Palladium(II) and Platinum(II) η^3-Methylallyl Trichlorotin Complexes. Part 3.* Crystal Structure Analysis of $[Pt(\eta^3\text{-}C_4H_7)(cod)]_2[Pt(\eta^3\text{-}C_4H_7)(SnCl_3)_3]$ (cod = cyclo-octa-1,5-diene)†

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The dimer $[\{Pt(\eta^3\text{-}C_4H_7)Cl\}_2]$ reacts with cyclo-octa-1,5-diene (cod) and $SnCl_2$ to give $[Pt(\eta^3\text{-}C_4H_7)(cod)]_2[Pt(\eta^3\text{-}C_4H_7)(SnCl_3)_3]$ (**1**). The compound crystallizes as discrete anionic and cationic platinum(II) complexes in space group $P\bar{1}$ with a = 13.256(4), b = 19.960(4), c = 8.615(3) Å, α = 101.75(2), β = 104.69(2), and γ = 86.62(2)°. The anionic complex displays a distorted square-pyramidal co-ordination while the two isostructural cations have irregular square-planar co-ordination. Analysis of bond distances using $SnCl_3$ as a probe suggests that the *trans* influence of the methylallyl ligand is comparable to that of olefin ligands. While no n.m.r. data are available for (**1**) due to its very poor solubility, n.m.r. results for the palladium(II) analogue (**2**) obtained by the same synthetic route are compatible with the structure determined for (**1**).

As a part of a research programme on transition-metal compounds containing the $SnCl_3$ group, we have recently reported[1,2] the preparation and characterization of $[M(\eta^3\text{-}C_4H_7)(SnCl_3)L]$ (M = Pt or Pd; L = olefin or CO; C_4H_7 = 2-methylallyl). The complexes are readily synthesized according to equation (1). This reaction has now been extended to

$$\tfrac{1}{2}[\{M(\eta^3\text{-}C_4H_7)Cl\}_2] + SnCl_2 + L \longrightarrow [M(\eta^3\text{-}C_4H_7)(SnCl_3)L] \quad (1)$$

diolefins. In this paper we report on the reaction with cyclo-octa-1,5-diene (cod) which yields sparingly soluble orange compounds $[M(\eta^3\text{-}C_4H_7)(cod)]_2[M(\eta^3\text{-}C_4H_7)(SnCl_3)_3]$ [M = Pt(**1**) or Pd(**2**)]. Although the palladium derivative (**2**) was sufficiently soluble to measure ^{1}H n.m.r. spectra, the limiting low-temperature spectra could not be obtained. Therefore an *X*-ray crystallographic study was deemed necessary to elucidate the structure of these products. Crystals suitable for *X*-ray analysis were grown for the compound (**1**).

Reaction (1) has been also run with norbornadiene and butadiene yielding with the former ligand an insoluble uncharacterized compound. The palladium–butadiene complex is exceedingly thermally unstable and proved to be difficult to characterize spectroscopically. Addition of triphenylphosphine to the product yielded $[Pd(\eta^3\text{-}C_4H_7)(SnCl_3)(PPh_3)]$. We therefore believe the butadiene ligand to be η^2-co-ordinated to the metal, *i.e.* structurally similar to the mono-olefin complex.[1]

Results and Discussion

The ^{1}H n.m.r. spectrum of compound (**2**) at room temperature (Figure 1) consists of five broad singlets [δ 6.04 (4 H), 4.74 (3 H), 3.4 (3 H), 2.5 (8 H), and 1.88 (4.5 H)], which were tentatively assigned as the resonances of the species $[Pd(\eta^3\text{-}C_4H_7)(\eta^2\text{-}C_8H_{12})(SnCl_3)]$ undergoing rapid fast exchange. Nevertheless the integrated areas of the signals as well as the spectral features were not consistent with the above hypothetical structure. The spectrum measured at −90 °C exhibits partial splitting of resonances at δ 3.4 and 1.88 into two sets of signals which, on going from high to low field, integrate as 1.5 H, 3 H, 1 H, and 2 H respectively. On the basis of these results, and taking into account the elemental analysis for (**2**) and the *X*-ray findings on the platinum compound obtained with the same synthetic procedure, we interpreted the spectrum as the superimposition of the subspectra due to $[Pd(\eta^3\text{-}C_4H_7)(SnCl_3)_3]^{2-}$ and $[Pd(\eta^3\text{-}C_4H_7)(cod)]^+$ in which the allylic resonances overlap at room temperature and partially split at −90 °C. Averaging occurs between the cod olefinic and CH_2 protons above and below the co-ordination plane, indicating the occurrence of a dynamic process and suggesting that cod, as reported elsewhere,[3] is weakly bound to Pd. To account for the observed fluxionality, the two most probable mechanisms are: (*i*) η^3–σ–η^3 on the methylallyl moiety, (*ii*) η^4–η^2–η^4 involving the cod ligand. No evidence of η^3–σ–η^3 allyl isomerization (which should equilibrate the *syn* and *anti* protons) was detected, and thus we suggest that the observed exchange may proceed *via* path (*ii*). In principle a further process, which implies complete exchange of the co-ordination sphere of the two different $Pd(\eta^3\text{-}C_4H_7)$ species, is consistent with our findings. In favourable circumstances this dynamic behaviour could be easily monitored by ^{119}Sn n.m.r. spectroscopy, either by direct observation or by ^{119}Sn satellite analysis. We failed however to rule out this third mechanism because of the very low solubility and the high fluxionality of (**2**). The platinum compound, was almost insoluble in all common solvents, therefore no n.m.r. data are available.

X-Ray Diffraction Structure Analysis of Compound (**1**).—In

* Part 2 is ref. 2.

† Bis[η-cyclo-octa-1,5-diene)(η-2-methylallyl)platinum(II)](η-2-methylallyl)tris(trichlorostannio)platinate(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

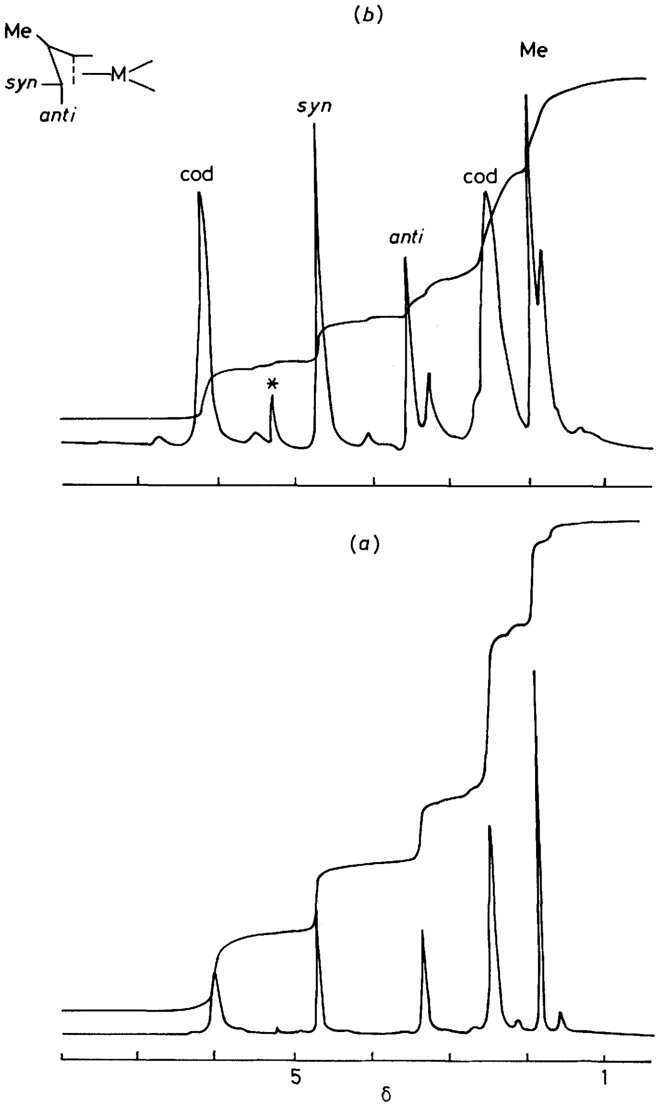

Figure 1. Proton n.m.r. spectrum of compound (**2**) at 80.01 MHz in CD_2Cl_2: (*a*) at 295, (*b*) at 183 K (* solvent impurity)

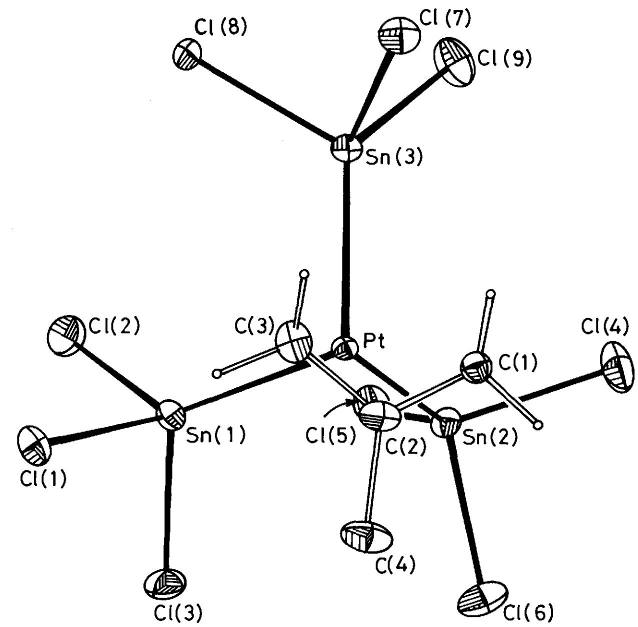

Figure 2. ORTEP view of anion (**1a**) (arbitrary orientation)

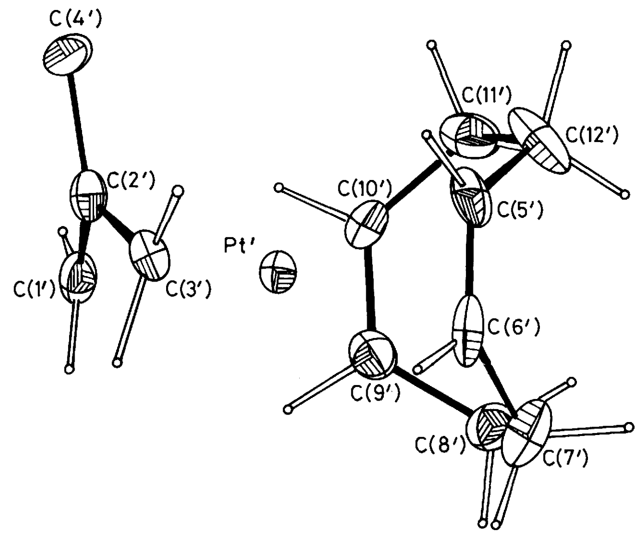

Figure 3. ORTEP view of cation (**1b**) (arbitrary orientation)

Figures 2 and 3 ORTEP views and numbering schemes respectively of the $[Pt(\eta^3\text{-}C_4H_7)(SnCl_3)_3]^{2-}$ moiety (**1a**) and of one of the $[Pt(\eta^3\text{-}C_4H_7)(cod)]^+$ cations (**1b**) are shown, the second cation being crystallographically independent but visually indistinguishable from the first. Final positional parameters are given in Table 1 while Table 2 presents a compilation of bond distances and angles.

The crystals obtained in the case of the palladium analogue (**2**) were unsuitable for *X*-ray diffraction and even attempts to determine the unit-cell parameters to verify isomorphism with (**1**) were unsuccessful.

$[Pt(\eta^3\text{-}C_4H_7)(SnCl_3)_3]^{2-}$. The co-ordination of anion (**1a**) can be described in terms of a distorted square pyramid, reminiscent of the structure of $[Pt(\eta^4\text{-cod})(SnCl_3)_3]^-$, complex (**3**).[4] In analogy to what was observed for that product, the apical Pt–Sn(3) bond length [2.615(1) in (**1a**) and 2.643(2) Å in (**3**) respectively] is markedly longer than the basal Pt–Sn bond distances [means 2.541(1) and 2.557(2) Å in (**1a**) and in (**3**) respectively]. This behaviour conforms to theoretical predictions for low-spin d^8 square-pyramidal species presented in the work of Rossi and Hoffmann.[5]

Despite similarities, (**1a**) and (**3**) display also interesting differences. (*i*) The square-pyramidal co-ordination in (**3**) is flatter than in (**1a**) as evidenced by the average $Sn_{apical}PtSn_{basal}$ bond angles [94.3 and 102.9° in (**3**) and in (**1a**) respectively]; accordingly the distance of the Pt atom from the plane defined by the basal Sn atoms and the centres of mass of the other basal ligands in (**1a**) has the rather large value of 0.647(1) Å. (*ii*) The corresponding bonding distances in (**1a**) are consistently shorter than in (**3**). While (*i*) should be accounted for essentially by steric causes, the cod ligand being bulkier than the methylallyl, for (*ii*) also electronic features may play a role.

In Table 3 selected Pt–Sn bond lengths in square-planar and in square-pyramidal $Pt(SnCl_3)$ complexes are listed. For the latter co-ordination geometry only basal ligand bond distances are listed. Specifically, the data relative to $Pt(C_4H_7)(SnCl_3)$ complexes suggest that, in the case of the two geometries which are considered, neither co-ordination mode plays a major role in determining Pt–Sn bond distances, nor the anionic character of anion (**1a**). The apical Pt–Sn distances in (**1a**) and in (**3**),[4] and the Pt–Sn bond lengths observed in $[Pt(SnCl_3)_5]^{3-}$,[6] [2.553(1)

Table 1. Fractional atomic co-ordinates for non-H atoms for compound (**1**) with estimated standard deviations (e.s.d.s) in parentheses

Atom	X/a	Y/b	Z/c
Anion (**1a**)			
Pt	0.279 30(3)	0.253 86(2)	0.544 95(5)
Sn(1)	0.109 81(5)	0.194 57(4)	0.523 08(8)
Sn(2)	0.209 90(5)	0.370 19(4)	0.654 53(9)
Sn(3)	0.406 65(5)	0.225 89(4)	0.810 35(8)
Cl(1)	0.078 2(2)	0.091 0(2)	0.320 1(4)
Cl(2)	0.059 3(2)	0.153 4(2)	0.730 7(3)
Cl(3)	−0.050 9(2)	0.248 4(2)	0.420 0(4)
Cl(4)	0.324 4(2)	0.462 6(2)	0.790 4(5)
Cl(5)	0.110 0(3)	0.376 8(2)	0.850 1(4)
Cl(6)	0.095 8(3)	0.430 2(2)	0.474 6(5)
Cl(7)	0.576 3(2)	0.187 1(2)	0.763 0(4)
Cl(8)	0.380 5(2)	0.128 9(2)	0.924 5(4)
Cl(9)	0.478 5(2)	0.301 4(2)	1.065 4(4)
C(1)	0.380 7(8)	0.293 0(6)	0.417 8(13)
C(2)	0.313 0(8)	0.241 7(7)	0.309 2(13)
C(3)	0.328 8(8)	0.177 4(6)	0.359 7(12)
C(4)	0.222 5(9)	0.256 2(8)	0.164 5(14)
Cation (**1b′**)			
Pt′	0.764 12(3)	0.404 69(2)	−0.106 99(5)
C(1′)	0.752 8(9)	0.343 1(6)	0.062 6(14)
C(2′)	0.858 9(9)	0.341 2(7)	0.056 8(13)
C(3′)	0.900 2(8)	0.408 1(7)	0.093 0(13)
C(4′)	0.913 8(10)	0.279 7(7)	−0.013 6(14)
C(5′)	0.826 0(9)	0.442 6(7)	−0.290 6(16)
C(6′)	0.778 4(10)	0.496 1(6)	−0.207 2(15)
C(7′)	0.672 0(13)	0.525 3(7)	−0.276 0(19)
C(8′)	0.582 9(12)	0.487 5(10)	−0.261 7(22)
C(9′)	0.599 4(10)	0.415 2(10)	−0.239 6(20)
C(10′)	0.642 1(12)	0.362 9(8)	−0.334 4(19)
C(11′)	0.678 4(16)	0.374 4(9)	−0.480 3(18)
C(12′)	0.780 2(13)	0.402 7(7)	−0.454 0(17)
Cation (**1b″**)			
Pt″	0.269 16(3)	−0.038 22(2)	−0.163 68(5)
C(1″)	0.311 8(8)	−0.020 1(6)	0.095 4(11)
C(2″)	0.202 0(7)	−0.029 0(5)	0.050 4(11)
C(3″)	0.147 8(8)	0.012 4(5)	−0.058 5(11)
C(4″)	0.151 3(8)	−0.090 7(6)	0.074 0(14)
C(5″)	0.186 0(8)	−0.079 0(6)	−0.426 9(11)
C(6″)	0.218 8(9)	−0.013 8(6)	−0.411 0(12)
C(7″)	0.315 1(10)	0.004 2(6)	−0.456 0(13)
C(8″)	0.413 2(8)	−0.036 3(6)	−0.391 8(13)
C(9″)	0.419 5(7)	−0.060 4(6)	−0.236 0(13)
C(10″)	0.381 1(8)	−0.121 9(6)	−0.224 6(14)
C(11″)	0.319 3(9)	−0.174 7(6)	−0.363 8(14)
C(12″)	0.241 4(8)	−0.143 6(6)	−0.496 8(13)

and 2.572(1) Å, average axial and equatorial value respectively], do not fit well with the data in Table 3, consistently with theoretical analysis.[5] Basal Pt–Sn bond distances can be interpreted essentially in terms of *trans* influence, extending the relationship also to square-pyramidal complexes. The data in Table 3 suggest that, with $SnCl_3$ as a probe, the *trans* influence of the methylallyl ligand is comparable to that of olefins. In this respect it is not surprising that literature data for pertinent chlorine derivatives* imply a different conclusion, *i.e.* a *trans* influence somewhat larger for allyl than for olefin ligands. These diverging conclusions can in fact be tentatively rationalized in terms of the different direction and magnitude of π interactions for the two probing ligands.[7]

* M-Cl interaction distances (M = Pt or Pd) for bonds *trans* to olefinic ligands average 2.31(1) Å from refs. 8(*a*)—(*d*), while those *trans* to allyl ligands average 2.36(1) Å from refs. 9(*a*)—(*d*).

Table 2. Bond lengths (Å) and selected bond angles (°) for compound (**1**) with e.s.d.s in parentheses *

Anion (**1a**)

Sn(1)–Pt	2.548(1)	Cl(5)–Sn(2)	2.373(4)
Sn(2)–Pt	2.535(1)	Cl(6)–Sn(2)	2.341(4)
Sn(3)–Pt	2.615(1)	Cl(7)–Sn(3)	2.440(3)
C(1)–Pt	2.200(13)	Cl(8)–Sn(3)	2.421(3)
C(2)–Pt	2.152(12)	Cl(9)–Sn(3)	2.402(3)
C(3)–Pt	2.175(11)	C(2)–C(1)	1.422(15)
Cl(1)–Sn(1)	2.400(3)	C(3)–C(2)	1.425(18)
Cl(2)–Sn(1)	2.365(4)	C(4)–C(2)	1.558(15)
Cl(3)–Sn(1)	2.375(3)	AL–Pt	1.913(20)
Cl(4)–Sn(2)	2.373(3)		
Sn(2)–Pt–Sn(1)	92.6(1)	Cl(4)–Sn(2)–Pt	121.0(1)
Sn(3)–Pt–Sn(1)	104.7(1)	Cl(5)–Sn(2)–Pt	117.9(1)
Sn(3)–Pt–Sn(2)	101.1(1)	Cl(5)–Sn(2)–Cl(4)	98.7(1)
C(1)–Pt–Sn(1)	147.6(2)	Cl(6)–Sn(2)–Pt	119.7(1)
C(1)–Pt–Sn(2)	95.4(3)	Cl(6)–Sn(2)–Cl(4)	96.3(1)
C(1)–Pt–Sn(3)	104.5(3)	Cl(6)–Sn(2)–Cl(5)	98.3(1)
C(2)–Pt–Sn(1)	111.0(3)	Cl(7)–Sn(3)–Pt	111.4(1)
C(2)–Pt–Sn(2)	116.0(4)	Cl(8)–Sn(3)–Pt	122.0(1)
C(2)–Pt–Sn(3)	125.9(3)	Cl(8)–Sn(3)–Cl(7)	95.1(1)
C(3)–Pt–Sn(1)	95.5(3)	Cl(9)–Sn(3)–Pt	129.1(1)
C(3)–Pt–Sn(2)	154.2(3)	Cl(9)–Sn(3)–Cl(7)	94.4(1)
C(3)–Pt–Sn(3)	100.4(3)	Cl(9)–Sn(3)–Cl(8)	97.0(1)
C(3)–Pt–C(1)	65.5(4)	C(3)–C(2)–C(1)	112.4(9)
Cl(1)–Sn(1)–Pt	114.2(1)	C(4)–C(2)–C(1)	123.7(12)
Cl(2)–Sn(1)–Pt	127.7(1)	C(4)–C(2)–C(3)	123.5(10)
Cl(2)–Sn(1)–Cl(1)	97.0(1)	AL–Pt–Sn(1)	119.6(6)
Cl(3)–Sn(1)–Pt	118.7(1)	AL–Pt–Sn(2)	122.8(6)
Cl(3)–Sn(1)–Cl(1)	95.8(1)	AL–Pt–Sn(3)	112.6(6)
Cl(3)–Sn(1)–Cl(2)	97.2(1)		

Cations (**1b**)

	(**1b′**)	(**1b″**)
C(1′)–Pt′	2.129(13)	2.118(9)
C(2′)–Pt′	2.196(12)	2.214(11)
C(3′)–Pt′	2.149(10)	2.146(11)
C(5′)–Pt′	2.229(16)	2.260(9)
C(6′)–Pt′	2.209(14)	2.211(11)
C(9′)–Pt′	2.213(13)	2.230(11)
C(10′)–Pt′	2.244(14)	2.239(11)
C(2′)–C(1′)	1.419(17)	1.420(13)
C(3′)–C(2′)	1.419(19)	1.408(15)
C(4′)–C(2′)	1.489(18)	1.508(17)
C(6′)–C(5′)	1.376(18)	1.366(18)
C(12′)–C(5′)	1.466(18)	1.536(16)
C(7′)–C(6′)	1.516(20)	1.507(19)
C(8′)–C(7′)	1.481(26)	1.532(16)
C(9′)–C(8′)	1.490(28)	1.497(18)
C(10′)–C(9′)	1.377(23)	1.387(19)
C(11′)–C(10′)	1.517(27)	1.519(14)
C(12′)–C(11′)	1.441(27)	1.542(15)
AL′–Pt′	1.898(21)	1.896(18)
DB1′–Pt′	2.109(22)	2.128(13)
DB2′–Pt′	2.119(19)	2.124(15)
C(3′)–Pt′–C(1′)	66.3(5)	67.6(4)
C(9′)–Pt′–C(6′)	81.0(6)	81.9(4)
C(10′)–Pt′–C(5′)	80.6(6)	80.9(4)
C(3′)–C(2′)–C(1′)	111.1(11)	114.0(10)
C(4′)–C(2′)–C(1′)	124.8(11)	122.5(9)
C(4′)–C(2′)–C(3′)	122.8(12)	121.1(8)
C(6′)–C(5′)–Pt′	71.1(9)	70.3(5)
C(12′)–C(5′)–C(6′)	125.8(11)	124.3(11)
C(5′)–C(6′)–Pt′	72.7(8)	74.2(6)
C(7′)–C(6′)–C(5′)	124.4(11)	124.6(10)
C(8′)–C(7′)–C(6′)	114.7(14)	114.8(11)
C(9′)–C(8′)–C(7′)	118.7(14)	116.4(10)
C(10′)–C(9′)–Pt′	73.3(8)	72.3(7)
C(10′)–C(9′)–C(8′)	127.0(18)	125.5(9)

Table 2 (*continued*)

C(9′)–C(10′)–Pt′	70.8(8)	71.6(7)
C(11′)–C(10′)–C(9′)	121.3(16)	127.1(11)
C(12′)–C(11′)–C(10′)	119.2(12)	114.0(9)
C(11′)–C(12′)–C(5′)	116.9(14)	113.2(8)
AL′–Pt′–DB1′	136.0(8)	135.7(7)
AL′–Pt′–DB2′	136.8(9)	136.8(7)
DB1′–Pt′–DB2′	85.9(8)	86.4(6)

* AL,AL′ respectively are the centres of gravity of the allylic carbons of (**1a**) and (**1b**), DB1′ and DB2′ the midpoints of the C(5′)–C(6′) and C(9′)–C(10′) double bonds.

Table 3. Bond distances Pt–Sn (Å) for square-planar and square-pyramidal (basal bonds) co-ordination

Complex		Ref.
syn-trans-$[\{Pt(SnCl_3)(PEt_3)Cl\}_2]$	2.487(3)	*a*
$[Pt(SnCl_3)(PEt_3)\{PhC(NH_2)=NOH\}Cl]$	2.501(1)	*b*
$[Pt(SnCl_3)(PEt_3)(NH_2C_6H_4Cl$-*p*$)]$	2.514(1)	*c*
$[Pt(\eta^3\text{-}C_4H_7)(H_2=CHPh)(SnCl_3)]$	2.539(1)	1
$[Pt(\eta^3\text{-}C_4H_7)(SnCl_3)_3]^{2-}$	2.542(1)	This work [d]
$[Pt(\eta^3\text{-}C_4H_7)(SnCl_3)(CO)]$	2.550(1)	2
$[Pt(SnCl_3)(cod)]^-$	2.557(1)	4, *d*
$[Pt(SnCl_3)(diop)Cl]$	2.599(1)	*e*
trans-$[Pt(SnCl_3)_2\{P(OPh)_3\}_2]$	2.602(2)	7
trans-$[Pt(SnCl_3)_2(COPh)(PEt_3)]$	2.634(1)	—

[a] A. Albinati, R. Naegeli, K. H. A. Ostoja Starzewski, P. S. Pregosin, and H. Rüegger, *Inorg. Chim. Acta*, 1983, **76**, L231. [b] A. B. Goel, S. Goel, and D. Vanderveer, *Inorg. Chim. Acta*, 1981, **54**, L5. [c] A. Albinati, H. Moriyama, H. Rüegger, P. S. Pregosin, and A. Togni, *Inorg. Chem.*, 1985, **24**, 4430. [d] Average for basal Pt–Sn bonds. [e] B. Consiglio, P. Pino, and M. Scallone, unpublished work quoted in ref. 1, diop = 2,3-*O*-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane. [f] A. Albinati, U. Von Gunten, P. S. Pregosin, and H. J. Ruegg, *J. Organomet. Chem.*, 1985, **295**, 239.

In Table 4 Pt–C bond distances for $Pt(\eta^3\text{-}C_4H_7)(SnCl_3)$ complexes are listed. Also in this case we note that the basal ligand positioning in the square-pyramidal complex (**1a**) does not appear to alter the Pt–C distances *trans* to $SnCl_3$, with respect to the values observed in species with square-planar co-ordination.

The $SnCl_3$ geometry is coherent with pertinent literature:[10] specifically the average Sn–Cl bond lengths and Cl–Sn–Cl angles have values which are respectively larger and smaller for apical than for basal $SnCl_3$. Finally a nearly perfectly staggered conformation around the Pt–C(2) bond is observed.

$[Pt(\eta^3\text{-}C_4H_7)(cod)]^+$. The two isostructural cations (**1b**) of idealized C_s symmetry, display only minor, probably packing-related differences, and will be therefore discussed together. The centre of gravity of the allyl ligand and the two double-bond midpoints define the metal co-ordination plane, details of the co-ordination geometry being presented in Table 5. Significant deviations from a perfectly planar co-ordination are observed: the Pt atom lies roughly 0.12 Å to the side of the co-ordination plane opposite to the methyl substituent of the methylallyl ligand. The dihedral angle between this plane and the allyl plane is close to the usual value of 115°, while that with the cyclo-octadiene ligand deviates slightly from orthogonality (average 93°), the double bonds being nearly perpendicular to the co-ordination plane. The platinum–terminal allyl carbon distances are in fair agreement with literature data for complexes of Pt^{II} and Pd^{II} where the methylallyl ligand is *trans* to an olefinic ligand: the average value of 2.136(11) Å in (**1b**) is to be compared with distances of 2.151(7) Å in $[Pt(\eta^3\text{-}C_4H_7)(CH_2=CHPh)(SnCl_3)]$,[1] of 2.175(13) Å in $[Pt(\eta^3\text{-}C_4H_7)(CH_2=CHPh)(PPh_3)]^+$,[11] and 2.154(3) Å in $[Pd(\eta^5\text{-}C_{10}H_{17})(MeCN)]^+$,[12] the observed differences being scarcely significant.

The co-ordination of the cyclo-octadiene ligand, in the normal tub conformation, is characterized by average Pt–C and C=C bond lengths of 2.230(12) and 1.376(16) Å respectively. These values are consistent with literature data for platinum(II) olefin complexes (Table 6). Caution appears necessary in a detailed interpretation of these data because of the experimental uncertainties and the possible importance of steric and packing effects. However, while $Pt\text{–}C_{cod}$ bond lengths in (**1b**) are significantly longer than in $[Pt(cod)Cl_2]$[8a] and hardly shorter than in $[Pt(cod)Me(C_9F_6H_5)]$,[13] they are in close agreement with values reported[11] for $[Pt(\eta^3\text{-}C_4H_7)(PPh_3)(Z\text{-}MeCH=CHMe)]^+$ and for $[Pt(\eta^3\text{-}C_4H_7)(PPh_3)(E\text{-}MeCH=CHMe)]^+$, *i.e.* 2.200 and 2.232 Å respectively.

The essential invariance of the $Pt\text{–}C_{allyl}$ bond distances on going from neutral to cationic complexes, with similar ligands in *trans* position, suggests a predominant σ contribution in $Pt\text{–}C_{allyl}$ bonds and unimportant reduction in π back donation for these bonds in cationic complexes; *vice versa*, in the case of olefinic ligands, the increased $Pt\text{–}C_{olefin}$ separation in cationic complexes appears to indicate significant reduction of π back bonding.[11]

Experimental

Preparations.—Complex (**2**). Tin(II) chloride (0.201 g, 1.06 mmol) was added to $[\{Pd(\eta^3\text{-}C_4H_7)Cl)\}_2]$ (0.205 g, 0.52 mmol) dissolved in methylene chloride (8 cm^3). The mixture was stirred for 30 min and then cod (0.108 g, 2.1 mmol) was added to the resulting yellow suspension. A clear red solution was obtained which was stratified with heptane. Wine-red crystals separated (0.420 g) (Found: C, 24.65; H, 3.35. $C_{28}H_{45}Cl_9Pd_3Sn_3$, requires C, 24.40; H, 3.25%).

Complex (**1**). This compound was prepared following a similar procedure (Found: C, 21.70; H, 2.95. $C_{28}H_{45}Cl_9Pt_3Sn_3$ requires C, 20.45; H, 2.75%).

N.M.R. Spectroscopy.—The n.m.r. spectra were measured using Bruker AM-250 and WP-80 spectrometers.

X-*Ray Structure Determination of Complex* (**1**).—Crystals were grown from CH_2Cl_2–heptane solution, and a single crystal measuring 0.20 × 0.10 × 0.06 mm was selected and used for all crystallographic analysis.

Crystal data. $C_{28}H_{45}Cl_9Pt_3Sn_3$, M = 1 642.08, triclinic, a = 13.256(4), b = 19.960(4), c = 8.615(3) Å, α = 101.75(2), β = 104.69(2), γ = 86.62(2)°, U = 2 159(1) Å^3, space group $P\bar{1}$, Z = 2, D_c = 2.526 g cm^{-3}, $F(000)$ = 1 500, μ(Mo-K_α) = 120.88 cm^{-1}, λ(Mo-K_α) = 0.710 63 Å.

Data collection and crystal structure analysis. Intensity data were recorded on an Enraf-Nonius CAD4 diffractometer, ω scan mode, using Mo-K_α graphite-monochromatized radiation. Lattice parameters were obtained from a least-squares refinement of 25 reflections (18 ⩽ 2θ ⩽ 26°). A set of three reflections was centred every 300 data to check the orientation of the crystal; three standard reflections were measured every 2 h during the collection to monitor the decay which at the end of the collection was *ca.* 40%. 5 946 Unique reflections ($\pm h, \pm k, l$) with 6 ⩽ 2θ ⩽ 46° were collected at room temperature, 3 833 with $I \geqslant 3\sigma(I)$ being used in the analysis. The empirical absorption correction was based on ψ scans of three suitable reflections at χ values close to 90°. Maximum and minimum transmission factors were 1.00 and 0.66 respectively. The SDP programs[14] were used for crystal decay and absorption corrections, and for the data reduction (Lorentz polarization corrections applied).

Table 4. Platinum–allyl carbon bond lengths (e.s.d.s in parentheses), for $Pt(\eta^3-C_4H_7)(SnCl_3)$ complexes

	Pt–C(1)	Pt–C(2)	Pt–C(3)	Ref.
$[Pt(\eta^3-C_4H_7)(CH_2{=}CHPh)(SnCl_3)]$	2.192(9) *	2.174(7)	2.151(7)	1
$[Pt(\eta^3-C_4H_7)(SnCl_3)_3]^{2-}$	2.200(13)	2.152(10)	2.175(11)	This work
$[Pt(\eta^3-C_4H_7)(SnCl_3)(CO)]$	2.197(8) *	2.194(7)	2.153(7)	2

* *trans* to $SnCl_3$.

Table 5. Geometric features of the co-ordination of cation (**1b**)

Distances (Å) from co-ordination plane[a]

	(**1b**′)	(**1b**″)
Pt′	0.125	0.115
C(1′)	0.24	0.18
C(2′)	−0.49	−0.45
C(3′)	0.24	0.27
C(4′)	−1.94	−1.91

Dihedral angles (°) between ligand and co-ordination plane

allyl	113.5	118.9
cod[b]	94.0	92.2

Angles (°) between double-bond lines and normal to co-ordination plane

C(5′)–C(6′)	5.9	5.8
C(10′)–C(11′)	2.6	8.2

[a] Plane through allyl centre of mass (AL) and double-bond midpoints. [b] Least squares plane through olefinic carbons.

Table 6. Average $Pt-C_{olefin}$ bond distances (Å) in selected platinum(II) complexes

Complex		Ref.
$[Pt(\eta^2-C_2H_4)Cl_3]^-$	2.132(3)	*a*
$[Pt(cod)Cl_2]$	2.170(6)	8*a*
$[Pt(\eta^3-C_4H_7)(CH_2{=}CHC_6H_4Cl\text{-}o)(PPh_3)]^+$	2.200(18)	11
$[Pt(\eta^3-C_4H_7)(SnCl_3)(CH_2{=}CHPh)]$	2.209(6)	1
cis-$[Pt(CH_2{=}CHPh)_2Cl_2]$	2.214(6)	*b*
$[Pt(\eta^3-C_4H_7)(PPh_3)(Z\text{-}MeCH{=}CHMe)]^+$	2.220(17)	11
$[Pt(\eta^3-C_4H_7)(cod)]^+$	2.229(16)	This work
$[Pt(\eta^3-C_4H_7)(PPh_3)(E\text{-}MeCH{=}CHMe)]^+$	2.232(16)	11
$[Pt(\eta^3-C_4H_7)(PPh_3)(C_2H_4)]^+$	2.238(16)	11
$[Pt(\eta^3-C_4H_7)(PPh_3)(E\text{-}MeCH{=}CHPh)]^+$	2.238(8)	11
$[Pt(SnCl_3)_3(cod)]^-$	2.24(2)	4
$[Pt(\eta^3-C_4H_7)(CH_2{=}CHPh)(PPh_3)]^+$	2.253(13)	11
$[Pt(cod)Me(C_9F_6H_5)]$	2.257(13)	13

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The positions of the three Pt atoms in complex (**1**) were determined from a Patterson synthesis, while other atoms were located by standard Fourier methods and the refinement was carried out by blocked-full-matrix least-squares methods using SHELX[15] with optimized weighting scheme in the final cycle. Atomic scattering factors corrected for anomalous dispersion effects[16] and, for all non-hydrogen atoms, anisotropic thermal parameters were used. Terminal allyl hydrogen atoms were located from Fourier difference maps and refined, while the other hydrogen atoms were placed at calculated positions refining only a common thermal parameter. Methyl hydrogens were omitted as attempts at refining a group thermal parameters suggested a disordered state. The refinement converged at a final $R = 0.026$ ($R' = 0.023$), with a goodness of fit of 1.31 and the maximum residual peak in the final difference Fourier of 1.3 e Å^{-3}, at 1.53 Å from Pt′.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond angles.

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