Crystallographic and Nuclear Magnetic Resonance Studies of Carbonyl(η^3-methylallyl)(trichlorostannyl) Complexes of Platinum(II) and Palladium(II) *

Maria Grassi
Department of Inorganic and Metallorganic Chemistry, University of Milan, Via Venezian 21, I-20133 Milano, Italy
Stefano V. Meille
Department of Chemistry, Polytechnic of Milano, Piazza Leonardo da Vinci 32, I-20133 Milano, Italy
Alfredo Musco and Roberto Pontellini
Institute of Chemical Sciences, University of Urbino, I-61029 Urbino, Italy
Angelo Sironi
Institute of Structural Inorganic Chemistry, via Venezian 21, I-20133 Milano, Italy

The complexes [M(η^3-C_4H_7)($SnCl_3$)(CO)] [C_4H_7 = 2-methylallyl, M = Pt(1) or Pd(2)] have been prepared and characterized. Their solution behaviour has been studied by n.m.r. spectroscopy, the compounds being dynamic through dissociation of the CO ligand. The *X*-ray structures of (**1**) and (**2**) are reported. Complex (**2**) is the first mononuclear palladium carbonyl to be characterized by *X*-ray diffraction. The different stabilities of the two isostructural complexes are correlated with the subtle differences in bonding observed in the crystal structures.

Trichlorostannate complexes of Pt^{II} and Pd^{II} play an important role in the hydroformylation of olefins.[1] π-Allyl complexes are also recognized to be useful intermediates in organic synthetic reactions.[2] While a number of π-allylic complexes of Pd^{II} and Pt^{II} containing tertiary phosphines or olefins have been studied in both the solution[3] and solid state,[4] studies of π-allylic complexes containing the $SnCl_3$ ligand are less extensive.[4a,e,5] Allylic palladium(II) complexes containing the CO ligand have been postulated as intermediates in carbonylation reactions of the allyl group but were not isolated.[6] Finally, while mononuclear carbonyl complexes of Pt^{II} have been characterized by *X*-ray structural studies,[7] no such complex of Pd^{II} has been reported.

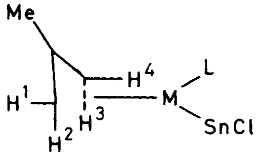
In view of our interest in this research area we have prepared and studied the complexes [M(η^3-C_4H_7)($SnCl_3$)(CO)] [C_4H_7 = 2-methylallyl; M = Pt (**1**) or Pd (**2**)]. A further interest of our study is the comparison of the strength of the ligand–metal bond in these two isostructural complexes.

Results and Discussion

The complexes are readily prepared as shown in equation (1).

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

They gave satisfactory analyses and were characterized by *X*-ray crystallographic studies and by multinuclear n.m.r. spectroscopy. Crystals suitable for *X*-ray analysis of both (**1**) and (**2**) were obtained by crystallization from toluene. Both complexes are white solids which are stable in an inert atmosphere at low temperature but rapidly decompose [particularly (**2**)] when exposed to air or warmed to room temperature. Compound (2) is slightly soluble in methylene chloride at room temperature, producing a colourless solution which almost immediately decomposes to palladium metal. The decomposition can partially be prevented by working at low temperature under an atmosphere of CO, however the solubility of the complex is very low under these conditions. This has hampered a full characterization of the compound in solution. Complex (**1**) behaves similarly but its solubility and stability are higher than that of (**2**). Solutions of (**1**) in an atmosphere of CO are stable at room temperature for a few hours. The labelling used for the ^1H and ^{13}C resonances is shown below.



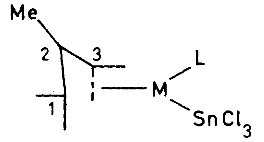


Figure 1 reports the low-temperature ^1H n.m.r. spectrum of complex (**1**). It shows four resonances for the allyl protons (H^1—H^4) besides the resonance of the CH_3 group. Corresponding n.m.r. parameters are reported in Table 1. The attribution was made following the usual criteria: (*i*) in allyl complexes the *syn* protons resonate at higher frequencies than *anti* protons;[8] (*ii*) $^4J(H_{syn}$–$H_{syn})$ is larger than $^4J(H_{anti}$–$H_{anti})$;[9,10] (*iii*) ^2J(H–X) (X = n.m.r.-active nucleus, Sn in our case) is larger for the protons *trans* to X than for those *cis*.[11–13] The assignment was confirmed by nuclear Overhauser effect (n.O.e.) and decoupling difference experiments. The geminal arrangement of the pairs H^1, H^2 and H^3, H^4 was confirmed by observing significant n.O.e. enhancements at δ 3.52 and 2.76 when the resonances at δ 5.23 and 4.66 respectively were irradiated. The *syn*/*anti* arrangements of the pairs H^1, H^4, and H^2, H^3 were demonstrated by decoupling difference experiments. The resonances at δ 5.23 and 4.66 appeared coupled to each other [$^4J(H^1$–$H^4)$ = 3.5 Hz] and to the resonances at δ 3.52 [$^2J(H^4$–$H^3)$ = 3 Hz] and at 2.76 [$^2J(H^1$–$H^2)$ = 2 Hz] respectively. At higher temperature (**1**) shows dynamic behaviour resulting in pairwise exchange of the *syn* and *anti* protons. The rate of the process is slow at room temperature as no significant broadening of the lines is observed. Nevertheless the fluxionality is clearly evident in the two-dimensional chemical exchange correlation spectrum. The contour plot in Figure 2 shows cross peaks between the exchanging protons H^1, H^4 and H^2, H^3. A similar allyl fluxionality has been previously observed for the analogous complexes [Pt(η^3-C_3H_5)($SnCl_3$)(PR_3)] (R = Ph, Et,

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* *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. N.m.r. data for the complexes $[M(\eta^3\text{-}C_4H_7)(SnCl_3)L]$[a]

M	L	H^1	H^2	H^3	H^4	Me			
Pt[b]	CO	4.66 $J(H^1H^4) = 3.5$ $J(H^1H^2) = 2$ [28] n.o.	2.76 n.o. (30.5)	3.52 $J(H^3H^4) = 3$ [84] (48)	5.23 [44] (16)	2.05 n.o. (68)			
		C^1	C^2	C^3	Me	L	Pt	Sn	Ref.
Pt[c]	CO	59.2 (93)	135.8 (39)	70.9 (77) [230]	25.1 (34)	176.5 (34)	−5 439	76.9 (29 287)	This work
Pt[d]	Styrene						−5 770	14.0 (28 496)	e
	$[Pt(\eta\text{-}C_3H_5)(SnCl_3)(PPh_3)]$[e]						−5 517	76.0 (28 504)	e

[a] Chemical shifts are in p.p.m. referred to: $SiMe_4$, H_2PtCl_6, and $SnMe_4$ for ^1H and ^{13}C, ^{195}Pt, and ^{119}Sn respectively; coupling constants are in Hz, in square brackets Sn, in parentheses to Pt. [b] At 400.13 MHz, in $CDCl_3$, 253 K; n.o. = not observed. [c] At 100.61 (^{13}C), 53.53 (^{195}Pt), or 93.27 MHz (^{119}Sn); in $CDCl_3$, 253 K. [d] At 53.53 (^{195}Pt) and 93.27 MHz (^{119}Sn), in $CDCl_3$, at room temperature (r.t.); resonances of major isomer. [e] M. Grassi, unpublished work.

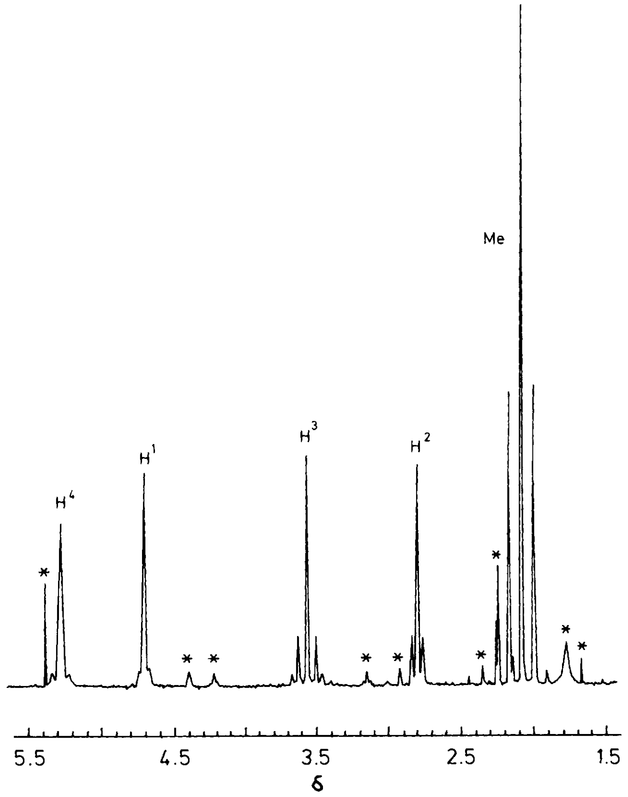


Figure 1. Proton n.m.r. spectrum of complex (**1**) at 400.13 MHz, in $CDCl_3$, 253 K. The asterisks indicate impurities

or Pr^i).[5a] We have proposed a dissociative mechanism involving $SnCl_3$–$SnCl_2$ species.[5a] The same mechanism may apply also for (**1**) and (**2**) albeit, due to the solutions of these complexes being stable only under an atmosphere of CO, CO dissociation appears a more viable pathway for the observed fluxionality. This second mechanism receives additional support from the observation of Sn–H couplings in the ^1H n.m.r. spectrum of (**1**) at room temperature (Table 1).

The spectrum of complex (**2**) at room temperature consists of two broad resonances at δ 4.49 (2 H) and 3.27 (2 H), and of a sharp resonance at 1.90 (3 H). At 183 K the spectrum reveals four resonances for the allyl protons at δ 5.28, 4.67, 3.68, and 3.04. The broadness of the signals suggests that some dynamic process is still operating. Accordingly, on irradiation of the signals at δ 5.28 and 3.68 we clearly observe magnetization transfer at δ 4.67 and 3.04 respectively. Analogously to the platinum case, this may be explained *via* a pairwise exchange of the *syn,syn* and *anti,anti* protons. Due to the very low solubility of (**2**), good quality spectra at temperatures lower than 183 K were not obtained. Consequently the resonances of (**2**) were not assigned.

The higher fluxionality of complex (**2**) relative to (**1**) suggests stronger bonds in the latter. An analogous trend on going from Pt to Pd has been observed in the above mentioned structurally related complexes $[M(\eta^3\text{-allyl})(SnCl_3)(PR_3)]$.[5a] As expected, third-row elements are stronger electron acceptors than the corresponding second-row elements.

The ^{13}C n.m.r. data for complex (**1**) are reported in Table 1. The assignment of the C^3 and the C^1 resonances respectively at δ 70.90 and 59.16 p.p.m. was made on the basis that $^2J(Sn\text{–}C_{trans})$ is larger (230 Hz) than $^2J(Sn\text{–}C_{cis})$ (*ca.* 0 Hz).[11–13]

The larger *trans* influence of $SnCl_3$ relative to CO, which is suggested by the ^1H n.m.r. data (H^4 and H^3 appear at higher frequencies than H^1 and H^2), is further supported by ^{13}C data: (*i*) the C^3 resonance (δ 70.90 p.p.m.) appears at higher frequencies than C^1 (δ 59.16); (*ii*) $^1J(Pt\text{–}C^1) = 93$ Hz is larger than $^1J(Pt\text{–}C^3) = 77$ Hz.

The observed value for the CO resonance (δ 176.45) is much closer to that observed for free CO (δ 180.3) rather than for strongly bonded CO {*e.g.* δ 150.0 p.p.m. for $[Pt(CO)_2Cl_2]$},[14,15] again indicating a rather weak Pt–CO bond. Both ^{195}Pt and ^{119}Sn spectra for (**1**) reveal $^1J(Pt\text{–}Sn)$ *ca.* 29 kHz which is typical of a direct Pt–Sn bond.[16,17] This coupling value is consistent with the intermediate *trans* influence of the allyl and a rather strong Pt–$SnCl_3$ bond.

The ^{195}Pt resonance (δ −5 439) appears shifted upfield by about 1 500 p.p.m. relatively to that of $[\{Pt(\eta^3\text{-}C_4H_7)Cl\}_2]$ as expected for the substitution of a Cl ligand with $SnCl_3$.[18,19] However, comparing the ^{195}Pt chemical shift of (**1**) and related compounds (Table 1), the nature of the ligand bound to the metal is not reflected in the ^{195}Pt chemical shift in this class of compound.

The ^{119}Sn spectrum of (**1**) deserves comment. Square-planar platinum complexes containing the $SnCl_3$ moiety *trans* to

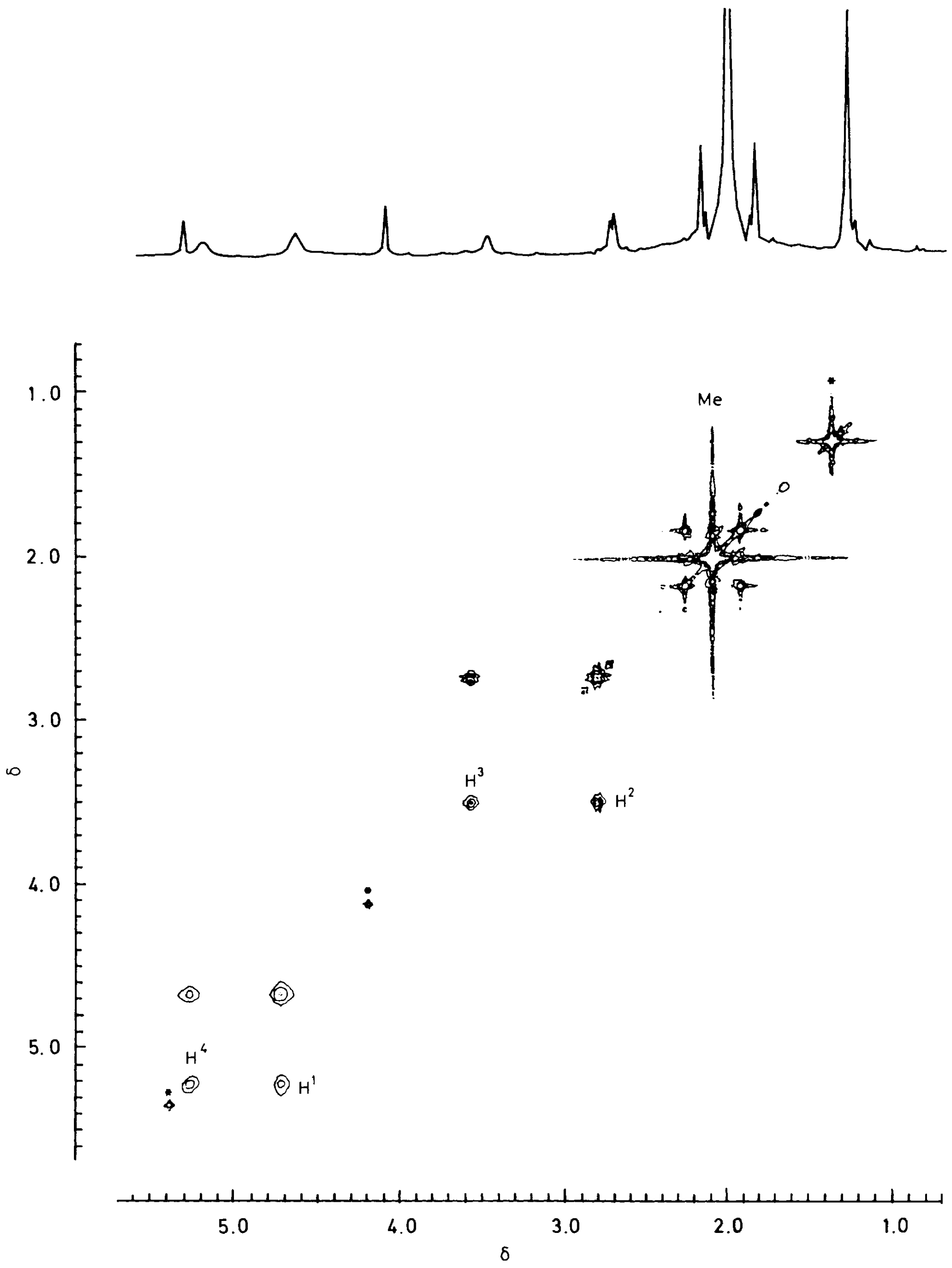


Figure 2. Contour plot of the chemical exchange-correlated two-dimensional ^{1}H n.m.r. spectrum of complex (**1**) at 200.13 MHz, in CDCl$_3$, room temperature. The asterisks indicate impurities

ligands with strong *trans* influence have a ^{119}Sn resonance between δ 0 and +200 p.p.m. (relative to SnMe$_4$) and ^1J(Pt–Sn) less than 10 kHz {*e.g.* *trans*-[Pt(SnCl$_3$)Me(PEt$_3$)$_2$] δ(^{119}Sn) = 140 p.p.m., ^1J(Pt–Sn) = 6 620 Hz[16]}. Conversely, negative δ (^{119}Sn) values and ^1J(Pt–Sn) > 10 kHz are observed in the presence of ligands which display a weak *trans* influence {*e.g.* *trans*-[Pt(SnCl$_3$)Cl(PEt$_3$)(H$_2$NC$_6$H$_4$Cl-*p*)] δ(^{119}Sn) = −243 p.p.m., ^1J(Pt–Sn) = 31 348 Hz}.[20] In our case complex (**1**) displays a positive δ (^{119}Sn) = 76.9 p.p.m. and a large ^1J(Pt–Sn) = 29 287 Hz. Similar values have been observed for the analogous complexes [Pt(η^3-allyl)(SnCl$_3$)L] where L = PR$_3$ or olefin (Table 1). This fact suggests that the linear correlation between the ^{119}Sn resonance and the magnitude of ^1J(Pt–Sn), usually observed in platinum–tin complexes,[21] does not apply to allyl derivatives.

X-*Ray Diffraction Structure Analysis*.—In Figure 3 a projection of the platinum derivative on the co-ordination plane is presented together with details of the co-ordination geometry. The isostructural palladium complex is not shown since it is visually indistinguishable. Crystal data and details of the data collection and refinement parameters are given in Table 2 together with the final disagreement factors, while Tables 3 and 4 present the final positional parameters for the two complexes. Bond distances and relevant bond angles are listed in Table 5.

The Sn atom, the centre of gravity of the bound methyl allyl

Table 2. Crystal data, data collection and refinement details for complexes (**1**) and (**2**)[a]

	(**1**)	(**2**)
Formula	$C_5H_7Cl_3OPtSn$	$C_5H_7Cl_3OPdSn$
M	503.2	414.6
$F(000)$	448	384
a/Å	8.912(2)	8.971(2)
b/Å	9.076(2)	9.032(2)
c/Å	7.263(1)	7.168(1)
α/°	98.92(1)	99.77(2)
β/°	105.80(2)	105.09(2)
γ/°	86.06(2)	86.34(2)
U/Å^3	558.2(2)	552.5(2)
D_c/g cm^{-3}	2.994	2.492
Crystal dimensions/mm	0.20 × 0.12 × 0.10	0.22 × 0.17 × 0.05
μ(Mo-K_α)/cm^{-1}	155.74	45.62
Max., min. transmission factors	1.00, 0.56	1.00, 0.89
2θ range/°	6—55	6—50
Unique data collected	2 573	2 079
Unique data	2 067 [$I > 3\sigma(I)$]	1 122 [$I > 2\sigma(I)$]
R^b	0.0206	0.0298
R'^c	0.0214	0.0256
Goodness of fit[d]	1.49	1.13
Max. peak in final Fourier difference/Å^{-3}	1.40 (0.79 Å from Pt)	0.62 [2.05 Å from Cl(3)]

[a] Details common to both complexes: space group $P\bar{1}$; $Z = 2$; radiation Mo-K_α (λ = 0.710 73 Å); graphite monochromator; CAD-4 diffractometer; temperature 298 K; ω scan mode, scan interval 0.9 + 0.347 tan θ; prescan speed 10° min^{-1}, prescan acceptance $[\sigma(I)/(I)] = 1.0$; required $[\sigma(I)/(I)] = 0.01$; max. time for one reflection measurement 80 s; data collected $\pm h$, $\pm k$, $+l$; three azimuthal reflections for absorption correction; final number of variables 126. [b] $R = \Sigma(k|F_o| - |F_c|)/\Sigma k|F_o|$. [c] $R' = \Sigma w^{\frac{1}{2}}(k|F_o| - |F_c|)/\Sigma w^{\frac{1}{2}}k|F_o|$, $w = a[\sigma^2|F_o| + bF_o^2]$. [d] $[\Sigma w(k|F_o| - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$, N_o = number of observations, N_v = number of variables.

Table 3. Final positional parameters (× 10^5, × 10^3 for H) for complex (**1**)

Atom	x	y	z
Pt	24 931(2)	26 481(2)	17 553(3)
Sn	53 341(4)	26 688(4)	16 758(5)
C(11)	67 843(18)	3 722(16)	18 941(23)
C(12)	70 442(19)	40 472(19)	43 509(23)
C(13)	61 554(20)	33 636(18)	−8 852(23)
C(1)	31 895(78)	18 101(81)	44 886(91)
C(2)	16 613(70)	13 437(67)	35 646(85)
C(3)	5 375(81)	24 962(82)	30 110(112)
C(4)	12 670(108)	−2 573(81)	28 218(127)
C(5)	15 126(76)	34 356(75)	−5 315(102)
O	8 939(71)	38 897(75)	−19 183(84)
H(1s)	379(7)	99(7)	455(8)
H(1a)	358(7)	288(7)	530(8)
H(3a)	51(8)	348(8)	385(9)
H(3s)	−59(11)	220(10)	220(12)
H(41)	220(11)	−83(9)	233(11)
H(42)	115(10)	−91(9)	370(12)
H(43)	53(10)	−36(10)	168(12)

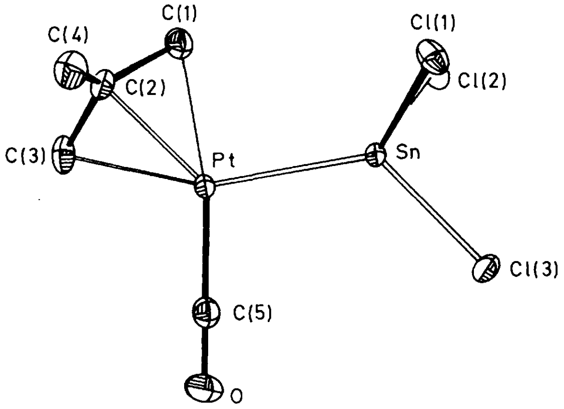


Figure 3. Projection of complex (**1**) on the co-ordination plane

carbon atoms (AL), and the carbonyl carbon C(5) define the co-ordination plane together with the metal atom [Pt in (**1**) and Pd in (**2**)]. The square-planar model, but also an irregular planar trigonal model, affords an acceptable description of the co-ordination geometry. The dihedral angles between the plane of the methylallyl and the co-ordination plane are in the usual range [115.5(6)° in (**1**) and 117.2(9)° in (**2**)]. The CO group lies practically in the co-ordination plane, the Pt–C(5) bond length [1.878(7) Å] being somewhat larger than in other mononuclear platinum carbonyl complexes.[7] The Pd–C(5) distance in complex (**2**) is 1.947(11) Å and no data are available for comparison. These findings are in agreement with the i.r. spectra in the ν(CO) region [2 105 (Pt), 2 125 cm^{-1} (Pd)] assuming that stronger C–O bonding means a weaker M–C interaction. A direct correlation of the i.r. data with the observed C–O bond lengths [1.133(9) and 1.113(14) Å in (**1**) and (**2**) respectively] is unreliable owing to the values of the standard deviations. The geometric features of the $SnCl_3$ ligands are similar to those found in analogous complexes. The non-homogeneity of the environment *trans* to the methylallyl produces in both the compounds significantly asymmetric binding of the methylallyl itself. The M–C bonds *trans* to $SnCl_3$ [2.197(8) Å in (**1**) and 2.187(13) Å in (**2**)] are longer than the corresponding bonds opposite to the CO ligand [2.153(7) Å and 2.132(12) Å].

The *trans* influence on π-allylic ligands in mononuclear palladium complexes was discussed many years ago in a pioneering work by Lippard and Morehouse.[22] In Table 6 more recent and accurate data (structural studies in which the pertinent bond lengths have standard deviations greater than 0.02 Å were omitted) are taken into consideration. The labilizing power with respect to the M–C bonds appears to increase in a similar manner to that found using different *trans* ligands as probes (*e.g.* Cl in ref. 7*e*). The following sequence results from an analysis of the data in Table 6: O < Cl < N ≅ CO ≅ C=C < C(ylide) < $SnCl_3$ ≅ S < PPh_3 < $P(C_6H_{11})_3$.

We also observe that, possibly also due to the values of the bond distance standard deviations, the *trans* influence with respect to allylic ligands both in palladium(II) and platinum(II) mononuclear complexes is comparable. The M–C distances for non-symmetrically substituted π-allyl ligands, except where steric factors are obviously relevant, also fit the general trend satisfactorily. The literature data quoted in Table 6 confirm that, notwithstanding significant co-ordination asymmetry, the differences between the C(1)–C(2) and the C(2)–C(3) bond lengths are not significant at room temperature.

Subtle variations in the bonding parameters of isostructural complexes of Pd and Pt can be rationalized on the basis of the hard–soft concept (Pt is softer than Pd) or, alternatively, on the basis of the π donor or acceptor abilities (Pt is a better donor than Pd). On this basis Ibers and co-workers[23] were able to predict stronger, *i.e.* shorter, M–L bonds for the metal which better match the particular character of a given ligand. In the present compounds and in the related $[M(\eta^3\text{-}C_4H_7)(SnCl_3)(CH_2{=}CHPh)]$ (M = Pt or Pd)[5b] all the ligands have π-acidic character and we should thus expect the platinum-ligand interactions to be stronger than the corresponding bonds involving Pd. This is indeed the case and pertinent data are reported in Table 7. The Pt/Pd differences are more evident with the stronger π-acidic ligands (CO and styrene) somewhat less important for $SnCl_3$ and negligible for the methylallyl moiety. The latter displays similar interactions with the two metals, being only slightly more symmetric when bound to Pt.

Table 4. Final positional parameters (× 10⁴, × 10³ for H) for complex (**2**)

Atom	*x*	*y*	*z*
Pd	2 516(1)	2 643(1)	1 782(1)
Sn	5 349(1)	2 660(1)	1 689(1)
Cl(1)	6 823(3)	356(3)	1 828(4)
Cl(2)	7 094(3)	4 049(3)	4 395(4)
Cl(3)	6 199(3)	3 377(3)	−893(4)
C(1)	3 200(12)	1 748(14)	4 452(16)
C(2)	1 666(10)	1 313(10)	3 574(13)
C(3)	588(12)	2 477(13)	3 072(17)
C(4)	1 264(16)	−270(13)	2 824(19)
C(5)	1 475(11)	3 475(12)	−568(16)
O	837(10)	3 927(10)	−1 912(12)
H(1s)	400(12)	107(12)	490(15)
H(1a)	336(10)	263(10)	540(12)
H(3a)	77(9)	338(10)	383(12)
H(3s)	−47(12)	204(12)	238(15)
H(41)	208(15)	−94(15)	266(19)
H(42)	119(15)	−50(15)	390(20)
H(43)	87(15)	−52(15)	155(18)

From the crystallographic and n.m.r. data reported here we conclude that, analogously to what was found in $[M(\eta^3\text{-}C_4H_7)(SnCl_3)(olefin)]$ (M = Pt or Pd), in the carbonyl complexes (**1**) and (**2**) a stronger co-ordination sphere is observed for Pt than for Pd.

Experimental

Synthesis of Complexes (**1**) *and* (**2**).—The complexes were prepared under dinitrogen purified by passage through BASF catalyst R3-11.

$[Pt(\eta^3\text{-}C_4H_7)(SnCl_3)(CO)]$. The complex $[\{Pt(\eta^3\text{-}C_4H_7)Cl\}_2]$ (0.285 g, 0.5 mmol) and $SnCl_2$ (0.197 g, 1.04 mmol) were stirred in toluene (8 cm³) for 30 min. Carbon monoxide was bubbled through the orange-yellow suspension. The pale yellow solution obtained was kept at −30 °C. An off-white crystalline material separated out. The solvent was siphoned off and the solid dried under vacuum (0.270 g) (Found: C, 12.05; H, 1.35. $C_5H_7Cl_3OPtSn$ requires C, 11.95; H, 1.40%).

The complex $[Pd(\eta^3\text{-}C_4H_7)(SnCl_3)(CO)]$ was prepared similarly in comparable yields (Found: C, 14.65; H, 1.75. $C_5H_7Cl_3OPdSn$, requires C, 14.50; H, 1.70%).

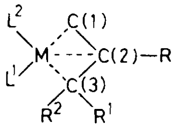
N.M.R. Spectroscopy.—The n.m.r. spectra were measured on Bruker AC-200, AM-250, and WH-400 spectrometers operating in Fourier-transform mode. One-dimensional ^1H, ^{13}C, ^{195}Pt, and ^{119}Sn spectra were measured at 400.13, 100.61, 53.53, and 93.27 MHz respectively. The two-dimensional experiment was performed at 200.13 MHz with a microprogram from the

Table 5. Bond lengths (Å) and selected bond angles (°) for complexes (**1**) and (**2**)*

	M = Pt	Pd		M = Pt	Pd
Sn–M	2.549 6(7)	2.560 7(12)	M–Sn–Cl(1)	117.01(5)	118.43(7)
Sn–Cl(1)	2.379(2)	2.395(2)	M–Sn–Cl(2)	116.47(5)	117.70(7)
Sn–Cl(2)	2.358(2)	2.373(2)	M–Sn–Cl(3)	124.29(5)	124.33(8)
Sn–Cl(3)	2.358(2)	2.372(3)	Cl(1)–Sn–Cl(2)	96.03(6)	94.99(9)
M–C(1)	2.153(7)	2.132(12)	Cl(1)–Sn–Cl(3)	97.23(6)	96.25(10)
M–C(2)	2.194(7)	2.197(11)	Cl(2)–Sn–Cl(3)	100.62(6)	99.27(10)
M–C(3)	2.197(8)	2.187(13)	Sn–M–C(5)	100.1(2)	101.8(5)
M–C(5)	1.878(7)	1.947(11)	Sn–M–C(3)	157.0(2)	156.4(3)
C(1)–C(2)	1.406(9)	1.407(14)	Sn–M–C(2)	123.8(2)	123.7(2)
C(2)–C(3)	1.423(9)	1.410(14)	Sn–M–C(1)	90.6(2)	89.8(3)
C(2)–C(4)	1.500(9)	1.472(14)	C(3)–M–C(5)	102.2(3)	101.1(4)
C(5)–O	1.133(9)	1.113(14)	C(2)–M–C(5)	133.2(3)	131.7(4)
C(1)–H(1s)	0.88(6)	0.94(10)	C(2)–M–C(3)	37.8(3)	37.5(4)
C(1)–H(1a)	1.08(6)	0.95(8)	C(1)–M–C(5)	169.1(3)	168.4(4)
C(3)–H(3a)	1.00(6)	0.90(8)	C(1)–M–C(3)	65.9(3)	67.3(4)
C(3)–H(3s)	1.04(9)	1.02(10)	C(1)–M–C(2)	37.7(2)	37.9(4)
C(4)–H(41)	1.07(9)	0.93(13)	C(1)–C(2)–C(4)	123.1(6)	121.8(10)
C(4)–H(42)	0.97(10)	0.86(15)	C(1)–C(2)–C(3)	115.8(6)	116.2(10)
C(4)–H(43)	0.90(8)	0.88(12)	C(3)–C(2)–C(4)	119.9(6)	121.8(10)
M–AL	1.917(14)	1.908(22)	M–C(5)–O	178.4(7)	177.7(10)
			Sn–M–AL	124.6(4)	124.2(6)
			AL–M–C(5)	135.2(4)	133.9(6)

* AL = Centre of gravity of the C(1), C(2), and C(3) allylic carbons.

Table 6. Selected literature metal–terminal allyl carbon (M = Pt or Pd) bond lengths with estimated standard deviations < 0.02 Å



L^{1a}	L^{2a}	M	R	Ref.	M–C(1)	M–C(3)
O	S	Pd	Me	*b*	2.08(1)	2.21(1)
O	S	Pd	R=Me, R^1=Bu^t	*c*	2.05(1)	2.18(1)
O	N	Pd	Me	*d*	2.07(2)	2.16(2)
Cl	Cl	Pd	H	*e*	2.123(7)	2.121(8)
Cl	Cl	Pd	Me	*f*	2.124(9)	2.077(9)
Cl	N	Pd	R=R^1=Me	*g*	2.133(15)	2.154(14)
Cl	N	Pd	H	*h*	2.124(7)	2.125(7)
N	N	Pd	Me	*i*	2.133(9)	2.186(9)
					2.149(8)	2.167(9)
N	N	Pd	H	*j*	2.125(8)	2.143(9)
					2.127(7)	2.165(8)
CO	$SnCl_3$	Pt	Me	This work	2.153(7)	2.197(8)
CO	$SnCl_3$	Pd	Me	This work	2.132(12)	2.187(13)
Styrene	$SnCl_3$	Pt	Me	5*b*	2.151(7)	2.192(9)
Styrene	$SnCl_3$	Pd	Me	5*b*	2.142(4)	2.197(4)
Olefin	MeCN	Pd	R=H, R^2=Me R^1 = CH_2–CH_2–CH=C(Me)$_2$	*k*	2.154(3)	2.149(9)
P(C_6H_{11})$_3$	$SnCl_3$	Pt	R = H, R′ = Me	4*a*	2.234(7)	2.170(5)
P(C_6H_{11})$_3$	P(C_6H_{11})$_3$	Pt	H	4*b*	2.24(2)	2.24(2)
PPh_3	Styrene	Pt	Me	4*c*	2.226(14)	2.175(13)
PPh_3	Cl	Pd	Me	4*d*	2.211(6)	2.120(5)
PPh_3	$SnCl_3$	Pd	H	4*e*	2.193(12)	2.201(16)
C(ylide)	Cl	Pd	Me	*l*	2.126(4)	2.180(4)

[a] Ligating atom; the full ligand and complex formula is reported in the appropriate reference. [b] [Pd(η^3-C_4H_7)(PhCOCHCSPh)]; ref. 22. [c] [Pd{η^3-Bu^{t}CHC(Me)CH$_2$}(PhCOCHCSPh)]; S. Lippard and S. Morehouse, *J. Am. Chem. Soc.*, 1972, **94**, 6956. [d] (η^3-2-Methylallyl)[2-(*R,S*)-α-phenylethyliminopent-3-en-4-olato]palladium; R. Claverini, P. Ganis, and C. Pedone, *J. Organomet. Chem.*, 1973, **50**, 327. [e] [{Pd(η^3-C_3H_5)Cl}$_2$]; A. E. Smith, *Acta Crystallogr.*, 1965, **18**, 331. [f] [{Pd(η^3-C_4H_7)Cl}$_2$]; G. Bandoli and D. A. Clemente, *Acta Crystallogr., Sect. B*, 1981, **37**, 490. [g] Chloro(η^3-1,2-dimethylallyl)(3-methylpyridine)palladium; H. A. Graf, R. Huttel, G. Nagorsen, and B. Rau, *J. Organomet. Chem.*, 1977, **136**, 389. [h] (η^3-Allyl)(2-amino-4-methylpyridine)chloropalladium; G. Reck, B. Heyn, and H. P. Schroer, *Cryst. Struct. Commun.*, 1982, **11**, 179. [i] [{Pd(η^3-C_4H_7)-(MeNNNMe}$_2$]; P. Hendriks, K. Olie, and V. Vrieze, *Cryst. Struct. Commun.*, 1975, **4**, 611. [j] [{Pd(η^3-C_3H_5)(*p*-MeC$_6$H$_4$NNNC$_6$H$_4$Me-*p*}$_2$]; S. Candeloro De Sanctis, N. V. Pavel, and L. Toniolo, *J. Organomet. Chem.*, 1976, **108**, 409. [k] [Pd(η^5-CH$_2$CHCMeCH$_2$CH$_2$CHCMe$_2$)]-(MeCN)][BF$_4$]; ref. 4*i*. [l] [PdCl(η^3-C_4H_7)(Ph$_3$PCHCOMe)]; G. Facchin, R. Bertani, M. Calligaris, G. Nardin, and M. Mari, *J. Chem. Soc., Dalton Trans.*, 1987, 1381.

Table 7. Metal–ligand bond distance (Å) comparison for compounds (**1**) and (**2**) and for the related [M(η^3-C_4H_7)($SnCl_3$)(CH_2CHPh)] complexes (M = Pd or Pt)[5b]

Ligand		M = Pt	M = Pd	Difference
CO		1.878(7)	1.947(11)	0.069(13)
$SnCl_3$		2.549 6(7)	2.560 7(12)	0.011 1(14)
Methylallyl	C(1)	2.153(7)	2.132(12)	−0.021(14)
	C(2)	2.194(7)	2.197(11)	−0.003(13)
	C(3)	2.197(8)	2.187(13)	0.010(15)
Styrene	C(5)	2.181(7)	2.249(4)	0.068(8)
	C(6)	2.236(7)	2.300(4)	0.064(8)
$SnCl_3$		2.539 3(7)	2.554 2(6)	0.014 9(9)
Methylallyl	C(1)	2.151(7)	2.142(6)	−0.009(8)
	C(2)	2.174(7)	2.178(3)	−0.004(8)
	C(3)	2.192(9)	2.197(4)	−0.005(10)

Bruker library using the pulse sequence $t_1 - \frac{\pi}{2} - t_0 - \frac{\pi}{2} - t_m - \frac{\pi}{2}$ − AQ where t_1 (relaxation delay) = 1 s, t_0 (incremental delay) = t_m (mixing time) = 2 s, and AQ = acquisition time. Solvents and temperatures are given in Table 1.

X-*Ray Diffraction*.—The data for the analysis of both structures were collected on an Enraf-Nonius CAD4 diffractometer using graphite monochromatized Mo-K_α radiation (λ = 0.710 73 Å). Crystal data and data collection parameters are summarized in Table 3. Lattice parameters were obtained in both cases from a least-squares refinement of 25 reflections (18 < 2θ < 26°). Three reflections were centred every 300 data to check the orientation of the crystal. Three standard reflections were monitored every 2 h during the collection, but no significant decay was detected. The empirical absorption correction was based on ψ scans of three suitable reflections at χ values close to 90°. The SDP programs[24] were used for crystal decay and absorption corrections, and for the data reduction (Lorentz polarization corrections applied).

The positions of the Pt and Sn atoms in complex (**1**) were determined from a Patterson synthesis, while the structure of (**2**) was solved by isomorphous substitution. Other atoms were located by standard Fourier methods and the refinement was carried out by full-matrix least-squares methods using SHELX.[25] Atomic scattering factors corrected for anomalous dispersion effects[26] and anisotropic thermal parameters for all non-hydrogen atoms were used. All hydrogen atoms were located from Fourier difference maps and refined. In each structure a single average thermal parameter was refined for the three methyl hydrogens, while for the other hydrogen atoms individual isotropic thermal parameters were refined.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond angles.

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