[8] R. G. Pearson and M. Laurent, *Israel J. Chem.*, 1977, **15**, 243.

[9] J. C. Huffmann, M. P. Laurent, and J. K. Kochi, *Inorg. Chem.*, 1977, **16**, 2639.

[10] J. A. Kaduk and J. A. Ibers, *J. Organometallic Chem.*, 1977, **139**, 199.

[11] M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 271; J. L. Spencer, *Inorg. Synth.*, 1979, **19**, 213.

[12] S. Numata, R. Okawara, and H. Kurosawa, *Inorg. Chem.*, 1977, **16**, 173.

[13] B. E. Mann, *Adv. Organometallic Chem.*, 1974, **12**, 135.

[14] D. A. White, *Synth. Inorg. Metal-org. Chem.*, 1971, **1**, 133.

[15] D. J. Mabbott, B. E. Mann, and P. M. Maitlis, *J.C.S. Dalton*, 1977, 294.

[16] H. C. Clark and H. Kurosawa, *Inorg. Chem.*, 1973, **12**, 357.

[17] P. W. N. M. van Leeuwen and A. P. Praat, *Chem. Comm.*, 1970, 365.

[18] M. T. Chicote, M. Green, J. L. Spencer, F. G. A. Stone, and J. Vicente, *J.C.S. Dalton*, 1979, 536.