Cationic (η^3-Allylic) (η^4-diene)-palladium and -platinum Complexes

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The syntheses, and the temperature-dependent ^{1}H and ^{13}C n.m.r. spectra of the complexes [Pd(η^3-all)(η^4-diene)]-[PF$_6$] [all = C_3H_5, 1-MeC_3H_4, 2-MeC_3H_4, or 2-PhC_3H_4, diene = cyclo-octatetraene (cot); all = 2-MeC_3H_4, diene = cyclo-octa-1,5-diene (cod), hexamethylbicyclohexa[2.2.0]diene (hmdb), hexa-1,5-diene, or cycloheptatriene], [Pt(η^3-2-MeC_3H_4)Cl]$_2$, and [Pt(η^3-2-MeC_3H_4)(η^4-diene)][PF$_6$] [diene = cot or cod] are reported. The platinum complexes are rigid at low temperatures but undergo $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ exchange on heating. The palladium complexes exhibit different behaviour; for the cot complexes the observations are consistent with a higher temperature exchange process involving solvent, $[Pd(all)(cot)]^+ + s \rightleftharpoons cot + [Pd(all)(s)_2]^+$, and a lower energy process which could not be frozen out and which is interpreted in terms of a solvated five-co-ordinate intermediate undergoing pseudorotation in which the two halves of the cot are made equivalent. The η-arene complexes [M(2-MeC_3H_4)(hmb)][PF$_6$] (M = Pd or Pt, hmb = hexamethylbenzene) have been prepared and their structures are discussed on the basis of their n.m.r. spectra. A stability sequence towards solvation by acetone for the palladium complexes is, cot ~ cod > hmdb > hexa-1,5-diene ~ cht ~ hmb; the Pt complexes are less stable than their Pd analogues.

CATIONIC allylic complexes of palladium and platinum $[M(all)L_2]^+$ have long been known for L = R_3P, R_3As, L_2 = bipy, *etc.*[1] The only complexes that appear hitherto to have been reported where L_2 is a diene or similar ligand are $[Pd(all)(cod)]^+$ [2,3] (cod = cyclo-octa-1,5-diene) and $[\{Pd(all)\}_2(cot)]^{2+}$ (cot = cyclo-octatetraene).[4]

We report here the preparation and the solution n.m.r. spectra of a series of palladium complexes [Pd(all)-(η^4-diene)][PF$_6$], [Pd(all)(hmb)][PF$_6$] (hmb = hexamethylbenzene), and the solvated species, [Pd(all)(s)$_2$]-[PF$_6$], one of which (s = MeCN) has been isolated and characterised. For comparison we have also prepared some related platinum complexes, [Pt(all)(diene)][PF$_6$] and [Pt(all)(hmb)][PF$_6$], derived from di-μ-chloro-bis-(η^3-2-methylallylplatinum), a convenient new synthesis of which is also described.

The cationic complexes were all prepared from the allylic chloro-complexes (I) by reaction with the appropriate ligand in dichloromethane in the presence of silver hexafluorophosphate to remove chloride. Except for the hexamethylbenzene complexes, the complexes were all relatively stable in the solid at least; their colours were white or pale yellow. Analytical and spectroscopic data are given in the Tables.

RESULTS AND DISCUSSION

Cyclo-octatetraene Complexes (IIa—d) *and* (III).—The ^{1}H n.m.r. spectrum of the platinum complex (III) (100 MHz in [^{2}H$_6$]acetone) showed, in addition to the resonances for the 2-methylallyl ligand, a multiplet composed of an AB pair and two singlets which are due to the cot proton resonances. The lower-field AB pair showed coupling to ^{195}Pt [δ 6.66, J(H–Pt) = 28 Hz; $J(H_a{-}H_{a'})$ = 8; δ 6.82, J(H–Pt) = 36 Hz] and is assigned to the protons on the co-ordinated carbon atoms while the two higher-field singlet resonances (δ 6.47, 6.53) are assigned to the protons on the unco-ordinated carbons. The ^{13}C n.m.r. spectrum showed the co-ordinated carbon atoms at δ 102.3 [J(C–Pt) = 79] and 104.8 (J = 101 Hz);

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[1] See, for example, G. Paiaro and A. Musco, *Tetrahedron Letters*, 1965, 1583; J. Powell and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 744; K. Vrieze and H. C. Volger, *J. Organometallic Chem.*, 1967, **9**, 537; S. R. Stevens and G. D. Shier, *ibid.*, 1970, **21**, 495.

[2] R. R. Shrock and J. A. Osborn, *J. Amer. Chem. Soc.*, 1971, **93**, 3089.

[3] D. A. White, *Inorg. Synth.*, 1972, **13**, 61.

[4] B. F. G. Johnson, J. Lewis, and D. A. White, *J. Chem. Soc.* (*A*), 1970, 1738.

TABLE 1

	^{1}H n.m.r. spectrum (in δ)					^{13}C n.m.r spectrum (in δ)					
	(syn)	(anti)	R^2	cot	Other	C(1)	C(2)	R^2	C(a) [h]	C(b) [h]	Other
(IIa) [a]	4.83 (6) [b]	3.82 (13) [b]	6.18 (13,8) [b]	6.45		[f] 80.6	125.9		114.9	135.0	
(IIb) [a]	4.96	3.98	2.21	6.42		[f] 79.4	141.7	22.9	114.6	135.0	
(IIc) [a]	5.37	4.18	7.60	6.34		[f] 75.9	139.9	127.3 130.0 132.0	115.0	135.0	
(IId) [a,c]											
(III) [a,d]	4.90 (20)	3.54 (32)	2.11 (92)	6.66[J(aa′) = 8] (28) 6.82 (36) } H_a, $H_{a'}$ 6.47, 6.53, (H_b,$H_{b'}$)		[g] 70.4 (142)	140.2 (43)	24.7 (44)	102.3 (79) 104.8 (101)	136.3	
(IV) [a]	4.95	3.68	2.09		2.6 (8 H, m) 6.40 (4 H, bd)	[a] 76.3	142.2	22.8			113.8 (–CH=) 29.8 (–CH_2–)
(V) [a,d]	4.80	3.22 (32)	2.02 (88)		2.5 (8 H, m) 6.23 (4 H, bd)	[f] 67.6 (154)	140.4 (47)	24.7 (43)			101.7, 103.9 (105) (127) (–CH=; a,a′) 30.4 (CH_2)
(VI) [e]	4.32	3.20	2.10		1.17 (3 H), 1.23 (3 H) 1.98 (6 H), 2.08 (6 H)						
(VII) [a]	4.96	3.70	2.08		2.72 (4 H, m) 4.88 (dd, 2 H, J = 3,16) 5.66 (dd, 2 H, J = 3,9) 6.34 (2 H, m)	[a] 75.8	138.4	22.4			32.4 (–CH_2–); 96.2 (–CH=) 129.5 (=CH_2)
(VIII) [a]	4.73	3.47	2.07		3.39 (2 H, m), 6.09 (4 H, m), 6.99 (2 H, m)						
(IX) [e]	3.93	2.89	2.06		2.47 (18 H, s)	[e] 62.9	131.0	22.0			125.3, 125.8 (>C=) 17.2, 17.7 (Me)
(X) [e,d]	3.81 (64)	2.71 (116)	2.22 (43)		2.47 (18 H, Me) (16)						
(XI) [a]	4.20	3.16	2.18		2.34 (6 H, Me)	[a] 62.9	122.3	22.6			2.0 (Me), 135.2 (CN)

[a] In [$^2H_6$]acetone at +35 °C. [b] J(H–H) in parentheses. [c] ^{1}H n.m.r. of (IId): δ 1.63 (3 H, d, J = 6), 3.89 [H$(3)_{anti}$,d, J = 12], 4.88 [H$(3)_{syn}$,d, J = 7), 5.09 [H(1), m, J = 6, 12], 6.22 [m, H(2)], 6.28 (s, cot); ^{13}C n.m.r. of (IId): 17.6 (Me), 76.3 [C(1)], 101.1 [C(3)], 125.8 [C(2)], 115.3 [cot, C(a,a′)], 134.9 [cot, C(b,b′)]. [d] $J(^{195}$Pt–H) or $J(^{195}$Pt–C) in parentheses. [e] In [$^2H_2$]dichloromethane at +35 °C. [f] In [$^2H_6$] acetone at −90 °C. [g] In [$^2H_6$]acetone at −30 °C. [h] In cot.

the unco-ordinated carbons appeared as a singlet at δ 136.3. These results are completely consistent with a rigid structure in which the observed asymmetry of the cot reflects the asymmetry of the complex, *i.e.* where a ≠ a′ and b ≠ b′.

By contrast, at +30 °C the palladium complexes (IIa—d) all showed sharp singlets in the ^{1}H n.m.r. spectra at δ *ca.* 6.3 due to the cot. The ^{13}C n.m.r. spectra (in [$^2H_6$]acetone) were all very broad at +30 °C but at −90 °C they showed two equal intensity resonances, which could be assigned to co-ordinated cot, together with a weak peak arising from free cot.

The 2-methylallylpalladium complex (IIb) was chosen for a more detailed study of the temperature-dependent ^{1}H n.m.r. spectrum. In acetone, on cooling from +35 °C the cot resonance at δ 6.49 slowly broadened until (at −50 °C) it had split into two lines of equal intensity at δ 6.46 and 6.64. Further cooling to −90 °C caused no further change. In [$^2H_2$]dichloromethane solution similar behaviour was observed on cooling except that the coalescence temperature was much higher and the two signals were completely resolved already at −5 °C; cooling to −35 °C, the temperature at which precipitation of the complex began, caused no further change. There was no change in $W_{\frac{1}{2}}$ of the signals of the *syn*- and *anti*- or the CH_3-protons of the allylic group from +30 to −90 °C.

The ^{13}C n.m.r. spectrum of (IIb) in [$^2H_2$]dichloromethane also showed two sharp resonances due to the cot (at δ 115.1 and 134.5) but here there was no change over the range +30 to −30 °C.

TABLE 2

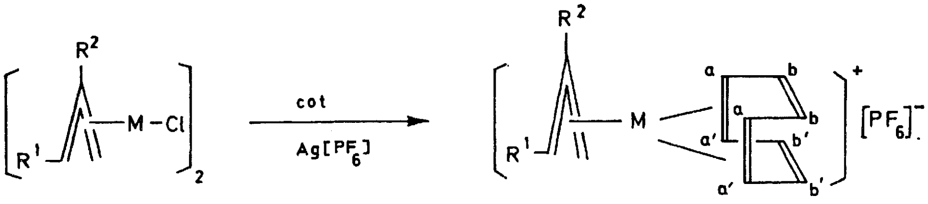
Analytical data (calculated values in parentheses)

Compound	C(%)	H(%)	Yield %
[Pd(C_3H_5)(cot)][PF_6] (IIa)	34.0 (33.3)	3.0 (3.3)	84
[Pd(2-MeC_3H_4)(cot)][PF_6] (IIb)	35.4 (35.1)	3.9 (3.7)	82
[Pd(2-PhC_3H_4)(cot)][PF_6] (IIc)	43.4 (43.2)	3.6 (3.6)	57
[Pd(1-MeC_3H_4)(cot)][PF_6] (IId)	35.4 (35.1)	3.8 (3.7)	88
[Pt(2-MeC_3H_4)(cot)][PF_6] (III)	28.9 (28.9)	3.1 (3.0)	91
[Pd(2-MeC_3H_4)(cod)][PF_6] (IV)	35.0 (34.8)	4.8 (4.6)	95
[Pt(2-MeC_3H_4)(cod)][PF_6] (V)	29.4 (28.6)	3.9 (3.8)	97
[Pd(2-MeC_3H_4)(hmdb)][PF_6] (VI)	41.1 (41.0)	5.4 (5.3)	78
[Pd(2-MeC_3H_4)(C_6H_{10})][PF_6] (VII)	30.7 (30.9)	4.4 (4.4)	97
[Pd(2-MeC_3H_4)(cht)][PF_6] (VIII)	32.9 (33.1)	3.9 (3.8)	78
[Pd(2-MeC_3H_4)(hmb)][PF_6] (IX)	40.4 (41.0)	5.3 (5.4)	86
[Pd(2-MeC_3H_4)(MeCN)$_2$][PF_6] (XI)	25.5 (24.7)	3.7 (3.4) [a]	70 [b]

[a] %N 7.2(7.2). [b] In acetonitrile as solvent.

Dilution studies at the coalescence temperature (−25 °C, $W_{\frac{1}{2}}$ = 13 Hz) in [$^2H_6$]acetone showed no changes in line-shape of the ^1H spectrum on dilution by a factor of 16. The process which caused signal averaging at ambient temperature was therefore unimolecular in complex *(IIb)*, but involving the solvent. Additional evidence for solvent participation was the observation that addition of $[^2H_6]$dimethyl sulphoxide (0.1 ml) to a concentrated solution of (IIb) in $[^2H_6]$acetone at −25 °C caused a dramatic sharpening ($W_{\frac{1}{2}} = 4$ Hz).

Addition of a small amount of cot to a solution of (IIb) in acetone at −25 °C caused further broadening and the ^1H spectrum showed that the free cot resonance was on the verge of coalescence with the co-ordinated cot. On warming this sample to +30 °C only one single resonance due to cot (at δ 6.06) was observed. On cooling to −45 °C three separate resonances (δ 6.47, 6.64, co-ordinated cot, and 5.83, free cot) were observed. Similar results were obtained in $[^2H_2]$dichloromethane, but in this case coalescence between free and co-ordinated cot only began to occur at +50 °C ($W_{\frac{1}{2}} = 24$ Hz); decomposition occurred at higher temperatures.



(I)

(II) M = Pd; a: $R^1 = R^2 = H$
b: $R^1 = H$, $R^2 = Me$
c: $R^1 = H$, $R^2 = Ph$
d: $R^1 = Me$, $R^2 = H$

(III) M = Pt, $R^1 = H$, $R^2 = Me$

$$[\{M(\eta^3\text{-}2\text{-}MeC_3H_4)Cl\}_2] + L_2 \xrightarrow{Ag[PF_6]} [M(\eta^3\text{-}2\text{-}MeC_3H_4)(L_2)][PF_6]$$

(IV) M = Pd, L_2 = cyclo-octa-1,5-diene (cod)
(V) M = Pt, L_2 = cyclo-octa-1,5-diene
(VI) M = Pd, L_2 = hexamethylbicyclohexa[2·2·0]diene (hmdb)
(VII) M = Pd, L_2 = hexa-1,5-diene
(VIII) M = Pd, L_2 = cycloheptatriene (cht)
(IX) M = Pd, L_2 = hexamethylbenzene (hmb)
(X) M = Pt, L_2 = hexamethylbenzene
(XI) M = Pd, L = MeCN

These results indicate that for the palladium-cot complexes: (i) free cot exchanges with co-ordinated cot in solution; (ii) free cot is involved in the exchange undergone by co-ordinated cot which averages out the co-ordinated and unco-ordinated cot carbons and their protons; (iii) the rate of the exchange process increases with the increasing nucleophilicity of the solvent.

Furthermore, even at the lowest temperatures attainable there was no sign of the resolution in either the ^1H or the ^{13}C spectra that was observed for the platinum complex (III) and a = a′, b = b′ throughout the accessible temperature range.

The higher temperature exchange process is presumably due to the following:

$$[Pd(all)(cot)]^+ + \text{solvent} \rightleftharpoons \text{cot} + [Pd(all)\text{solvent}]^+$$

The observed equivalence of H_a and $H_{a'}$, and H_b and $H_{b'}$, even at −90 °C could be due to an accidental overlapping of signals; however, since this is also observed in the low temperature ^{13}C spectra of all the four complexes (IIa—d) this explanation is very unlikely.

A more plausible explanation is that there is also a very low-energy exchange process occurring in these complexes, which does *not* involve the η^3-allylic group, but which effectively averages a and a′, b and b′. This could occur through a rotation of the allyl (or the cot) about the metal-ligand axis or alternatively solvent may again participate to give a five-co-ordinate intermediate which can undergo a Berry pseudorotation. Dynamic behaviour involving the allylic group ($\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$) is ruled out here since no averaging of the *syn*- and *anti*-protons of the 2-methylallyl group was observed. A similar suggestion has been made to explain the intramolecular exchange of the two ends of co-ordinated cyclo-octa-1,5-diene in $[RhMe(cod)(PPh_3)]$.[5]

On warming a solution of the platinum complex (III) in $[^2H_6]$acetone to +60 °C the *syn*- and *anti*-allylic protons began to coalesce to a single resonance [δ 4.13]

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[5] J. R. Shapley and J. A. Osborn, *J. Amer. Chem. Soc.*, 1970, **92**, 6976.

while the cot resonances now coalesced to two signals [δ 6.29 and 6.54]. This is the behaviour expected if the complex is undergoing conventional $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ dynamic behaviour involving a σ-allylic intermediate.[6]

Attempts to cause the platinum complex to mimic the behaviour of the palladium complexes by using more nucleophilic solvents failed. In the presence of 0.5 equivalents of dimethyl sulphoxide the spectrum in [$^2H_6$]acetone merely showed the presence of static (III) together with free cot.

The differing behaviour of the platinum and the palladium complexes may be reconciled, in terms of the explanation for the dynamic behaviour that we offer for the palladium complex, with a greater tendency for the palladium complex to achieve five-co-ordination with weak ligands such as acetone or dimethyl sulphoxide.

We assign a 1,2:5,6-η^4-bonding to cot in the complexes (II) and (III) rather than the alternative 1–4-η^4-bonding for the following reasons.

(a) This agrees better with the observed n.m.r. spectra; 1—4-η^4-bonded cot complexes show fluxional behaviour leading to a singlet resonance, and sharp symmetrical doublets are not observed.[7]

(b) The *X*-ray crystal structure of [Pd(cot)Cl_2] shows that the cot is 1,2:5,6-bonded there.[8]

(c) Both Pd^{II} and Pt^{II} show a strong tendency to bind to chelating dienes and less to conjugated ones; attempts to prepare palladium complexes of cyclo-octa-1,3-diene or cyclohexa-1,3-diene analogous to (V)—(IX) all failed.

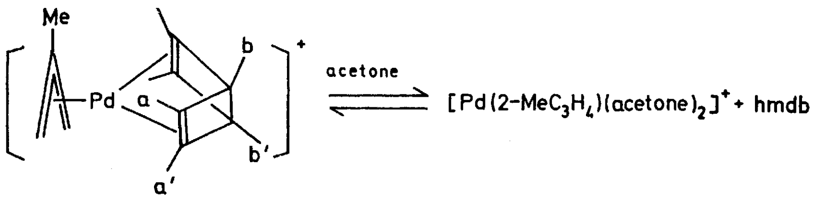
η^4-*Cyclo-octa*-1,5-*diene*(η^3-2-*methylallyl*)-*palladium and -platinum Hexafluorophosphates* (IV) *and* (V).—The palladium complex (IV) has already been described [2,3] but the platinum complex (V) is new. The ^1H n.m.r. spectra (Table 1) were similar to each other at +30 °C except that the resonances arising from the cyclo-octa-1,5-diene (cod) olefinic protons as well as the *syn*- and *anti*-protons of the methylallyl were all broadened in the platinum complex (V). The cod olefinic carbons were also broad in the ^{13}C spectrum of (V) at +30 °C but at −90 °C a clean and sharp spectrum was obtained which showed these carbons as two singlets (with platinum satellites). This complex therefore appeared to be static at low temperature and hence similar to the platinum–cot complex (III).

The palladium complex (IV) showed sharp *syn*- and *anti*-proton resonances, and an olefinic cod resonance, which was broader due to H–H coupling, in the ^1H spectrum at +30 °C. The ^{13}C spectrum was invariant from +30 to −90 °C in [$^2H_6$]acetone and showed only one type of cod olefinic carbon, but in [$^2H_2$]dichloromethane the singlet (δ 113.5) at +30 °C broadened at lower temperatures and was split into a closely spaced doublet (δ 112.8, 113.6) at −50 °C, while the cod CH_2 carbon remained as a singlet (δ 29.5). This suggests that (IV) exists as the frozen-out form at low temperatures in dichloromethane but that at higher temperature and in acetone exchange processes similar to those suggested for the cot–palladium complex (IIb) occur.

η^4-*Hexamethylbicyclo*[2.2.0]*diene*(η^3-2-*methylallyl*)*palladium Hexafluorophosphate* (VI).—In [$^2H_2$]dichloromethane at +30 °C the ^1H n.m.r. spectrum showed that the molecule was quite rigid and that no exchange process were occurring. In particular, the signals of the methyls of the hexamethyl Dewar benzene (hmdb) were separated into two pairs (a/a′ and b/b′) as required by the symmetry of the complex. Low solubility precluded ^{13}C measurements in this solvent.

However, in [$^2H_6$]acetone the ^1H n.m.r. spectrum showed the presence of free hmdb [at δ 1.05 (6 H) and 1.57 (12 H)] as well as a hmdb complex in which the methyl groups a and a′, and b and b′ were now equivalent [δ 1.26 (6 H), 2.12 (12 H), 2.17 (3 H), 3.38 (2 H_{anti}), and 4.58 (2 H_{syn})]. In addition, resonances ascribed to [Pd(2-MeC_3H_4)(acetone)$_2$]$^+$ were observed at δ 2.31 (3 H), 3.20 (2 H_{anti}), and 4.16 (2 H_{syn}). The ratio of complexed to uncomplexed hmdb was 7 : 3.

Clearly the situation in acetone is analogous to that which is observed for the palladium–cot complex except that here the position of the equilibrium favours the free ligand more. The observed equivalence of a and a′, and b and b′, in acetone probably arises through the reversible dissociation:



(VI)

Attempts to prepare the platinum analogue of (VI) were unsuccessful.

η^4-*Hexa*-1,5-*diene*(η^3-2-*methylallyl*)*palladium Hexafluorophosphate* (VII).—The ^1H and ^{13}C n.m.r. spectra in acetone (Table 1) were consistent with either one form, (VIIa) *or* (VIIb), or with fast exchange between them. It was not possible to differentiate between these possibilities.

η-*Cycloheptatriene*(η^3-2-*methylallyl*)*palladium Hexa-*

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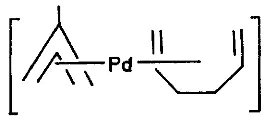
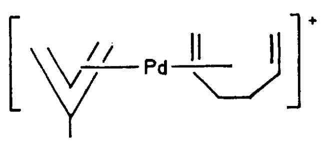
[6] K. Vrieze, 'Dynamic Nuclear Magnetic Resonance Spectroscopy,' eds. L. M. Jackman and F. A. Cotton, Academic Press, New York, 1975, p. 454.

[7] F. A. Cotton, 'Dynamic Nuclear Magnetic Resonance Spectroscopy,' eds. L. M. Jackman and F. A. Cotton, Academic Press, New York, 1975, p. 403.

[8] C. V. Goebel, *Diss. Abstr.*, 1967, **28**, 625B.

fluorophosphate (VIII).—^{13}C N.m.r. studies on this complex were not possible owing to low solubility and the ^1H spectra gave only a little information. In [$^2H_2$]dichloromethane the complex appeared to be stable and a spectrum was obtained (Table 1); however, in [$^2H_6$]acetone it had completely dissociated and the resonances observed could be entirely ascribed to free cycloheptatriene [δ 2.28 (2 H, t, $J = 6$), 5.37 (2 H, m), 6.17 (2 H, m), and 6.60 (m, 2 H)] and the acetone complex [Pd(2-MeC_3H_4)-(acetone)$_2$]$^+$ [see complex (VI) above]. The mode of bonding of the cht to the metal is not known but is expected to be 1,2:5,6-η^4.


(VIIa)


(VIIb)

η-*Hexamethylbenzene*(η^3-2-*methylallyl*)-*palladium and -platinum Hexafluorophosphates* (IX) *and* (X).—On addition of silver hexafluorophosphate to a dichloromethane solution of di-μ-chloro-bis(2-methylallylpalladium) and hexamethylbenzene (hmb), an immediate colour change from yellow to orange was observed. An orange granular solid was isolated from the solution which was stable under nitrogen both in the solid and in dichloromethane, chloroform, or benzene solution. However, the substance immediately turned colourless on contact with even weakly co-ordinating solvents, such as water, acetone, or diethyl ether, to give free hmb and the appropriate solvent complex.

At +35 °C in [$^2H_2$]dichloromethane the hmb methyl resonances were observed as a singlet ($W_{\frac{1}{2}} = 5$ Hz) at δ 2.47 in the ^1H n.m.r. spectrum. On cooling, the allylic resonances retained their sharpness and their chemical shifts [δ 2.06 (Me), 2.89 (H_{anti}), and 3.93 (H_{syn})] but the hmb resonance broadened until at −50 °C two sharp resonances were present, at δ 2.45 and 2.22*; no further change occurred down to −80 °C. The low-temperature ^{13}C n.m.r. spectrum at −90 °C showed two resonances for the hmb ring carbons (δ 125.3, 125.8*) and two for the hmb methyl carbons (δ 17.2*, 17.7).

The platinum analogue (X) was also prepared (at 0 °C) but it proved extremely unstable and could only be characterised through a low-temperature ^1H n.m.r. spectrum in [^2H]chloroform. This was temperature invariant over the range 0 to −30 °C (at which temperature the complex precipitated from solution) and showed co-ordinated hmb at δ 2.47 [J(H–Pt) = 16 Hz] as well as unco-ordinated hmb at δ 2.19.

The available information does not allow an unambiguous assignment of structure to (IX) or (X). Two possibilities may reasonably be considered; one that the hmb is 1—4-η-bonded in the manner which has been observed for some Rh^I and Ir^I complexes [9,10] (to give a 16-electron complex), and the other that the hmb is η^6-bonded, giving an 18-electron complex. The ^1H n.m.r. spectrum of the platinum complex (X) is hard to reconcile with the former structure unless the hmb were dynamic with a very low $\Delta G^\ddagger$ and even then the great differences between J(H–Pt), for H_{syn}, H_{anti}, and the allylic methyl in (X) and those for the diene–platinum complexes (III) and (V) are hard to understand. Accordingly we favour the 18-electron η^6-bonded structure for (X), and the lack of exchange between co-ordinated and unco-ordinated hmb at 0 °C is consistent with the observations on the cot–platinum complex (III).

The similarity in the chemical shifts of H_{syn}, H_{anti}, and the allylic methyl of (X) and (IX) and the differences between these values and the corresponding ones for the diene complexes (II)—(VIII) again argues that the bonding is similar in (X) and (IX) and different from that in (II)—(VIII).

On this interpretation one set of hmb resonances in both the ^1H and the ^{13}C low-temperature spectra (marked *) of (IX) must be due to free hmb and exchange between co-ordinated and free hmb occurs at ambient temperatures. This picture is again consistent with the behaviour observed for the cot–palladium complex, (IIb).

η^6-Benzene complexes are not known for Pd^{II} or Pt^{II} but the nickel complex $[Ni(C_3H_5)(C_6H_6)]^+$ has been reported briefly without any discussion of the bonding.[11] 18-Electron complexes of the type $[Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)]$ are, however, well-known and well-characterised [12] and are moreover red–brown in contrast to most other η^3-allylic compounds which are yellow. The very much deeper colours of (IX) and (X) compared to the other complexes may be noted.

Conclusion.—The diene- and hmb-palladium complexes readily undergo exchange with free ligand, particularly in acetone, which leads to the observation of equivalence of the ligand sites in L_2:

$$[Pd(all)L_2]^+ + 2s \rightleftharpoons [Pd(all)s_2]^+ + L_2$$

For the series $[Pd(2\text{-}MeC_3H_4)(L_2)][PF_6]$ the stability towards displacement of L_2 by solvent (acetone) is found to be L_2 = hmb ~ cht ~ hexa-1,5-diene < hexamethylbicyclo[2.2.0]hexadiene < cyclo-octa-1,5-diene ~ cyclo-octatetraene. The platinum complexes are less stable in this respect than their palladium analogues.

There is also a low-energy intramolecular exchange process, which has been most closely defined for [Pd(2-MeC_3H_4)cot]$^+$, probably involving a solvated five-co-ordinate intermediate which makes the ligand sites in L_2 equivalent *via* a Berry pseudorotation.

The platinum complexes do not undergo comparable dynamic behaviour involving the diene ligand but there

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is some evidence for a $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ dynamic process involving the allylic ligand at higher temperatures.

EXPERIMENTAL

All experiments were carried out under nitrogen. The allylic palladium chloride complexes (I) were prepared by published methods.[13] Yields and analytical data for the cationic complexes are presented in Table 2, and details of a typical preparation are given below.

Di-μ-chloro-bis(η^3-2-methylallylplatinum).—A hot solution of potassium tetrachloroplatinate(II) (3.8 g, 9.1 mmol) in water (40 ml) was added to a boiling solution of 1-chloro-2-methylprop-2-ene (20 ml) in ethanol (95%, 300 ml) containing suspended sodium acetate (14 g, 0.18 mol). The resultant solution was refluxed for 2.2 h during which time the colour changed from red to pale yellow; it was then cooled, and the solvent removed *in vacuo* on a rotary evaporator. The solid residue was extracted with dichloromethane (1 × 100 ml, 2 × 50 ml); the extracts were dried (Na_2SO_4) and the solvent removed. After washing with light petroleum and air-drying, di-μ-chloro-bis(η^3-2-methylallylplatinum) was obtained as a buff solid (2.2 g, 7.8 mmol, 85%) which was suitable for further reaction. The ^1H n.m.r. spectrum was identical to the published one.[14] The ^{13}C spectrum showed resonances at δ 22.4 [Me, J(C–Pt) = 57 Hz], 45.0 [C(1), J 279], and 109.6 [C(2)].

(1,2:5,6-η^4-Cyclo-octa-1,5-diene)(1—3-η-2-methylallyl)palladium Hexafluorophosphate (IV).—Silver hexafluorophosphate (0.55 g, 2.2 mmol) was added in one portion to a stirred solution of di-μ-chloro-bis(2-methylallylpalladium) (0.42 g, 2.1 mmol) and cyclo-octa-1,5-diene (1.5 ml) in dichloromethane (40 ml). An immediate reaction took place with the precipitation of silver chloride; this was filtered off after 5 min and the filtrate was evaporated to dryness on a rotary evaporator. The solid was purified by reprecipitation from acetone and diethyl ether to yield (IV) as a white solid (0.84 g, 2.0 mmol, 95%). The analytical sample was purified by dissolving the solid in acetone, and filtering the solution through a short column of cellulose, after which it was crystallised from acetone–diethyl ether.

The bis-acetonitrile complex (XI) was prepared similarly but using acetonitrile as solvent.

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