

REACTIONS OF DIMETHYLDIVINYLSILANE, DIMETHYLDIVINYLTIN AND ALLYLTRIMETHYLTIN WITH DIETHYLENE (TERTIARY PHOSPHINE)PLATINUM COMPLEXES

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Summary

The compounds $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$ [$\text{PR}_3 = \text{P}-t\text{-Bu}_2\text{Me}, \text{P}(\text{C}_6\text{H}_{11})_3, \text{PPh}_3$] react with dimethyldivynylsilane or dimethyldivinylnin to give chelate complexes $[\text{Pt}\{(\text{CH}_2=\text{CH})_2\text{MMe}_2\}(\text{PR}_3)]$ ($\text{M} = \text{Si}$ or Sn). Allyltrimethyltin reacts with various diethylene (tertiary phosphine)platinum compounds with cleavage of the allyl group to afford complexes $[\text{Pt}(\text{SnMe}_3)(\eta^3\text{-C}_3\text{H}_5)(\text{PR}_3)]$. The NMR spectra (^{13}C , ^1H and ^{31}P) of the new compounds have been recorded, and the data are discussed in terms of the structures proposed.

Introduction

The complexes $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$ [1] have been used to synthesise a variety of organoplatinum compounds [1–5]. Recently we have found [6] that these diethylene(tertiary phosphine)platinum complexes oxidatively cleave both of the phenylethynyl groups from dimethylbis(phenylethynyl)silane to give diplatinum complexes. $[\text{Pt}_2(1-\sigma\text{-C}\equiv\text{CPh})\{\mu(1-\sigma-1,2-\eta\text{-C}\equiv\text{CPh})\}(\mu\text{-SiMe}_2)(\text{PR}_3)_2]$ (I). This result prompted an investigation of the reactions described herein between the species $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$ and the compounds $\text{Me}_2\text{M}(\text{CH}=\text{CH}_2)_2$ and $\text{Me}_3\text{MCH}_2\text{CH}=\text{CH}_2$ ($\text{M} = \text{Si}$ or Sn). These studies were carried out in order to establish whether cleavage of the vinyl or allyl groups would occur, as was the case with the alkynylsilicon compounds, or whether the vinyl or allyl groups would η^2 -coordinate to platinum without rupture of the carbon–silicon or –tin bonds.

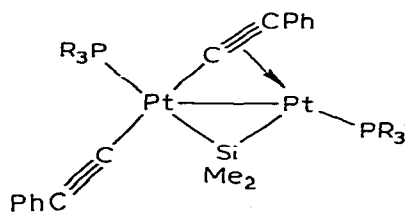
* Dedicated to Professor Eugene Rochow on the occasion of his 70th birthday on October 4th, 1979.

Several years ago [7] dimethyldivinylsilane was employed in reactions with the hexacarbonyls of molybdenum and tungsten to demonstrate that these metals were able to η^2 -bond olefinic groups in the chelate complexes (IIa). More recently, dodecacarbonyl triiron was shown [8] to behave similarly to give compound IIb. In contrast, however, iron carbonyls cleave vinyl groups from dimethyldivinyltin, affording diiron compounds [$\{\text{Fe}(\mu\text{-SnMe}_2)(\text{CO})_4\}_2$] [9]. Examples of the cleavage or non-cleavage of unsaturated groups from silicon are found with platinum chemistry. A series of stable η^2 -complexes $[\text{Pt}(\text{CH}_2=\text{CHSiR}_3)(\text{PPh}_3)_2]$ ($\text{R} = \text{Me}$ or OEt) is produced by treatment of $[\text{Pt}(\text{CH}_2=\text{CH}_2)(\text{PPh}_3)_2]$ with vinylsilanes [10]. In contrast, with $[\{\text{PtCl}(\mu\text{-Cl})\text{-}(\text{C}_2\text{H}_4)\}_2]$ initial substitution of ethylene by $\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ is subsequently followed by cleavage of the Si—C bond. With $[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{py})]$ ($\text{py} = \text{pyridine}$), however, allyltrimethylsilane yields the stable η^2 -complex $[\text{PtCl}_2(\text{py})(\text{CH}_2=\text{CHCH}_2\text{SiMe}_3)]$ [11]. The interaction of π -ligands containing organosilicon groups with low valent transition metal complexes has recently been reviewed [12].

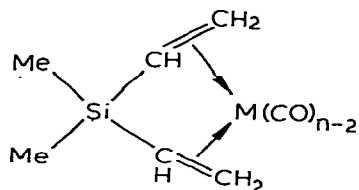
Results and discussion

The compound $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{P-t-Bu}_2\text{Me})]$, prepared in situ by treating an ethylene saturated light petroleum solution of bis(cycloocta-1,5-diene)platinum with one mole of di-*t*-butylmethylphosphine, reacted rapidly with dimethyldivinylsilane at room temperature to give a white crystalline solid (III). On the basis of elemental analysis, and the ^{31}P NMR spectrum (Table 1) showing a singlet resonance with one set of ^{195}Pt satellites, the complex is formulated as a mono-platinum chelate in which the vinyl groups of $(\text{CH}_2=\text{CH})_2\text{SiMe}_2$ are η^2 -coordinated to the metal. Similar compounds, IV and V, were formed from $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$ ($\text{R} = \text{cyclo-C}_6\text{H}_{11}$ and Ph).

In their ground state molecular structure the bis-olefin compounds $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$ adopt a configuration in which the ethylenic carbon atoms, the phosphorus atom, and the platinum atom are co-planar. However, the activation energy for olefin rotation is relatively low ($10\text{--}13 \text{ kcal mol}^{-1}$) [1]. When the ethylene ligands in $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$ are replaced by $(\text{CH}_2=\text{CH})_2\text{SiMe}_2$ a structure in which the Pt, P and C atoms of the vinyl groups are all co-planar is not possible because in this configuration the π orbitals of the C=C groups are not directed towards the platinum atom. For the latter requirement to be met, so that σ, π -bonding can occur, two alternative conformations could be adopted, illustrated as IIIa and IIIb for the case in which $\text{PR}_3 = \text{P-t-Bu}_2\text{Me}$. Examination of the ^1H NMR spectrum of compound III allowed a distinction between the two conformations to be made. In IIIa, the protons of the Me_2Si groups are in equivalent environments whereas in IIIb they are not. Moreover, in IIIa the *t*-Bu groups are non-equivalent whereas in IIIb they are equivalent. The spectrum shown resonances at τ 7.69 (m, 6 H, $\text{CH}=\text{CH}_2$), 8.40 [d, 3 H, MeP, $J(\text{PH})$ 6, $J(\text{PtH})$ 32 Hz], 8.82 [d, 9 H, *t*-Bu, $J(\text{PH})$ 14 Hz], 8.84 [d, 9 H, *t*-Bu, $J(\text{PH})$ 14 Hz] and 10.34 [s, 6 H, Me_2Si]. Thus the appearance of only one signal for the Me_2Si group and two for the *t*-Bu groups favours structure IIIa as being the conformation adopted in solution. Interestingly, the stereochemistry of the C=C groups relative to each other and to the platinum atom

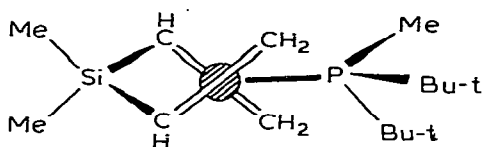


(I)

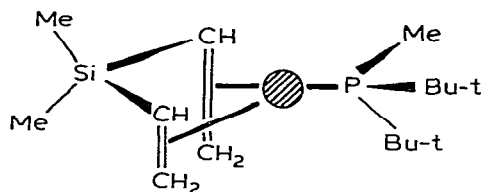


(IIa, M = Mo or W, n = 6)

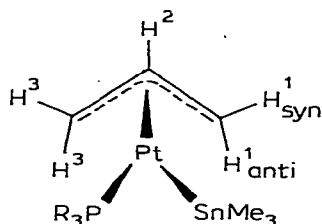
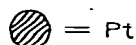
(IIb, M = Fe, n = 5)



(III a)



(III b)

(VIII), $PR_3 = PPh_3$;IX, $PR_3 = P(C_6H_{11})_3$;X, $PR_3 = P-t-Bu_2Me$;XI, $PR_3 = PPh_2Me$;XII, $PR_3 = PPhMe_2$)

in IIIa is similar to the conformation of the C=C groups with respect to the nickel atom in the sixteen electron nickel(0) complex $[Ni(t,t,t-cdt)]$ (cdt = cyclododeca-1,5,9-triene) [13]. Recently the complex $[Pt_3(cod)_2(cot)_2-(C_2H_4)]$ (cod = cycloocta-1,5-diene, cot = cyclooctatetraene) has been isolated [14]. A single crystal X-ray diffraction study has revealed that one of the metal atoms is η^2 -bonded to the ethylene ligands and also to one C=C bond of each of the two cot groups in a trigonal manner, but such that there is a dihedral angle of 23° between the plane $Pt \cdot CH_2 \cdot CH_2$ and either of the two planes defined by the metal atom and the η^2-C_2 groups of the cot ligands. Evidently this structure, as well as IIIa, reflects a tendency towards adopting the preferred trigonal "planar" configuration for 16 electron platinum species [15]. In IIIb the double bonds of the dimethyldivinylsilane ligand have a conformation similar to those of cycloocta-1,5-diene in the eighteen electron complex $[Pt(cod)_2]$ [16], an expected arrangement for four-rather than three-coordinate platinum(0).

TABLE 1
 PHOSPHORUS-31 AND CARBON-13 NMR DATA

Complex	^{31}P <i>a</i>	^{13}C <i>b</i>
III $[\text{P}\{(\text{CH}_2=\text{CH})_2\text{SiMe}_2\}(\text{P}-t\text{-Bu}_2\text{Me})] \text{ c,d}$	-32.9[s, J(PiP)3372]	45.2[d, CH ₂ , J(PC)7, J(PiC)160], 39.2[d, CH, J(PC)12, J(PiC)146], 35.2[d, CMe ₃ , J(PC)17, J(PiC)36], 29.1[s, t-Bu], 28.9[s, t-Bu], 8.0[d, MeP, J(PC)22, J(PiC)34], ~0.0(m, Me ₂ Si)
IV $[\text{P}\{(\text{CH}_2=\text{CH})_2\text{SiMe}_2\}(\text{C}_6\text{H}_4)_3] \text{ c}$	-25.4[s, J(PiP)3358]	43.2[d, CH ₂ , J(PC)7], 37.6[d, CH, J(PC)12], 36.7[d, CP, J(PC)21], 29.9[d, CH ₂ , J(PC)8], 27.7[d, CH ₂ , J(PC)9], 26.7(s, CH ₂), 0.0(m, Me ₂ Si)
V $[\text{P}\{(\text{CH}_2=\text{CH})_2\text{SiMe}_2\}(\text{Ph})_3] \text{ c}$	-22.4[s, J(PiP)3457]	
VI $[\text{P}\{(\text{CH}_2=\text{CH})_2\text{SiMe}_2\}(\text{P}-t\text{-Bu}_2\text{Me})] \text{ c,d}$	-34.7[s, J(PiP)3400, J(SnP)28]	47.0[d, CH ₂ , J(PC)6, J(PiC)160], 36.5[d, CH, J(PC)14, J(PiC)144], 35.5[d, CMe ₃ , J(PC)18, J(PiC)37], 29.0[s, t-Bu], 28.8[s, t-Bu], 8.3[d, MeP, J(PC)22, J(PiC)33], -8.9[d, Me ₂ Sn, J(PC)5, J(PiC)20]
VII $[\text{P}\{(\text{CH}_2=\text{CH})_2\text{SiMe}_2\}(\text{C}_6\text{H}_4)_3] \text{ c}$	-27.4[s, J(PiP)3342, J(SnP)30]	
VIII $[\text{P}(\text{SnMe}_3)(\eta^3\text{-C}_3\text{H}_5)(\text{Ph})_3] \text{ e,f}$	-27.5[s, J(PiP)4165, J(SnP)136 and 142]	133.1[d, C _{ortho} , J(PC)12, J(PiC)31], 130.1(C _{para}), 128.2[d, C _{meta} , J(PC)10], 103.3(C(2)), 73.3(C(3)), 46.0[d, C(1), J(PC)27], -6.4[Me ₃ Sn, J(PiC)101]
IX $[\text{P}(\text{SnMe}_3)(\eta^3\text{-C}_3\text{H}_5)\{\text{C}_6\text{H}_4\}_3] \text{ e,f}$	-40.6[s, J(PiP)4011, J(SnP)122 and 126]	106.5(C(2)), 64.6(C(3), J(PiC)13], 47.5[d, C(1), J(PC)33, J(PiC)83], 38.5[d, CP, J(PC)27, J(PiC)43], 30.4[d, CH ₂ , J(PC)8, J(PiC)28], 27.7[d, CH ₂ , J(PC)11], 26.7(s, CH ₂), -4.5[Me ₃ Sn, J(PiC)114]
X $[\text{P}(\text{SnMe}_3)(\eta^3\text{-C}_3\text{H}_5)(\text{P}-t\text{-Bu}_2\text{Me})] \text{ e,f}$	-47.1[s, J(PiP)4011, J(SnP)129]	105.4(C(2)), 66.2(C(3), J(SnC)132], 46.4[d, C(1), J(PC)33, J(PiC)88], 29.0(Me ₃ C), 12.2[d, MeP, J(PC)31], -4.7[Me ₃ Sn, J(PiC)108]
XI $[\text{P}(\text{SnMe}_3)(\eta^3\text{-C}_3\text{H}_5)(\text{PMePh}_2)] \text{ e,f}$	-5.0[s, J(PiP)3998, J(SnP)140 and 146]	138.2[d, (Ph)C-P, J(PC)50], 132.0[d, C _{ortho} , J(PC)12, J(PiC)30], 129.8(C _{para}), 128.1[d, C _{meta} , J(PC)14], 108.3(C(2)), 70.2(C(3), J(SnC)115], 46.3[d, C(1), J(PC)36, J(PiC)100], 19.1[d, MeP, J(PC)37], -6.0[Me ₃ Sn, J(PiC)103]
XII $[\text{P}(\text{SnMe}_3)(\eta^3\text{-C}_3\text{H}_5)(\text{PMe}_2\text{Ph})] \text{ e,f,g}$		108.4(C(2)), 66.2(C(3)), 46.5[d, C(1), J(PC)34], 20.6[d, MeP, J(PC)35], -5.9(Me ₃ Sn)

a Chemical shifts in δ ppm, to low frequency of 85% H₃PO₄ external; coupling constants in Hz. *b* Chemical shifts in δ ppm, relative to internal Me₄Si, positive values indicating signals to high frequency of the reference; coupling constants in Hz. *c* Measured in CDCl₃. *d* In the ^{13}C spectrum two resonances are assigned to C-CH₃ atoms of individual t-Bu groups. However, these signals may result from accidental coincidence of the two C-CH₃ resonances with the observed separation (ca. 6 Hz) then being due to coupling to ^{31}P . *e* Measured in C₆D₆. *f* For notation of ^{13}C chemical shift assignments C(1), C(2) and C(3) see structural formulae VIII-XII (text). Phenyl carbons of C₆H₅P groups are designated *ortho*, *meta*, and *para*. *g* This complex was identified only by its ^{13}C and ^1H NMR spectra. In the ^{13}C spectrum the Ph signals were obscured by solvent, for ^1H spectrum see Experimental.

Dimethyldivinyltin reacted at room temperature with the compounds $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$ [$\text{PR}_3 = \text{P}-t\text{-Bu}_2\text{Me}$ or $\text{P}(\text{C}_6\text{H}_{11})_3$], in a manner analogous to the silicon compound, to give the adducts $[\text{Pt}\{(\text{CH}_2=\text{CH})_2\text{SnMe}_2\}(\text{PR}_3)]$ (VI and VII). The vinyl groups are not cleaved from the tin, as in the reaction with iron carbonyls [9]. The ^1H NMR spectrum of VI showed a single signal for the protons of the SnMe_2 group and two resonances for the $t\text{-Bu}$ groups, thus implying a configuration similar to IIIa.

Allyltrimethylsilane reacts with Zeise's salt $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ to displace ethylene and give $\text{K}[\text{PtCl}_3(\text{CH}_2=\text{CHCH}_2\text{SiMe}_3)]$ [17]. We were unable to isolate stable compounds from reactions between $\text{CH}_2=\text{CHCH}_2\text{SiMe}_3$ and $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$ which is perhaps not surprising since stable complexes of the type $[\text{Pt}(\text{C}_2\text{H}_4)(\text{olefin})(\text{PR}_3)]$ or $[\text{Pt}(\text{olefin})_2(\text{PR}_3)]$ seem only to be isolable under ambient conditions when the ligated carbon atoms of the olefin ligand carry electron withdrawing substituents, e.g. $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{F}_4)]$, $[\text{Pt}(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$ [1] or $[\text{Pt}(\text{def})_2(\text{PPh}_3)]$ (def = diethyl fumarate) [5]. In contrast, allyltrimethyltin reacts with the complexes $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$ at room temperature to afford η^3 -allylplatinum compounds $[\text{Pt}(\text{SnMe}_3)(\eta^3\text{-C}_3\text{H}_5)(\text{PR}_3)]$ (VIII–XII) (Table 1). The nature of these allyl complexes was established by their NMR spectra. The ^{31}P spectra (singlet signals with one set of ^{195}Pt satellites) were in accord with the compounds being mono-platinum species. The ^1H NMR spectra were typical of those observed in the spectra of other η^3 -allylplatinum complexes [18]. Thus for VIII the observed resonances may be assigned: τ , 2.2–3.0 (m, 15 H, Ph), 5.86 (m, 1 H, H^2), 6.16 (m, 2 H, $\text{H}^{1,3}_{\text{syn}}$), 7.21 [d, 1 H, H^3_{anti} , $J(\text{HH})$ 13, $J(\text{PtH})$ 45 Hz], 8.14 (m, 1 H, H^1_{anti}) and 9.71 [s, 9 H, Me_3Sn , $J(\text{PtH})$ 12, $J(\text{SnH})$ 40 Hz]. The ^{13}C spectra were also in agreement with the assigned platinum(II) structures which result from oxidative cleavage of the tin–carbon bond of allyltrimethyltin. The latter thus reacts with platinum(0) compounds in a manner similar to allyl halides [18].

Experimental

General

All operations were carried out under dry oxygen-free nitrogen in Schlenk tubes. Light petroleum refers to the fraction b.p. 40–60°C. Infrared spectra were recorded as Nujol mulls on a Perkin–Elmer 457 spectrometer. ^1H decoupled ^{31}P and ^{13}C NMR spectra (Table 1) were obtained with a JEOL PFT-100 Fourier transform spectrometer using a ^2H lock. ^1H NMR spectra were recorded on a JEOL PS-100 spectrometer. Analytical and other data for new compounds are given in Table 2.

Reactions of $(\text{CH}_2=\text{CH})_2\text{SiMe}_2$ with the compounds diethylene(tertiary phosphine)platinum

The synthesis of the compound $[\text{Pt}\{(\text{CH}_2=\text{CH})_2\text{SiMe}_2\}(\text{P}-t\text{-Bu}_2\text{Me})]$ (III) is described in detail to illustrate the general method employed for all the compounds (III–VII).

The compound bis(cycloocta-1,5-dien)platinum (0.20 g, 0.5 mmol) was dissolved in light petroleum (10 cm^3) saturated with ethylene gas. To this solution

TABLE 2
 MELTING POINTS, COLOUR AND ANALYSES

Compound	M.p. ^a (°C)	Colour	Analysis found (calcd.) (%)	
			C	H
III	158–160	White	39.1(38.5)	7.6(7.1)
IV	138–139	White	49.4(49.0)	7.8(7.7)
V		White	50.2(50.6)	5.0(4.8)
VI	107	White	33.0(32.3)	6.2(6.0)
VII	134	White	43.9(42.5)	7.0(6.7)
VIII	122–126	Yellow	43.5(43.6)	5.0(4.4)
IX	142–145	Yellow	42.5(42.4)	7.0(7.0)
X	78–80	White	34.1(32.2)	6.6(6.3)

^a With decomposition.

was added di-*t*-butylmethylphosphine (0.5 mmol) in light petroleum (1 cm³). Solvent was removed in vacuo and the residue dissolved in diethyl ether (10 cm³) and treated with dimethyldivinylsilane (0.12 g, 1 mmol) at room temperature for 0.5 h. Solvent was removed in vacuo and the white solid crystallised from light petroleum to give III (0.15 g, 62%). IR spectrum (cm⁻¹): 3014m, 1364m, 1288s, 1242s, 1234s, 1189s, 1182s, 1020s, 955w, 934w, 911w, 890s, 885s, 878s, 826vs, 815s, 788m, 774m, 760m, 750m, 722s, 701s, 598w, 572w, 474m. ¹H NMR spectrum (CDCl₃ solution): τ , 7.69 (m, 6 H, CH=CH₂), 8.40 [d, 3 H, MeP, *J*(PH) 6, *J*(PtH) 32 Hz], 8.82 [d, 9 H, *t*-Bu, *J*(PH) 14 Hz], 8.84 [d, 9 H, *t*-Bu, *J*(PH) 14 Hz], 10.34 (s, 6 H, Me₂Si).

Similarly, [Pt(C₂H₄)₂{P(C₆H₁₁)₃}] (0.26 g, 0.5 mmol) suspended in diethyl ether (10 cm³), reacted with Me₂Si(CH=CH₂)₂ (0.12 g, 1 mmol) to give a pale yellow solution. Evaporation in vacuo afforded an oil which on treatment with light petroleum (2 cm³) gave after refrigeration for several hours the compound IV (0.18 g, 60%). IR spectrum (cm⁻¹): 3015m, 1402w, 1290s, 1241s, 1180s (br), 1138w, 1111w, 1062w(br), 1004m, 955w, 914w, 900w, 889w, 840vs, 822vs, 774s, 762s, 754s, 742m, 722m, 710m, 688w, 532w, 519m, 495w, 442w, 416m, 389m. ¹H NMR spectrum (CDCl₃ solution): τ , 6.95 (m, 2 H, CH=), 7.4–8.9 (complex m, 37 H, CH₂= and C₆H₁₁), 9.74 (s, Me₂Si).

Compound V (0.12 g, 42%) was prepared by adding [Pt(cod)₂] (0.21 g, 0.5 mmol) to (CH₂=CH)₂SiMe₂ (1 mmol) in light petroleum (10 cm³) at -30° C, followed by PPh₃ (0.13 g, 0.5 mmol). Diethyl ether was added in sufficient amount to dissolve the triphenylphosphine and the mixture was stirred for 1 h and filtered through an alumina pad (1 × 1 cm²). Evaporation and crystallisation gave V. IR spectrum (cm⁻¹): 3053w, 3018w, 1582w, 1496m, 1444s, 1410w, 1297s, 1256s, 1188m, 1102s, 1036w, 1020w, 1008w, 976w, 920w, 916w, 836vs, 811s, 774s, 710vs, 706s, 645vs, 620s, 609m, 564w.

Compound VI (80 mg, 28%) was obtained from [Pt(cod)₂] (0.20 g, 0.5 mmol), *P-t*-Bu₂Me (0.5 mmol) and (CH₂=CH)₂SnMe₂ (1 mmol). IR spectrum (cm⁻¹) 3010m, 1362s, 1266m, 1260m, 1184m(br), 1020m, 1001m, 947w, 934w, 912w, 903w, 890vs, 886vs, 878vs, 813m, 750sh, 734sh, 722s, 589w, 572m, 520m, 506m, 475m. ¹H NMR (CDCl₃ solution): τ , 7.24–7.9 (complex

m, 6 H, CH=CH₂), 8.38 [d, 3 H, MeP, *J*(PH) 7, *J*(PtH) 32 Hz], 8.83 [d, 9 H, t-Bu, *J*(PH) 13 Hz], 8.85 [d, 9 H, t-Bu, *J*(PH) 13 Hz], 10.38 [s, 6 H, Me₂Sn, *J*(SnH) 49 Hz].

Compound VII (0.12 g, 35%) was similarly obtained from [Pt(C₂H₄)₂{P(C₆H₁₁)₃}] (0.26 g, 0.5 mmol). IR spectrum (cm⁻¹): 3000m, 1292w, 1267m, 1222w, 1187m(br), 1172m, 1125m, 1108w, 1000m(br), 920w, 898w, 878w, 854m, 846m, 735m(br), 558w, 529w, 517s, 500m, 380s. ¹H NMR (CDCl₃ solution): τ, 7.3–8.9 (complex m, 39 H, CH=CH₂ and C₆H₁₁), 10.31 [s, Me₂Sn, *J*(SnH) 50 Hz].

Reactions of CH₂=CHCH₂SnMe₃ with the compounds diethylene(tertiary phosphine)platinum

The synthesis of compound VIII is illustrative of the preparation of the complexes [Pt(SnMe₃)(η³-C₃H₅)(PR₃)] (VIII–XII). The compound [Pt(C₂H₄)₂(PPh₃)] (0.38 g, 0.75 mmol) suspended in toluene (10 cm³) was treated with CH₂=CHCH₂SnMe₃ (0.15 g, 0.75 mmol) in hexane (10 cm³). The mixture was stirred at room temperature for 15 h. Solvent was removed in vacuo and the residue was recrystallised from hexane to give VIII (0.24 g, 48%). IR spectrum (cm⁻¹): 3050w, 1477s, 1433vs, 1260s, 1179w, 1166w, 1152w, 1095vs, 1025s, 998w, 915w, 876w, 802s, 750s, 746s, 606s, 657vs, 540vs, 502vs, 496s, 490s, 452w, 442w, 432w. ¹H NMR (C₆D₆ solution): τ, 2.2–3.0 (m, 15 H, Ph), 5.86 (m, 1 H, H²), 6.16 (m, 2 H, H¹_{syn} and H³_{syn}), 7.21 [d, 1 H, H³_{anti}, *J*(HH) 13, *J*(PtH) 45 Hz], 8.14 (m, 1 H, H¹_{anti}), 9.71 [s, 9 H, Me₃Sn, *J*(PtH) 12, *J*(SnH) 40 Hz].

Compound IX was obtained (0.4 g, 78%) from [Pt(C₂H₄)₂{P(C₆H₁₁)₃}] (0.75 mmol) and CH₂=CHCH₂SnMe₃ (0.75 mmol). IR spectrum (cm⁻¹): 1293m, 1273m, 1180s, 1135m, 1115m, 1058m, 1013s, 930s, 910m, 895m, 886m, 863s, 857s, 833m, 850vs(br), 550s, 533s, 509vs. ¹H NMR (C₆D₆ solution): τ, 6.0 (m, 3 H, H², H¹_{syn} and H³_{syn}), 7.7–9.0 (m br, 35 H, C₆H₁₁, H¹_{anti} and H³_{anti}), 9.34 [s, 9 H, Me₃Sn, *J*(PtH) 12 and *J*(SnH) 39 Hz].

Compounds X, XI and XII were similarly prepared. ¹H NMR (C₆D₆ solution): Compound X, τ 5.62 (m, 1 H, H²), 6.18 (m, 2 H, H¹_{anti} and H³_{anti}), 7.59 [d, 1 H, H³_{anti}, *J*(PH) 12, *J*(PtH) 44 Hz], 8.22 [d, 3 H, MeP, *J*(PH) 8, *J*(PtH) 56 Hz], 8.92 [d, 9 H, t-Bu, *J*(PH) 14 Hz], 8.97 [d, 9 H, t-Bu, *J*(PH) 14 Hz], 9.39 [s, 9 H, Me₃Sn, *J*(PtH) 12, *J*(SnH) 39 Hz]. Compound XI, τ, 2.4–3.0 (m, 10 H, Ph), 5.92 (m, 1 H, H²), 6.21 (m, 2 H, H¹_{syn} and H³_{syn}), 7.42 [d, 1 H, H³_{anti}, *J*(HH) 13, *J*(PtH) 46 Hz], 8.00 [d, 3 H, MeP, *J*(PH) 9, *J*(PtH) 48 Hz], 9.67 [s, 9 H, Me₃Sn, *J*(PtH) 12, *J*(SnH) 40 Hz]. Compound XII, τ, 2.4–3.0 (m, 5 H, Ph), 6.1 (m, 3 H, H², H¹_{syn} and H³_{syn}), 7.50 [d, 1 H, H³_{anti}, *J*(HH) 14, *J*(PtH) 46 Hz], 8.39 [d, 6 H, MeP, *J*(PH) 9, *J*(PtH) 42 Hz], 9.60 [s, 9 H, Me₃Sn, *J*(PtH) 12, *J*(SnH) 40 Hz].

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