The Synthesis, Reactions, and Dynamic Behaviour of Allyl(cyclopentadienyl)platinum Complexes

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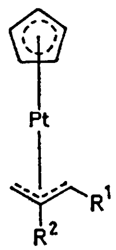
Reaction of [PtCl(σ-allyl)(cod)] [allyl = $CH_2CH{=}CH_2$, $CH_2C(Me){=}CH_2$, $CH_2CH{=}CHMe$, or $CH_2CH{=}CHPh$; cod = cyclo-octa-1,5-diene] with $Tl[C_5H_5]$ affords the crystalline complexes [Pt(η^3-allyl)(η-C_5H_5)]. In the case of the cinnamyl ligand the precursor, [Pt(σ-$CH_2CH{=}CHPh$)(cod)(σ-C_5H_5)], of the η^3-allyl species could be isolated as an orange crystalline material. Treatment of the η^3-allylic species with an excess of $CNBu^t$ affords the complexes *trans*-[Pt($CNBu^t$)$_2$(σ-allyl)(σ-C_5H_5)], there being no evidence for the intermediacy of isocyanide analogues of [Pt(CO)(σ-allyl)(η-C_5H_5)]. The *trans*-isocyanide complexes rearrange in solution to give thermodynamically controlled mixtures whose major component is the *cis* isomer. The mechanisms of these reactions are discussed, together with the ^1H and ^{13}C n.m.r. spectra of the complexes isolated.

ALTHOUGH complexes of the type [Pt(η^3-allyl)(η-C_5H_5)] [allyl = $CH_2CH{=}CH_2$ or $CH_2C(Me){=}CH_2$] have been known[1] for several years, and were synthesised by the reaction of allylplatinum halides with sodium or thallium(I) cyclopentadienide, the general lack of suitable precursors has limited the further development of this area of chemistry. The recent synthesis[2] of the complexes [PtX(σ-allyl)(cod)] (cod = cyclo-octa-1,5-diene) *via* oxidative addition of allylic halides to [Pt(cod)$_2$] prompted the study of the reactions of these new allylic species with $Tl[C_5H_5]$.

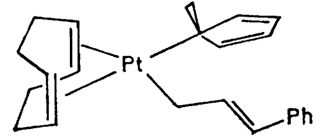
RESULTS AND DISCUSSION

Reaction of the compounds [PtCl(σ-allyl)(cod)] [allyl = $CH_2CH{=}CH_2$, $CH_2C(Me){=}CH_2$, or $CH_2CH{=}CHMe$] with $Tl[C_5H_5]$ in tetrahydrofuran at room temperature afforded the complexes (1)—(3). The compounds were isolated as yellow crystalline materials by sublimation and characterised as η^3-allyl(η^5-cyclopentadienyl)platinum complexes by elemental analysis, and by ^1H (Table 1) and ^{13}C (Table 2) n.m.r. spectroscopy. The spectroscopic data obtained for (1) and (2) were in agreement with those previously reported[1] for these molecules. Whereas, compounds (1)—(3) readily sublime in good yield at room temperature onto a water-cooled probe, the cinnamyl derivatives (4), prepared in an analogous manner from [PtCl(σ-$CH_2CH{=}CHPh$)(cod)], required sublimation from the reaction mixture at 50 °C onto a −78 °C probe. This resulted in extensive decomposition, and the complex was only identified by ^1H n.m.r. spectroscopy (Table 1).

In an attempt to increase the yield of (4), the reaction mixture was extracted with light petroleum and cooled, thereby yielding an orange crystalline compound (5) which from elemental analysis still contained co-ordinated cyclo-octa-1,5-diene, and was evidently the precursor of (4). Evidence for the structural identity of (5) was obtained from a spectroscopic study. The characteristic ν(C=C) of a σ-allyl group was observed at 1 613 cm^{-1} in the i.r. spectrum. The ^1H n.m.r. spectrum demonstrated that the cyclopentadienyl group was σ bound because a platinum–hydrogen coupling constant of 41 Hz was observed which is characteristic of such a mode.[3] Moreover, a value of 15 Hz for the coupling between the olefinic allyl protons is indicative of a *trans* configuration of that ligand. The ^1H n.m.r. and ^{13}C n.m.r. spectra both showed the presence of two cyclo-octa-1,5-diene methine environments. The signals due to the double bond *trans* to the cinnamyl group [^1H n.m.r.: τ 4.19 {^2J(PtH) 34 Hz}; ^{13}C n.m.r.: 106.2 p.p.m. {^1J(PtC) 55 Hz}] are identified by comparison with those in the spectrum of [PtCl(σ-$CH_2CH{=}CHPh$)(cod)].[2] The larger coupling constants of the double bond *trans* to the σ-cyclopentadienyl ligand [^1H n.m.r.: τ 5.66 {^2J(PtH) 51 Hz}; ^{13}C n.m.r.: 94.2 p.p.m. {^1J(PtC) 114 Hz}] indicate that the latter ligand has a smaller *trans* influence than a σ-allyl, but larger than a halide. This is in accord with a comparison made between chloride, σ-cyclopentadienyl, and methyl ligands *trans* to cyclo-octa-1,5-diene by Clark and Shaver.[3]



	R^1	R^2
(1)	H	H
(2)	H	Me
(3)	Me	H
(4)	Ph	H



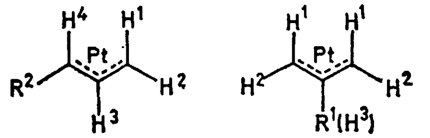
(5)

The ^1H n.m.r. spectrum of complex (3) and that of (4) are indicative of the substituent being in the *syn* position, since the coupling between the central allyl proton (H^3) and H^4 (Table 1) is that expected if H^4 is in the *anti* position. The ^1H n.m.r. spectrum of the crotyl derivative (3) exhibits several very small peaks characteristic of the *anti* isomer. Leaving the solution for several days produced no increase in the intensity of these signals.

The ^{13}C n.m.r. allylic chemical shifts of complexes (1)—(3) (Table 2), although comparable to those we have found for other σ-allyl compounds,[4] are all at rather high field with larger platinum–carbon coupling constants. These effects are possibly due to the higher electron density on platinum(II) in the 18-electron species as opposed to the more usual 16-electron configuration, as well as the difference in structures.

TABLE 1

Hydrogen-1 n.m.r. data for the complexes $[Pt(\eta^3\text{-}CH_2CR^1CHR^2)(\eta\text{-}C_5H_5)]$

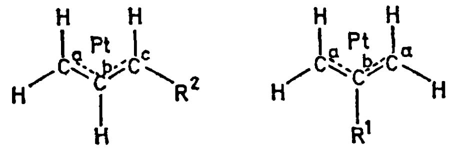


Complex	R¹	R²	τ [a] H¹	H²	H³	H⁴	Me	C_5H_5
(1)	H	H	7.95 d, $^3J(H^3)$ 9, J(Pt) 110	6.40 d, $^3J(H^3)$ 5, J(Pt) 62	6.08 m, J(Pt) 54			4.25 s, J(Pt) 22
(2)	Me	H	7.79 s, J(Pt) 112	6.48 s, J(Pt) 61			7.84 s, J(Pt) 33	4.24 s, J(Pt) 21
			7.83 [b] s, J(Pt) 110	6.44 s, J(Pt) 62			7.70 s, J(Pt) 30	4.20 s, J(Pt) 20
(3)	H	Me	8.04 d of d of d, $^2J(H^2)$ 1, $^3J(H^3)$ 9, $^4J(H^4)$ 1, J(Pt) 107	6.57 d of d, $^2J(H^1)$ 1, $^3J(H^3)$ 6, J(Pt) 60	6.20 d of d of d, $^3J(H^1)$ 9, $^3J(H^2)$ 6, $^3J(H^4)$ 8, J(Pt) 57	7.34 d of d of q, $^3J(H^3)$ 8, $^4J(H^1)$ 1, ^3J(Me) 7, J(Pt) 111	8.52 d, $^3J(H^4)$ 7, J(Pt) 49.5	4.25 s, J(Pt) 21.5
(4)	H	Ph [c]	7.87 d of d, $^2J(H^2)$ 1, $^3J(H^3)$ 9, J(Pt) 106	6.53 d of d, $^2J(H^1)$ 1, $^3J(H^3)$ 5, J(Pt) 57	5.69 d of d of d, $^3J(H^1)$ 9, $^3J(H^2)$ 5, $^3J(H^4)$ 8, J(Pt) 58.5	6.43 d, $^3J(H^3)$ 8, J(Pt) 114		4.44 s, J(Pt) 21.5

[a] Measured in $[^2H_6]$benzene at 26 °C unless otherwise indicated, coupling constants in Hz. [b] Measured in $[^2H_1]$chloroform. [c] Ph at τ 2.57—3.01.

TABLE 2

Carbon-13 n.m.r. data for the complexes $[Pt(\eta^3\text{-}CH_2CR^1CHR^2)(\eta\text{-}C_5H_5)]$ *

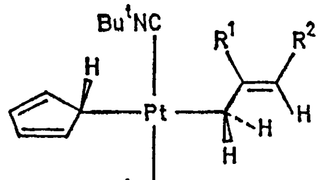


Complex	R¹	R²	δ/p.p.m. Cᵃ	Cᵇ	Cᶜ	Me	C_5H_5
(1)	H	H	26.7 (382)	70.2 (74)			90.7 (31)
(2)	Me	H	28.2 (391)	86.2 (90)		22.3 (39)	90.5 (28)
(3)	H	Me	24.3 (407)	73.4 (76)	45.8 (374)	22.9 (29)	90.9 (31)

* Measured in $[^2H_6]$benzene at 26 °C, J(PtC) given in parentheses in Hz.

As a corollary to this observation, the ^{13}C n.m.r. spectrum of $[Pt(CO)(\sigma\text{-}CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)]$ (6), prepared by bubbling carbon monoxide through solutions of $[Pt(\eta^3\text{-}CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)]$, was measured and found to contain an anomalous shift for the allyl carbon directly bound to platinum. This occurs at —12.0 p.p.m. which, although as a result of the allylic double bond does not appear at so high a shift as related species (Table 3), is clearly a related phenomenon. These complexes also exhibit very small or zero platinum coupling (^1H and ^{13}C) to the cyclopentadienyl ligand but very large platinum coupling to the co-ordinated carbonyl group.

Addition (—40 °C) of an excess of $CNBu^t$ to a solution of (1) in light petroleum resulted, on warming the reaction mixture to room temperature, in the precipitation of a pale yellow microcrystalline complex (7), which analysed for a species with the molecular formula $[Pt(CNBu^t)_2(\sigma\text{-}CH_2CH{=}CH_2)(\sigma\text{-}C_5H_5)]$. The i.r. spec-



	R¹	R²
(7)	H	H
(8)	Me	H
(9)	H	Me

trum of (7) showed a single strong band at 2 188 cm^{-1} attributable to a terminal isocyanide stretch, and an absorption at 1 605 cm^{-1}, which could be assigned either to an imino or to a σ-allyl group.

Examination of the ^{1}H n.m.r. spectrum of (7) showed that in solution the complex exists as a mixture of isomeric species in the ratio of *ca.* 1 : 6. Since a fast scan of the ^{1}H spectrum prior to spectrometer tuning indicated a different isomer ratio it was suspected that rapid isomerisation occurred in solution. Both isomers had cyclopentadienyl signals whose platinum–hydrogen coupling constants were in agreement with a σ-bonding mode (Table 4). However, apart from the cyclopentadienyl and tertiary butyl resonances, the dominant features were two sets of doublets in an isomeric ratio at *ca.* τ 7.20, with a platinum–hydrogen coupling constant of *ca.* 90 Hz. This is reminiscent of signals for protons on a carbon atom bound directly to platinum in σ-allyl platinum complexes, *e.g.* as in *trans*-[Pt(CNBu^t)$_2$(PPh$_3$)(σ-CH$_2$CH=CH$_2$)][BF$_4$][4] [τ 7.35 {^2J(PtH) 80 Hz}]. If complex (7) contained a σ-allyl ligand then the mixture of isomers can be explained as being due to *cis,trans* isomerisation (see below). Closer examination of the ^{195}Pt–^{1}H coupling constants of the cyclopentadienyl resonances supported this hypothesis. Whilst that of the major isomer had a value of 38 Hz, the coupling constant of the minor isomer was less (23 Hz). Since a σ-allyl group has a large *trans* influence,[5] the minor isomer can be assigned the *trans* configuration and the major isomer to the *cis* configuration. However, the

TABLE 3

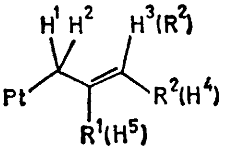
Comparison of ^{13}C n.m.r. data for (6) with those for related complexes

Complex	δ/p.p.m.[a] CH$_2$/Me	C$_5$H$_5$	CO
[Pt(CO)(Me)(η-C$_5$H$_5$)] [b]	−44.1 (691)	94.1 (8)	163.4 (2 459)
[Pt{P(OMe)$_3$}(Me)(η-C$_5$H$_5$)] [b]	−47.8 (795)	93.2 (4)	
[Pt(CO)(σ-allyl)(η-C$_5$H$_5$)] [c,d] (6)	−12.0 (654)	94.5	163.8 (2 525)

[a] J(PtC) given in parentheses in Hz. [b] Ref. 3 measured in [^{2}H$_8$]dioxan. [c] Measured in [^{2}H$_6$]benzene with [Cr(acac)$_3$] added. [d] Other allyl resonances: 146.7 [*C*H, ^2J(PtC) 76], 109.0 p.p.m. [*C*H$_2$, ^3J(PtC) 69 Hz].

TABLE 4

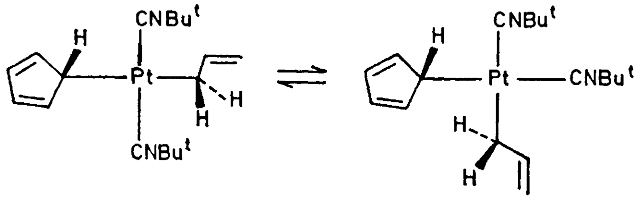
Hydrogen-1 n.m.r. data for the complexes [Pt(CNBu^t)$_2$(σ-CH$_2$CR^{1}CHR^2)(σ-C$_5$H$_5$)]



Complex	R^1	R^2	Structure	τ[a] H^1/H^2	H^3	H^4	H^5	Me	C$_5$H$_5$	Bu^t
(7)	H	H	*trans*	7.29 d, ^3J(H^5) 8, ^2J(Pt) 85	4.86 d of d, ^2J(H^4) 2, ^3J(H^5) 15, ^4J(Pt) 27	5.46 d of d, ^2J(H^3) 2, ^3J(H^5) 12, ^4J(Pt) 24	unobs.		3.54 s, ^2J(Pt) 22.5	9.09 s
			cis	7.16 d, ^2J(H^5) 9, ^2J(Pt) 91	4.86 d of d, ^2J(H^4) 3, ^3J(H^5) 17, ^4J(Pt) 23	5.17 d of d, ^2J(H^3) 3, ^3J(H^5) 10, ^4J(Pt) 22	3.41 d of d of t, ^3J(H^{1,2}) 9, ^3J(H^3) 17, ^3J(H^4) 10		3.65 s, ^2J(Pt) 38	9.04 (9 H) s 9.07 (9 H) s
(8)	Me	H	*trans*	7.30 s, ^2J(Pt) 85	5.46 d of q, ^2J(H^4) 3, ^4J(Me) 1, ^4J(Pt) 18	5.22 d, ^2J(H^3) 3, ^4J(Pt) 19.5		7.95 d, ^4J(H^3) 1, ^4J(Pt) 8	3.55 s, ^2J(Pt) 23	9.06 s
			cis	7.14 s, ^2J(Pt) 95	5.35 d of q, ^2J(H^4) 3, ^4J(Me) 1, ^4J(Pt) 19	5.09 d, ^2J(H^3) 3, ^4J(Pt) 20		7.87 d, ^4J(H^3) 1, ^4J(Pt) 4	3.65 s, ^2J(Pt) 38	8.99 (9 H) s 9.06 (9 H) s
(9)	H	Me	*trans* [b]	7.27 d, ^3J(H^5) 8, ^2J(Pt) 83	*ca.* 4.5 [c] m		*ca.* 3.8 [c] m	8.15 d, ^3J(H^3) 5, ^5J(Pt) 12	3.47 s, ^2J(Pt) 22.5	9.90 s
			cis [b]	7.14 d, ^3J(H^5) 5, ^2J(Pt) 91	*ca.* 4.5 [c] m		*ca.* 3.8 [c] m	8.10 d, ^3J(H^3) 5, ^5J(Pt) 12	3.55 s, ^2J(Pt) 39	9.05 (9 H) s 9.08 (9 H) s
			cis [d]	7.23 d, ^3J(H^5) 9, ^2J(Pt) 85		*ca.* 4.5 [c] m	*ca.* 3.8 [c] m	8.15 d of d, ^3J(H^3) 5, ^4J(H^5) 2, ^5J(Pt) 12	3.54 s, ^2J(Pt) 38	9.06 (9 H) s 9.10 (9 H) s

[a] Measured in [^{2}H$_6$]benzene at 26 °C, coupling constants in Hz. [b] Stereochemistry at metal centre, with ligand in (*E*)-CH$_2$CH=CHMe configuration. [c] J(Pt) unobserved. [d] Stereochemistry at the metal centre, with ligand in (*Z*)-CH$_2$CH=CHMe configuration.

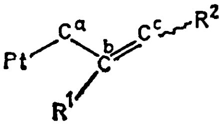
original i.r. spectrum (in Nujol) had only a single isocyanide stretch indicative of a *trans* isomer (*viz.* the minor isomer). Nevertheless, when the solution used for the n.m.r. study was taken to dryness *in vacuo*, the residue had two isocyanide bands in the i.r. (2 205 and 2 174 cm^{-1}) as expected for the *cis* isomer. This would



suggest that the original complex isolated is the *trans* isomer, which rearranges in solution to give a thermodynamically controlled mixture whose major component is the *cis* isomer. Similarly prepared were the 2-methylallyl (8) and crotyl (9) analogues, also isolated in the solid state as the *trans* isomers, but in solution existing in equilibrium with the *cis* forms. Hydrogen-1 n.m.r. data are given in Table 4.

TABLE 5

Carbon-13 n.m.r. data for the complexes $[Pt(CNBu^t)_2(\sigma\text{-}CH_2CR^1CHR^2)(\sigma\text{-}C_5H_5)]$



Complex	R^1	R^2	Structure	δ (p.p.m.) [a]					
				C^a	C^b	C^c	Me	C_5H_5	Bu^t
(7)	H	H	*trans*	9.8 [b]	148.4 [b]	104.9 (64)		111.4 (35)	30.2
			cis	18.4 (519)	147.3 (76)	106.0 (53)		114.9 (76)	30.2
(8)	Me	H	*trans*	13.6 (438)	154.4 [b]	102.7 (41)	26.1 [b]	110.9 (34)	29.6
			cis	22.3 (532)	154.7 (46)	103.0 (40)	26.5 (22)	114.6 (74)	29.6
(9)	H	Me	*trans* [c,d]	6.4 (439)	138.3 (54)	116.3 (54)	18.2 (16)	109.9 (28)	29.5
			trans [d]	7.3 (439)	140.3 (51)	unobs.	18.6	111.0 (32)	29.6
			cis [d]	16.2 (520)	139.5 (72)	115.9 (61)	18.6	114.5 (76)	29.6
			cis [e]	10.5 (402) or (530)	138.9 (51)	unobs.	13.3	114.4 (74)	29.6

[a] Measured in $[^2H_6]$benzene at 26 °C unless otherwise indicated, *J*(PtC) given in parentheses in Hz. [b] *J*(PtC) unobserved. [c] Measured in $[^2H_1]$chloroform at -60 °C, Me_3CNC at 57.0 p.p.m. (13 Hz). [d] Stereochemistry at the metal centre, with ligand in (*E*)-$CH_2CH{=}CHMe$ configuration. [e] Stereochemistry at the metal centre, with ligand in (*Z*)-$CH_2CH{=}CHMe$ configuration.

The ^{13}C n.m.r. spectra (Table 5) are also in full agreement with the existence in solution of equilibrium mixtures. Thus for (8) two resonances attributable to the contact carbons of the σ-allyl bound to platinum were detected [*cis*: 22.3 p.p.m. {^1J(PtC) 532 Hz}; *trans*: 13.6 p.p.m. {^1J(PtC) 438 Hz}], the higher value of *J*(PtC) for the *cis* isomer reflecting the *trans* influence of $CNBu^t$ and σ-cyclopentadienyl ligands respectively.

Complex (8) [ν(C=C) 1 615 cm^{-1}] isomerised more slowly than the allyl derivative (7); 105 min (26 °C) being required to obtain an equilibrium mixture of the *trans–cis* species (*ca.* 1 : 6) (Figure 1). Apart from this difference the spectroscopic data parallel that of (7).

It was felt that, due to increased steric hindrance, complex (9) would not rearrange. However, this species also undergoes *cis,trans* isomerisation, albeit slightly more slowly than the 2-methylallyl complex (8). In order to gain unambiguous n.m.r. evidence for the structure of these complexes, the ^{13}C n.m.r. spectrum of the crotyl derivative (9) was measured in $[^2H_1]$chloroform at -60 °C immediately after synthesis. The resonances observed for the allylic ligand (Table 5) have the expected shifts and coupling constants for a σ-allyl moiety and compare directly with other σ-allyl complexes, apart from the shift of the allyl contact carbon to slightly higher field, caused by the *trans*-σ-cyclopentadienyl ligand.

The necessity of recording the ^{13}C n.m.r. spectrum over extended periods in $[^2H_6]$benzene at 26 °C revealed that complex (9) underwent an isomerisation process more complicated than simple *cis–trans* conversion at the metal since additional peaks were observed in due course. Measurement of the ^1H n.m.r. spectrum 24 h after dissolution elucidated the dynamic process. The cyclopentadienyl region of the spectrum illustrates this most clearly (Figure 2). Resonances A and B (satellites marked as primes) can be assigned to *trans*- and *cis*-$[Pt(CNBu^t)_2(\sigma\text{-}CH_2CH{=}CHMe)(\sigma\text{-}C_5H_5)]$, respectively, by comparison with spectra recorded immediately and 2 h after dissolution. Since the starting η^3-complex (3) has the methyl substituent in the *syn* position, then the complexes giving rise to signals A and B are expected to contain *E*-crotyl groups. It is thought, therefore, that this ligand isomerises at a rate slower then *cis–trans* conversion at the metal centre, and hence resonance C is due to a species containing a *Z*-crotyl group (*i.e.* $\text{Pt}\cdot\text{CH}_2\text{-}\overset{cis}{\text{CH=}}\text{CHMe}$). This is supported in the ^{1}H n.m.r. spectrum by the observation of a small coupling of 1.5 Hz to the allyl-methyl protons. This is attributed to a *trans*-allylic coupling to the central allyl proton H^5 and is not observed for the *E*-crotyl methyl protons since they are *cis* to H^5. Because the platinum–hydrogen coupling constant of resonance C is comparable to that of resonance B (Table 4), the former signal is assigned to *cis*-$[\text{Pt(CNBu}^t)_2\{\sigma\text{-}(Z)\text{-CH}_2\text{CH=CHMe}\}(\sigma\text{-C}_5\text{H}_5)]$. No resonance could be detected for *trans*-$[\text{Pt(CNBu}^t)_2\{\sigma\text{-}(Z)\text{-CH}_2\text{CH=CHMe}\}(\sigma\text{-C}_5\text{H}_5)]$.

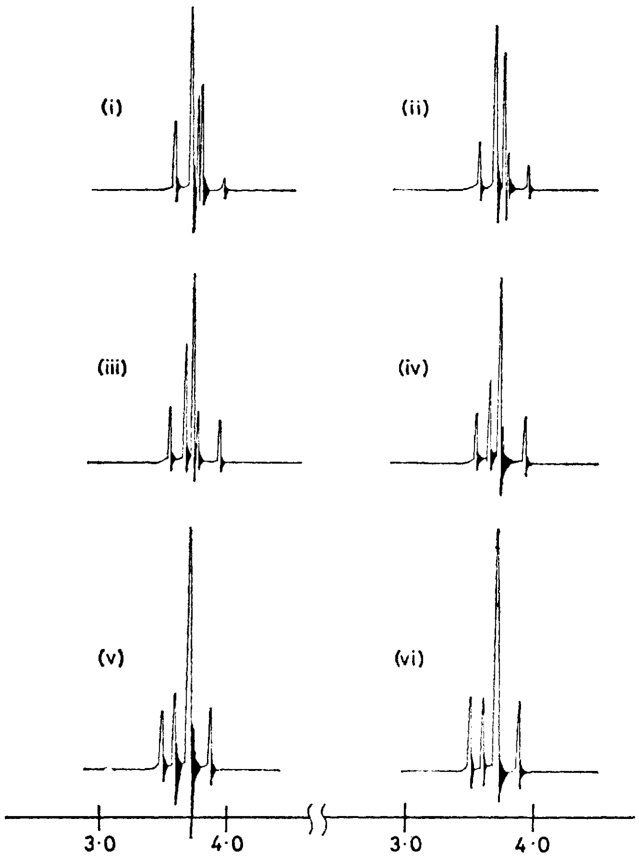


FIGURE 1 Changes in the cyclopentadienyl region of the ^{1}H n.m.r. spectrum of (8) (in $[^2\text{H}_6]$benzene) as a function of time: (i) 5, (ii) 15, (iii) 30, (iv) 50, (v) 65, and (vi) 105 min

Reassessment of the ^{13}C n.m.r. spectrum enabled a fairly satisfactory interpretation (Table 5). Unfortunately, due to signal overlap, it is not possible to assign an unambiguous platinum–carbon coupling constant to the allyl contact carbon resonance of *cis*-$[\text{Pt(CNBu}^t)_2\{\sigma\text{-}(Z)\text{-CH}_2\text{CH=CHMe}\}(\sigma\text{-C}_5\text{H}_5)]$. A value of *ca.* 520 Hz would be expected by comparison with *cis*-$[\text{Pt(CNBu}^t)_2\{\sigma\text{-}(E)\text{-CH}_2\text{CH=CHMe}\}(\sigma\text{-C}_5\text{H}_5)]$. However, it was not possible to observe a clean pair of satellites. The values given in Table 5 result from observation of only one member of two possible pairs, the other member being obscured by other signals.

The formation of a disubstituted complex on reacting CNBu^t with (1) is in contrast to the reaction of t-butyl isocyanide with $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\eta\text{-C}_5\text{H}_5)]$ which affords the cluster species $[\{\text{Pd(CNBu}^t)_2\}_n]$.[6] Similar types of reaction are observed on treatment of $[\text{M}(\eta^3\text{-C}_3\text{H}_5)_2]$ (M = Ni, Pd, or Pt) with an excess of triphenylphosphine. Whereas the nickel and palladium complexes form the zerovalent $[\text{M(PPh}_3)_4]$ species,[7,8] platinum gives the bis(σ-allyl) complex $[\text{Pt(PPh}_3)_2(\sigma\text{-CH}_2\text{CH=CH}_2)_2]$, emphasising the stability of platinum–carbon σ bonds.

Tertiary phosphines and phosphites (L) react with allyl(cyclopentadienyl)palladium complexes to form the zerovalent $[\text{PdL}_3]$ and $[\text{PdL}_4]$ species. This approach has been used[9] to generate $[\text{Pt(PEt}_3)_4]$. Parker and Werner[10] have studied the palladium system and have shown that formation of the zerovalent metal complexes occurs through reductive elimination of an allylcyclopentadiene group. Since a *cis*-square-planar complex is required for reductive elimination to take place, it has generally been assumed that the *cis* isomer is formed. This is identified by a small coupling of the cyclopentadienyl protons to the *trans* phosphorus. However, under certain conditions an unidentified cyclopentadienyl containing species is also observed. In view of the isolation of complexes (7)—(9) this is probably *trans*-$[\text{PdL}_2(\sigma\text{-allyl})(\sigma\text{-C}_5\text{H}_5)]$.

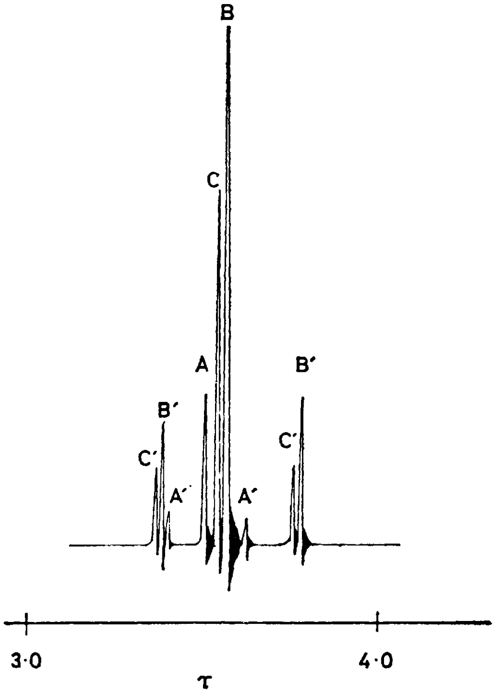
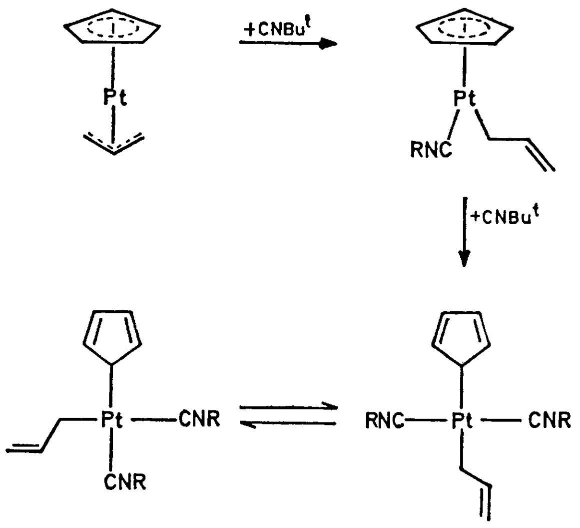


FIGURE 2 Cyclopentadienyl region of the ^{1}H n.m.r. spectrum of (9) measured after 24 h in $[^2\text{H}_6]$benzene. For peak assignments see text

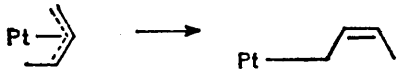
Reaction of t-butyl isocyanide with the compounds $[\text{Pt}(\eta^3\text{-allyl})(\eta\text{-C}_5\text{H}_5)]$ is considered to be similar to the reaction of tertiary phosphines and phosphites with the complexes $[Pd(\eta^3\text{-allyl})(\eta\text{-}C_5H_5)]$ although there are some significant differences. Even though stepwise addition must occur, the t-butyl isocyanide analogues of $[Pt(CO)(\sigma\text{-}CH_2CH{=}CH_2)(\eta\text{-}C_5H_5)]$ cannot be isolated, and attempts to do so led to the formation of solutions containing equimolar amounts of the compounds $[Pt(\eta^3\text{-allyl})(\eta\text{-}C_5H_5)]$ and $[Pt(CNBu^t)_2(\sigma\text{-allyl})(\sigma\text{-}C_5H_5)]$. Therefore, reaction with isocyanide is regarded as non-reversible (Scheme 1).



SCHEME 1

cis–trans Isomerisation of the isocyanide species is envisaged as occurring through a five-co-ordinate η^3-allyl intermediate which can undergo Berry rotations. Such a process (Scheme 2) has been described [4] for $[Pt\{P(OMe)_3\}_3(\sigma\text{-}CH_2CH{=}CH_2)][BF_4]$, but an important difference is that while isomerisation is fast for the trimethyl phosphite species resulting in the terminal allyl carbons being time averaged in the ^{13}C n.m.r. spectrum, the isocyanide complexes only undergo slow exchange on the n.m.r. time scale. This reaction scheme adequately describes the dynamic process in (7) and (8), the differences in rates probably being due to increased steric hindrance of the 2-methylallyl group in the five-co-ordinate intermediate. It also describes the isomer interconversion in the crotyl species (9). However, the situation is a little more complex and requires to be explained in detail.

Formation of the square-pyramidal intermediate from *trans*-$[Pt(CNBu^t)_2(\sigma\text{-}CH_2CH{=}CHMe)(\sigma\text{-}C_5H_5)]$ (Scheme 2) occurs as in the allyl case.[4] However, unlike the allyl or 2-methylallyl complexes, the intermediate can convert into two products. If the η^3-crotyl group undergoes an η^3–σ transformation with the unsubstituted carbon forming a σ bond in an axial position (Scheme 2, equilibrium II), then a straightforward *cis,trans* isomerisation of the isocyanide ligands is observed. However, another mode of opening is possible. If the crotyl group opens up with the substituted carbon forming a σ bond in an axial position (Scheme 2, equilibrium III), then the species *cis*-$[Pt(CNBu^t)_2(\sigma\text{-}CHMeCH{=}CH_2)(\sigma\text{-}C_5H_5)]$ results. Rotation of the platinum–carbon bond allows formation of an η^3-allyl intermediate in which the methyl group is in the *anti* position. In order to isolate a σ-(*Z*)-crotyl group, it is a pre-requisite that an η^3-allyl group of the type shown below be formed. Further steps in the sequence then allow formation of the observed *cis*-$[Pt(CNBu^t)_2\{\sigma\text{-}(Z)\text{-crotyl}\}(\sigma\text{-}C_5H_5)]$.



The reason why *cis*-$[Pt(CNBu^t)_2\{\sigma\text{-}(Z)\text{-crotyl}\}(\sigma\text{-}C_5H_5)]$ is formed slowly is easily understood. Whereas formation of platinum–carbon bonds to unsubstituted carbons is reasonably facile, formation of $[Pt(CNBu^t)_2(\sigma\text{-}CHMeCH{=}CH_2)(\sigma\text{-}C_5H_5)]$ (Scheme 2, equilibrium III) is relatively slow since it is sterically hindered. Exchange between *cis*- and *trans*-$[Pt(CNBu^t)_2\{\sigma\text{-}(E)\text{-crotyl}\}(\sigma\text{-}C_5H_5)]$, however, is relatively fast since it proceeds through intermediates with unsubstituted contact carbons (equilibria I and II). Nevertheless, $[Pt(CNBu^t)_2(\sigma\text{-}CHMeCH{=}CH_2)(\sigma\text{-}C_5H_5)]$ is slowly formed, and, once formed, allows isomerisation (*Z*/*E*) of the crotyl group. Although no *trans*-$[Pt(CNBu^t)_2\{\sigma\text{-}(Z)\text{-crotyl}\}(\sigma\text{-}C_5H_5)]$ could be detected, it is likely that the *Z*-crotyl complexes also undergo relatively fast *cis,-trans* isomerisation. Thus the equilibria can be summarised as follows, *cis,trans* isomerisation at the metal centre is relatively fast, but isomerisation of the $CH_2CH{=}CHMe$ moiety is slow since it is necessary to form the high-energy intermediate $[Pt(CNBu^t)_2(\sigma\text{-}CHMeCH{=}CH_2)(\sigma\text{-}C_5H_5)]$.

EXPERIMENTAL

The instrumentation used and techniques employed were as previously described in ref. 2. Carbon-13 chemical shifts in p.p.m. are relative to $SiMe_4$, positive values to high frequency. Infrared spectra were measured in Nujol mulls. Bis(cyclo-octa-1,5-diene)platinum was prepared by the published method.[11] Light petroleum refers to that fraction with b.p. 30—40 °C.

Preparation of the Complexes $[Pt(\eta^3\text{-allyl})(\eta\text{-}C_5H_5)]$.—A mixture of $[PtCl(\sigma\text{-}C_3H_5)(cod)]$[2] (2.44 g, 6.44 mmol) and $Tl[C_5H_5]$ (1.75 g, 6.5 mmol) was stirred in tetrahydrofuran (thf) (50 cm^3) in darkness for 3 h. The mixture was then filtered through a pad of Celite and the solvent removed *in vacuo* at 0 °C. The residue was extracted with diethyl ether–light petroleum (50 : 50, 70 cm^3). The yellow extract was again filtered through Celite, and taken to dryness *in vacuo* (0 °C). Sublimation onto a water-cooled probe (0.1 mmHg, 25 °C) * gave yellow *crystals* of $[Pt(\eta^3\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$ (1) (1.45 g, 75%) (Found: C, 31.4; H, 3.0. Calc. for $C_8H_{10}Pt$: C, 31.9; H, 3.3%); $\nu_{max.}$ at 3 035w, 1 398m, 1 283w, 1 255w, 1 202m, 1 151w, 1 101w, 1 012s, 984m, 962m, 796s, 756s, 611m, 595m, 456w, and 430w cm^{-1}.

Complex (2) was prepared in a similar manner to (1), with $[PtCl(\sigma\text{-}CH_2CMeCH_2)(cod)]$ (0.20 g, 0.5 mmol) and

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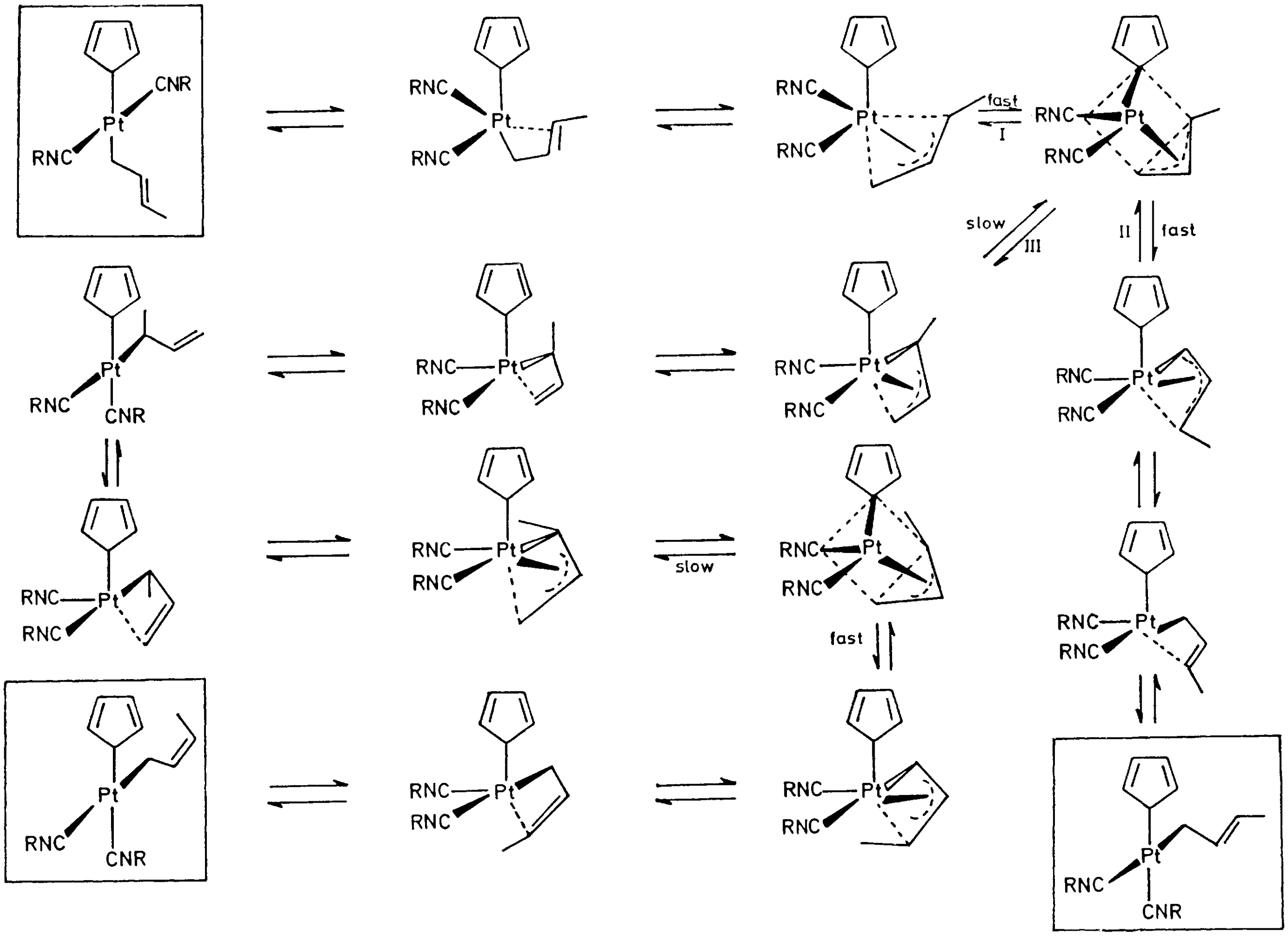
* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

$Tl[C_5H_5]$ (0.14 g, 0.52 mmol) affording yellow *crystals* of $[Pt\{\eta^3\text{-}CH_2C(Me)CH_2\}(\eta\text{-}C_5H_5)]$ (2) (0.1 g, 63%) (Found: C, 33.9; H, 3.6. Calc. for $C_9H_{12}Pt$: C, 34.3; H, 3.8%); $\nu_{max.}$ at 3 098w, 3 037w, 1 431m, 1 398m, 1 378s, 1 331w, 1 255w, 1 102w, 1 035w, 1 028m, 1 007w, 982m, 973(sh), 955m, 847m, 827m, 811m, 796m, 787m, 755m, 743w, 591w, 458w, and 441w cm^{-1}.

In a similar manner to (1), using $[PtCl(\sigma\text{-}CH_2CHCHMe)(cod)]$ (0.34 g, 0.85 mmol) and $Tl[C_5H_5]$ (0.24 g, 0.89 mmol), sublimation gave yellow *crystals* of $[Pt(\eta^3\text{-}CH_2CHCHMe)(\eta\text{-}C_5H_5)]$ (3) (0.16 g, 60%), m.p. *ca.* 30 °C (Found: C, 34.2; H, 3.7. $C_9H_{12}Pt$ requires C, 34.3; H, 3.8%); $\nu_{max.}$ at 3 098w, 3 068w, 3 046w, 3 015w, 1 459m,br, 1 424w, 1 404m, 1 373s, 1 282w, 1 255w, 1 215m, 1 152w, 1 112m, 1 102m, 1 040s, 1 010s, 986s, 967m, 940w, 888m, 867m, 833m, 792vs, 744s,br, 594m,br, 495w, 455w, and 411w cm^{-1}.



SCHEME 2 Rearrangement pathways for $[Pt(CNBu^t)_2(\sigma\text{-}CH_2CH{=}CHMe)(\sigma\text{-}C_5H_5)]$; the isomer *trans*-$[Pt(CNBu^t)_2\{\sigma\text{-}(Z)\text{-crotyl}\}(\sigma\text{-}C_5H_5)]$ is omitted for clarity

Preparation of $[Pt(\sigma\text{-}CH_2CHCHPh)(\sigma\text{-}C_5H_5)(cod)]$ (5).—A mixture of $[PtCl(\sigma\text{-}CH_2CHCHPh)(cod)]$ (0.36 g, 0.8 mmol) and $Tl[C_5H_5]$ (0.23 g, 0.86 mmol) was stirred in thf (15 cm^3) in darkness for 4 h. All volatiles were then removed *in vacuo* and the residue extracted with light petroleum (20 cm^3). Filtration through Celite and cooling (−20 °C) afforded orange *crystals* of $[Pt(\sigma\text{-}CH_2CHCHPh)(\sigma\text{-}C_5H_5)(cod)]$ (5) (0.13 g, 33%) (Found: C, 53.6; H, 5.1. $C_{22}H_{26}Pt$ requires C, 54.4; H, 5.4%); $\nu_{max.}$ at 3 078w, 3 064w, 3 016w, 1 613m (C=C), 1 590m, 1 490m, 1 476w, 1 443m, 1 430m, 1 333w, 1 328w, 1 305w, 1 299w, 1 259w, 1 222w, 1 153w, 1 123w,br, 1 081w,br, 1 070w, 1 026w, 1 001w, 993w, 984m, 980(sh), 957m, 906m, 882w, 868m, 855s, 839m, 825m, 819w, 813m, 794m, 771s, 764s, 752s, 721m, 693s, 661m, 612w, 545w,br, 489w, and 459w cm^{-1}. N.m.r.: ^1H ($[^2H_6]$benzene), τ 2.50—2.95 (m, 5 H, Ph), 3.25 [d(AB) of t, 1 H, CH_2CH, ^3J(HH) 8; ^3J(AB) 15], 3.57 [s, 5 H, C_5H_5, ^2J(PtH) 41], 3.55 [d(AB), 1 H, CHPh, ^3J(AB) 15], 5.66 [s, 2 H, CH, ^2J(PtH) 51], 4.19 [s, 2 H, CH, ^2J(PtH) 34], 7.31 [d, 2 H, CH_2, ^3J(HH) 8; ^2J(PtH) 108 Hz], 8.35 (s, br, 8 H, CH_2); ^{13}C ($[^2H_6]$benzene), δ 139.5 (s, Ph, α-C), 136.1 [s, CH_2CH, ^2J(PtC) 62], 126.6 (s, Ph, δ-C), 126.0, 125.8 (s + s, Ph, β- + γ-C), 124.9 [s, CHPh, ^3J(PtC) 54], 115.8 [s, C_5H_5, ^1J(PtC) 91], 106.2 [s, CH, ^1J(PtC) 55], 94.2 [s, CH, ^1J(PtC) 114 Hz], 30.5 (s, CH_2), 28.6 (s, CH_2), 28.3 [s, CH_2, ^1J(PtC) unobserved].

Preparation of $[Pt(CO)(\sigma\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$ (6).—Carbon monoxide was bubbled (20 h, −10 °C) through a solution of compound (1) (0.30 g, 1 mmol) in light petroleum (35 cm^3). The volatile material was removed *in vacuo*, and the residue distilled (70 °C, 0.01 mmHg) onto a water-cooled probe to give [Pt(CO)(σ-CH_2CHCH_2)(η-C_5H_5)] (6) a light yellow *oil* (0.28 g, 90%) (Found: C, 32.8; H, 3.0. $C_9H_{10}OPt$ requires C, 31.8; H, 2.8%), $\nu_{max.}$ (CO) 2 033s cm^{-1}. ^1H n.m.r. (measured in [$^2H_6$]benzene, protons labelled as in Table 4), τ 3.98 [d of d of t, 1 H, H^5, $^3J(H^{1,2}, H^5)$ 8, $^3J(H^3, H^5)$ 10, $^3J(H^4, H^5)$ 16, J(PtH) unobserved], 4.69 [s, 5 H, C_5H_5, ^2J(PtH) 13], 5.08 [d br, 1 H, $^3J(H^4, H^5)$ 16, ^4J(PtH) unobserved], 5.34 [d of d, 1 H, H^3, $^3J(H^3, H^5)$ 10, $^2J(H^3, H^4)$ 2, ^4J(PtH) 32], 6.89 [d br, 2 H, $^3J(H^{1,2}, H^5)$ 8, ^2J(PtH) 114 Hz].

Preparation of trans-[Pt(CNBu^t)$_2$(σ-C_3H_5)(σ-C_5H_5)] (7).—To a solution of (1) (0.21 g, 0.7 mmol) in light petroleum (20 cm^3) at −40 °C was added an excess of CNBu^t (0.2 cm^3). The solution was allowed to warm up to room temperature over 45 min, a white precipitate starting to form at −35 °C. The supernatant liquid was removed, the product washed with light petroleum (3 × 5 cm^3) and dried *in vacuo* affording pale yellow *microcrystals* of [Pt(CNBu^t)$_2$(σ-CH_2CHCH_2)(σ-C_5H_5)] (7) (0.28 g, 89%) (Found: C, 46.2; H, 6.0; N, 6.0. $C_{18}H_{28}N_2Pt$ requires C, 45.8; H, 6.3; N, 5.9%); $\nu_{max.}$ at 3 066(sh), 3 052w, 2 188vs (NC), 2 057w, 1 605s (C=C), 1 426w, 1 412m, 1 233m, 1 192s,br, 1 076w, 1 030w, 990w, 966w, 929w, 866s,br, 819m, 746s, 682w, 643m, 547s, 531w, 489w, and 466m cm^{-1}.

Preparation of trans-[Pt(CNBu^t)$_2${σ-$CH_2C(Me)CH_2$}(σ-C_5H_5)] (8).—This was prepared in a similar manner to complex (7) using (2) (0.18 g, 0.57 mmol) giving off-white *microcrystals* of [Pt(CNBu^t)$_2${σ-$CH_2C(Me)CH_2$}(σ-C_5H_5)] (8) (0.235 g, 92%) (Found: C, 47.3; H, 6.6; N, 5.7. $C_{19}H_{36}N_2Pt$ requires C, 47.4; H, 6.3; N, 5.8%); $\nu_{max.}$ at 3 067m, 3 054m, 2 188vs (NC), 2 054m, 1 615m (C=C), 1 425m, 1 412m, 1 372s, 1 367s, 1 278m, 1 233m, 1 194s,br, 1 074w, 1 029w, 991w, 967w, 927w, 875s, 865s, 855(sh), 822m, 746m, 644s, and 546s cm^{-1}.

Preparation of trans-[Pt(CNBu^t)$_2$(σ-$CH_2CHCHMe$)(σ-C_5H_5)] (9).—This was synthesised in an analogous manner to complex (7), from (3) (0.14 g, 0.44 mmol) which afforded off-white *microcrystals* of [Pt(CNBu^t)$_2$(σ-$CH_2CHCHMe$)(σ-C_5H_5)] (9) (0.20 g, 94%) (Found: C, 47.2; H, 6.4; N, 5.7. $C_{19}H_{36}N_2Pt$ requires C, 47.4; H, 6.3; N, 5.8%), $\nu_{max.}$ at 3 066w, 3 050w, 2 186vs (NC), 2 063w, 1 638w, 1 597w, 1 422m, 1 296w, 1 233m, 1 200s,br, 1 072w, 1 032w, 967m, 905w, 873s, 859s, 818m, 744s, 640m, 544m, 531w, and 446w cm^{-1}.

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