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REACTIONS OF ALKYNES WITH BIS(TRIPHENYLPHOSPHINE)PLATINUM-ETHYLENE: A ^{31}P-{^{1}H} NMR STUDY *

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Summary

Internally consistent assignments of the ^{31}P-{^{1}H} NMR parameters of the complexes $[Pt(RC{\equiv}CR')(PPh_3)_2]$ are proposed, based on the premise that the magnitude of $^{1}J(PtP)$ depends mainly on the nature of the moiety ≡CR *trans* to P. For a given R, $^{2}J(PP)$ correlates with $^{1}J(PtP)$ for the bond *trans* to ≡CR. The alkynes $PhC{\equiv}CSnEt_3$, $PhC{\equiv}CSnPh_3$, $Me_3SiC{\equiv}CCl$, $Me_3SiC{\equiv}CBr$, $Et_3SiC{\equiv}CI$ and $MeC{\equiv}CI$ undergo oxidative addition reactions with $[Pt(C_2H_4)(PPh_3)_2]$; the intermediate alkyne complex was detected for $PhC{\equiv}CSnEt_3$, $Me_3SiC{\equiv}CCl$ and $Me_3C{\equiv}CBr$. The triyne $Me(C{\equiv}C)_3Me$ forms platinum(0) complexes by coordination with the central or terminal C≡C bond and appears also to give a platinum(II) complex by oxidative addition.

Introduction

The complexes $[Pt(RC{\equiv}CR')(PPh_3)_2]$ have an approximately square planar arrangement of 2C and 2P donor atoms with a small dihedral angle between the PtCC and PtPP planes [1]. The ^{31}P-{^{1}H} NMR spectra of several complexes with $R \neq R'$ are known to show the presence of non-equivalent PPh_3 ligands, but the chemical shifts δ and coupling constants $^{1}J(PtP)$ have not been assigned to particular PPh_3 ligands [2,3]. We have now recorded the ^{31}P-{^{1}H} NMR spectra of a large number of these complexes and we propose assignments of the spectra based on the premise that the coupling constants $^{1}J(PtP)$ show a strong dependence on the nature of the ≡CR group in the *trans* relationship to the PPh_3 ligand. The coupling constants $^{1}J(PtP)$ are known to depend strongly on the *trans* ligand for platinum(II) and platinum(IV) complexes [4], and although the complexes $[Pt(RC{\equiv}CR')(PPh_3)_2]$ are formally complexes of platinum(0), their electronic structures are regarded as being intermediate between representations A and B, where B is a platinum(II) complex of the dianion

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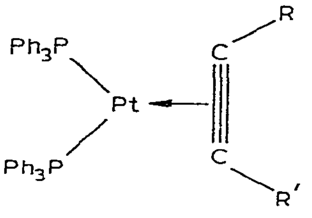
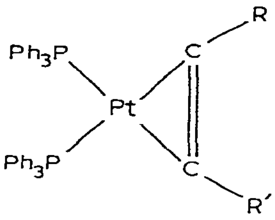


(A)



(B)

$[RC{\equiv}CR]^{2-}$. It is, however, possible that the couplings ^1J(PtP) in these complexes depend mainly on the nature of the ≡CR group in the *cis* relationship to the PPh_3 ligand, since a group R could have a smaller effect on the relevant electron density at the carbon to which it is attached than on that at the other carbon atom of the multiple bond; in that case our assignments would be reversed.

Results and discussion

The complexes $[Pt(RC{\equiv}CR')(PPh_3)_2]$ were prepared by treatment of $[Pt(C_2H_4)(PPh_3)_2]$ in dichloromethane with an excess of alkyne, and the ^{31}P-$\{^1H\}$ NMR spectra were recorded in situ. Our results together those available from the literature [2,3,5,6] are given in Table 1. The assignments in Table 1, which are discussed in detail in sections (a)—(d) below, are internally consistent, but reliability is not claimed for a number of assignments (indicated by Footnote *f* of Table 1) in cases in which the values of the coupling constants for the two PPh_3 ligands of a complex differ by only small amount. In Table 1, the complexes have been arranged in groups of complexes with substituents R in common, and within each group in order of decreasing ^2J(PP). Where complexes have identical values of ^2J(PP) or R = R' (when ^2J(PP) cannot be determined from the spectrum), the complexes are ordered with respect to the magnitude of ^1J(PtP) *trans* to the common ≡CR moiety.

Assignment of the ^{31}P-$\{^1H\}$ NMR parameters

(a) Coupling constants ^1J(PtP) *trans* to ≡CPh (3454 Hz), $≡CSiMe_3$ (3731 Hz); ≡CMe (3420 Hz) and $≡CC(OH)Me_2$ (3406 Hz) are taken from the results for the symmetrical complexes (R = R') VIII, XIV, XXV and XXXI. The coupling constants for II (R = Ph, R' = $SiMe_3$) differ substantially, and from the results for the symmetrical complexes and the assumed dependence of ^1J(PtP) on the nature of the *trans* moiety, ^1J(PtP) 3528 Hz is assigned to the P *trans* to ≡CPh and ^1J(PtP) 3791 Hz is assigned to the P *trans* to $≡CSiMe_3$. The parameters for complexes I, III, and IV (R = Ph, R' = SiX_3, GeX_3) are close to those of II and are similarly assigned. For each of the complexes V and VI one coupling constant ^1J(PtP) has a value which is very close to that in VIII and is, therefore, assigned to P *trans* to ≡CPh. Also, for VII the coupling ^1J(PtP) for the PtP bond *trans* to ≡CMe is smaller than that *trans* to ≡CPh, which is the order expected from the relative magnitudes of the coupling constants for VIII and XXV. The assignment for IX [R = Ph, R' = $C(OH)Me_2$] is based on the relative magnitudes of the coupling constants for VIII (R = R' = Ph) and XXXI [R = R' = $C(OH)Me_2$].

TABLE 1

^{31}P-{^1H}NMR PARAMETERS FOR COMPLEXES [$Pt(R-C\equiv C-R')(PPh_3)_2$] [a]

Complex	R	$-\delta$(ppm) [b] (PPh$_3$ *trans* to CR)	^1J(PtP)(Hz)	R′	$-\delta$(ppm) [b] (PPh$_3$ *trans* to CR′)	^1J(PtP)(Hz)	^2J(PP) (Hz)
I	Ph	112.7	3579	$GeEt_3$	111.1	3716	44
II	Ph	113.0	3528	$SiMe^3$	111.4	3791	44
III	Ph	112.3	3560	$SiPh_3$	112.5	3774	42
IV	Ph	112.5	3538	$GePh_3$	112.5	3645	42
V [c]	Ph	113.9	3469	H	109.9	3555	34
VI [d]	Ph	113.3	3457	$SnEt_3$	109.0	3506	32
VII [e]	Ph	112.8	3456	Me	111.7	3376	32
VIII [e]	Ph	112.9	3454	Ph			
IX [e]	Ph	113.7	3482	$C(OH)Me_2$	116.7	3431	27
X	$SiMe_3$	110.9	3826	Pr^n	112.5	3472	49
XI	$SiMe_3$	112.1	3772	$C_6H_4C\equiv CSiMe_3$-3	112.7	3550	42
XII	$SiMe_3$	112.2	3767	C_6H_4Br-3	112.8	3569	42
XIII	$SiMe_3$	113.5	3758	(η-Ph)$Cr(CO)_3$	113.1	3584	39
XIV	$SiMe_3$	106.3	3731	$SiMe_3$			
XV [f]	$SiMe_3$	114.2	3701	$C\equiv CSiMe_3$	113.0	3687	37
XVI	$SiMe_3$	114.0	3623	Cl	115.2	3359	20
XVII [g]	$SiMe_3$	113.5	3633	Br	115.7	3384	17
XVIII [f]	H	109.1	3706	$SiEt_3$	112.6	3774	46
XIX [c]	H	109.9	3563	C_6H_4Me-4	113.8	3451	35
XX	H	109.8	3552	C_6H_4F-4	113.8	3447	34
XXI [f]	H	110.9	3528	C_6H_4Br-4	113.9	3499	32
XXII [e]	H	112.2	3561	C(OH)HMe	113.6	3478	32
XXIII [e]	H	113.5	3547	C(OH)HPh	114.9	3479	27
XXIV [f]	H	114.2	3501	$C(OH)Ph(C\equiv CH)$	115.8	3533	23
XXV	Me	111.0	3420	Me			
XXVI [g]	Me	111.7	3357	$(C\equiv C)_2Me$	113.2	3708	32
XXVII	$GeEt_3$	110.8	3764	C_6H_4Me-2	112.9	3599	44
XXVIII	$GeEt_3$	110.9	3716	C_6H_4Me-3	112.6	3579	44
XXIX	$C(OH)Ph_2$	115.2	3394	$C\equiv CC(OH)Ph_2$	116.6	3657	22
XXX	$C(OH)Me_2$	114.2	3374	$C\equiv CC(OH)Me_2$	116.3	3633	22
XXXI [e]	$C(OH)Me_2$	116.5	3406	$C(OH)Me_2$			
XXXII	$C(OH)H_2$	113.9	3501	$C(OH)H_2$			
XXXIII [c]	Et	110.5	3430	Et			
XXXIV [c]	C_6H_4Me-4	112.8	3449	C_6H_4Me-4			
XXXV [g]	$C\equiv CMe$	113.7	3569	$C\equiv CMe$			
XXXVI [h]	$(CH_2)_5$	111.1	3420				
XXXVII [i]	$(CH_2)_4$	110.1	3409				
XXXVIII [j]	CF_3	120.6	3590	CF_3			

[a] Solutions in dichloromethane at 30° C unless stated otherwise. [b] Positive shifts are to high frequency of the external reference $(MeO)_3P$ in C_6D_6. [c] Result from ref. 3. [d] At —30° C. [e] Result from ref. 2. [f] Tentative assignment, see text. [g] In a mixture, see text. [h] Cycloheptyne, result from ref. 5. [i] Cyclohexyne, result from ref. 5. [j] Result from ref. 6.

(b) The results for complex XIV (R = R′ = $SiMe_3$) and complexes I—IV imply that ^1J(PtP) *trans* to $\equiv CMX_3$ (M = Si, Ge) is relatively large and this feature has been used to assign the parameters of complexes X—XIII, XVI, XVII, XXVII and XXVIII. For complex X (R′ = Pr^n) the coupling *trans* to $\equiv CPr^n$ agrees satisfactorily with the results for XXV and XXXIII (R = R′ = Me or Et), and for complexes XI—XIII, XXVII and XXVIII the couplings *trans* to $\equiv$CAr (Ar = aryl) are consistent with the results for P *trans* to $\equiv$CPh from complexes I—IX and for P *trans* to $\equiv CC_6H_4Me$-4 from complex XXXIV. The coupling constants ^1J(PtP) for the complex XV differ by only 14 Hz, so it is not possible to make a reliable assignment for this complex.

(c) Results for the unsubstituted acetylene complex (R = R′ = H) are not available, so the assignments for complexes XVIII—XXIV (R = H) must be based mainly on the magnitudes ^1J(PtP) *trans* to the moieties ≡CR′. For each of the complexes XIX and XX (R′ = Ar) one coupling constant ^1J(PtP) is very similar to those in VIII and XXXIV (R = R′ = Ar); the other coupling constants are larger by ca. 100 Hz and are assigned to P *trans* to ≡CH. For complexes XXII and XXIII one coupling constant is similar to those assigned to the P *trans* to ≡CH in complexes XIX and XX, and the other coupling constant is close to the mean of the coupling constants for XXXI [R = C(OH)Me_2] and XXXII [R = C(OH)H_2] (3454 Hz), which is presumed to provide an estimate for ^1J(PtP) *trans* to ≡C(OH)HR. From the results for complexes X—XVII (R = $SiMe_3$) it appears probable that the larger coupling constant ^1J(PtP) for complex XVIII (R′ = $SiEt_3$) should be assigned to the P *trans* to ≡$CSiEt_3$, but the relatively small difference between the coupling constants for complex XVIII and for the complexes XXI and XXIV precludes definite assignments.

(d) One coupling constant ^1J(PtP) for complex XXVI (R = Me, R′ = $(C{\equiv}C)_2Me$) has a similar magnitude to those for P *trans* to ≡CMe for complexes VII and XXV, and the smaller coupling constants for complexes XXIX [R = C(OH)Ph_2] are assigned to P *trans* to ≡CC(OH)X_2 by comparison with ^1J(PtP) for XXXI [R = R′ = C(OH)Me_2]. The couplings assigned to P *trans* to ≡CC≡CR for complexes XV, XXIX, XXX and XXXV agree satisfactorily with each other.

With the assignments given in Table 1 we have found an approximate linear correlation between ^2J(PP) and ^1J(PtP) for P *trans* to ≡CR for each of the groups of complexes with R = Ph (complexes I—VII, IX), with R = $SiMe_3$ (complexes II, X—XIII, XV—XVII) and with R = H (complexes XVIII—XIV). The

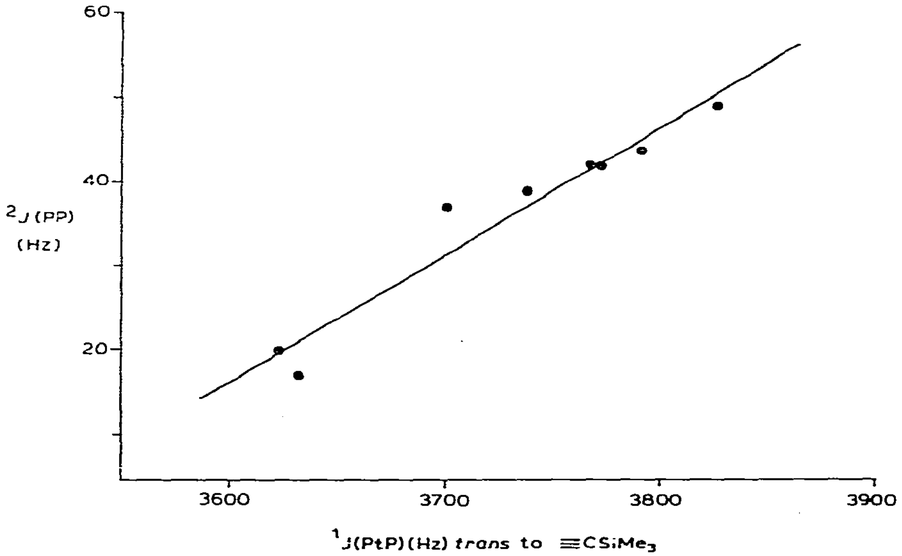


Fig. 1. Graph of ^2J(PP) against ^1J(PtP) *trans* to ≡$CSiMe_3$ for the complexes [Pt($Me_3SiC{\equiv}CR$)$(PPh_3)_2$].

correlation for R = $SiMe_3$ (correlation coefficient 0.990) is typical and is shown in Fig. 1; for all three correlations larger values of ^2J(PP) are associated with large coupling constants ^1J(PtP) *trans* to the common ≡CR moiety. The correlations may reflect a dependence of the relative contributions of structures A and B on the nature of R′ within the groups of complexes. Structure B resembles that for a *cis*-bis(triphenylphosphine)platinum(II) complex with σ-carbyl ligands for which both ^1J(PtP) (ca. 1800 Hz) and ^2J(PP) (<20 Hz) are relatively small [4]. For (triphenylphosphine)platinum(0) complexes, which are normally represented by structures analogous to A, the coupling constants ^1J(PtP) and ^2J(PP) are generally larger [4], so these parameters should increase as the substituent R′ favours a larger contribution from structure A. Since the alkyne ligand is formally anionic in structure B, structure A should be favoured by electron-releasing substituents R′. Thus, in contrast to platinum(II) complexes, where electron-releasing substituents increase the *trans* influence of ligands [4], electron-releasing substituents R′ for the alkyne complexes favour structure A and tend to increase ^1J(PtP) for the *trans* related PPh_3 ligand. Whilst the order of electron release by substituents R′ derived on this basis is reasonable (SiR_3, GeR_3 > H, aryl > $C(OH)R_2$) for R = Ph or H, the order is somewhat different for R = $SiMe_3$, so other factors, possibly steric, may also be involved.

It is noteworthy that the diynes $R(C{\equiv}C)_2R$ [R = $SiMe_3$, $C(OH)Ph_2$, $C(OH)Me_2$] each gave only a single platinum(0) product with non-equivalent PPh_3 ligands, indicating that the diynes are monodentate (complexes XV, XXIV, XXX) under our conditions. For the triyne $Me(C{\equiv}C)_3Me$ the ^{31}P-{^1H} NMR spectrum showed the presence of two complexes with coupling constants ^1J(PtP) of the magnitude expected for alkyne complexes. In one complex (XXVI) the PPh_3 ligands are nonequivalent, as expected for coordination by a terminal C≡C group, and the other complex (XXXV) has equivalent phosphines, indicating coordination of the central C≡C group. Also present was a minor component with non-equivalent PPh_3 ligands, the ^{31}P-{^1H} parameters of which (δ −123.5 ppm, ^1J(PtP) 2378 Hz; δ −124.7 ppm, ^1J(PtP) 2290, ^2J(PP) 19 Hz), and in particular the small values of ^1J(PtP), indicate the formation of a platinum(II) complex with both PPh_3 ligands *trans* to ligands of high *trans* influence. This complex is tentatively formulated as *cis*-$[Pt(C{\equiv}CMe)(C{\equiv}CC{\equiv}CMe)(PPh_3)_2]$, a product of oxidative addition of the alkyne.

Oxidative addition reactions

At room temperature alkynyl-tin compounds $PhC{\equiv}CSnR_3$ (R = Me, Et) and alkynyl iodides RC≡CI (R = Ph, I) add oxidatively to (phosphine)platinum(0) complexes. With polyhalogeno-alkenes the oxidative addition reaction is known to be preceded by coordination of the olefin [4], so we examined the products of reactions between $[Pt(C_2H_4)(PPh_3)_2]$ and $PhC{\equiv}CSnEt_3$, $PhC{\equiv}CSnPh_3$, R_3Si-C≡CX (X = Cl, Br, I) or MeC≡CI. A solution of $[Pt(C_2H_4)(PPh_3)_2]$ in dichloromethane was treated with $PhC{\equiv}CSnEt_3$ at ca. −30°C and examined at the same temperature by ^{31}P-{^1H} NMR spectroscopy. The spectrum showed the presence of the alkyne complex VI and a second complex with non-equivalent PPh_3 ligands. The latter complex was the only product at room temperature. The ^{31}P-{^1H} NMR spectrum establishes the formula *cis*-$[Pt(C{\equiv}CPh)(SnEt_3)(PPh_3)_2]$: the parameters (δ −116.2 ppm, ^1J(PtP) 1780, $^2J(^{119}SnP)$ 1426, $^2J(^{117}SnP)$ 1352

Hz; δ −114.3 ppm, ^{1}J(PtP) 2996, ^{2}J(SnP) 103, ^{2}J(PP) 17 Hz) are similar to those of the complex *cis*-$[\mathrm{PtPh(SnMe_3)(PPh_3)_2}]$ (δ −114.3 ppm, ^{1}J(PtP) 2060, $^{2}J(^{119}\mathrm{SnP})$ 1718, $^{2}J(^{117}\mathrm{SnP})$ 1640 Hz; δ −115.2 ppm, ^{1}J(PtP) 2129, ^{2}J(SnP) 145, ^{2}J(PP) 13 Hz [10]), but the value of ^{1}J(PtP) *trans* to C≡CPh (2996 Hz) is larger than that *trans* to Ph (2129 Hz), as is expected from the greater *trans* influence of the Ph ligand [4]. The configuration of the complex $[\mathrm{Pt(C{\equiv}CPh)(SnMe_3)(PPh_3)_2}]$, obtained from the reaction at room temperature between $[\mathrm{Pt(PPh_3)_4}]$ and $\mathrm{PhC{\equiv}CSnMe_3}$ has been assigned *trans* from the observation of a weak single resonance in a relatively low-resolution ^{31}P NMR spectrum [7]. Since our results for $\mathrm{PhC{\equiv}CSnEt_3}$, $\mathrm{PhC{\equiv}CSnPh_3}$ (see below) and a variety of tetraorganotin compounds show that *cis*-complexes are invariably obtained from reactions with platinum(0) complexes, it is probable that the complex obtained previously was *cis*, perhaps with only a small chemical shift (which was not resolved) between the non-equivalent nuclei. The reaction at room temperature between $[\mathrm{Pt(C_2H_4)(PPh_3)_2}]$ and $\mathrm{PhC{\equiv}CSnPh_3}$ gave *cis*-$[\mathrm{Pt(C{\equiv}CPh)(SnPh_3)(PPh_3)_2}]$ (δ −115.9 ppm, ^{1}J(PtP) 2058, $^{2}J(^{119}\mathrm{SnP})$ 1841, $^{2}J(^{117}\mathrm{SnP})$ 1760 Hz; δ −118.4 ppm, ^{1}J(PtP) 2856, ^{2}J(SnP) 114, ^{2}J(PP) 18 Hz).

The $^{31}\mathrm{P}$-$\{^{1}\mathrm{H}\}$ NMR spectrum of the mixture obtained after 30 min at room temperature from $[\mathrm{Pt(C_2H_4)(PPh_3)_2}]$ and $\mathrm{Me_3SiC{\equiv}CBr}$ showed the presence of the alkyne complex XVII, the parameters of which are similar to those of complex XVI which was obtained as the only product from $\mathrm{Me_3SiC{\equiv}CCl}$ when the same procedure was used. Also present in the reaction mixture from $\mathrm{Me_3SiC{\equiv}CBr}$ were *cis*-$[\mathrm{PtBr(C{\equiv}CSiMe_3)(PPh_3)_2}]$ [δ −121.3 ppm, ^{1}J(PtP) 2295 Hz; δ −129.4 ppm, ^{1}J(PtP) 3740, ^{2}J(PP) 18 Hz] and a *trans* complex [δ −119.6 ppm, ^{1}J(PtP) 2656 Hz] which is probably *trans*-$[\mathrm{PtBr(C{\equiv}CSiMe_3)(PPh_3)_2}]$. The reaction at room temperature or at −45°C between $\mathrm{Et_3SiC{\equiv}CI}$ or $\mathrm{MeC{\equiv}CI}$ and $[\mathrm{Pt(C_2H_4)(PPh_3)_2}]$ gave mixtures of *cis*- and *trans*-$[\mathrm{PtI(C{\equiv}CR)(PPh_3)_2}]$ [R = $\mathrm{SiEt_3}$, *cis* complex: δ −124.5 ppm, ^{1}J(PtP) 2334 Hz; δ −131.5 ppm, ^{1}J(PtP) 3594, ^{2}J(PP) 17 Hz; *trans* complex: δ −121.1 ppm, ^{1}J(PtP) 2617 Hz, R = Me, *cis* complex: δ −125.7 ppm, ^{1}J(PtP) 2341 Hz; δ −130.5 ppm, ^{1}J(PtP) 3591, ^{2}J(PP) 15 Hz; *trans* complex: δ −122.0 ppm, ^{1}J(PtP) 2617 Hz]. Since the reaction mixture from $[\mathrm{Pt(C_2H_4)(PPh_3)_2}]$ and an excess of $\mathrm{Me_3SiC{\equiv}CCl}$ appeared to contain *trans*-$[\mathrm{PtCl(C{\equiv}CSiMe_3)(PPh_3)_2}]$ [δ −117.8 ppm, ^{1}J(PtP) 2688 Hz] after 5 days at room temperature, it is evident that the rate of oxidative addition increases in the expected order $\equiv$C—Cl < $\equiv$C—Br < $\equiv$C—I. The rate for $\equiv$C—Sn most closely resembles that for $\equiv$C—Br. For $\mathrm{PhC{\equiv}CSnR_3}$ and $\mathrm{R_3SiC{\equiv}CX}$ (X = Cl, Br) the rates of displacement of ethylene from $[\mathrm{Pt(C_2H_4)(PPh_3)_2}]$ exceed that for oxidative addition; kinetic studies have shown that the rate of displacement of ethylene by PhC≡CH ($k^{25^\circ\mathrm{C}} = 2.8 \times 10^{2}\ M^{-1}\ \mathrm{sec}^{-1}$) exceeds the rate of oxidative addition of MeI ($k^{25^\circ\mathrm{C}} = 1.3 \times 10^{-2}\ M^{-1}\ \mathrm{sec}^{-1}$) or $\mathrm{PhCH_2Br}$ ($k^{25^\circ\mathrm{C}} = 1.4 \times 10^{-1}\ M^{-1}\ \mathrm{sec}^{-1}$) [11].

Experimental

Reactions were carried out under dry, oxygen-free nitrogen. Solvents were dried and distilled before use. The $^{31}\mathrm{P}$-$\{^{1}\mathrm{H}\}$ NMR spectra were recorded on a JEOL PFT-100 Fourier Transform spectrometer at 40.48 Hz. An external reference of $\mathrm{(MeO)_3P}$ in $\mathrm{C_6D_6}$ or of $\mathrm{(MeO)_3PO}$ in $\mathrm{CD_2Cl_3}$ (for samples at low temperature) also provided the ^{2}H lock signal. Complexes examined in situ were prepared by addition of an excess of the alkyne to [Pt(C_2H_4)(PPh_3)$_2$] (0.05 g) in CH_2Cl_2 (1 cm^3) in an 8 mm NMR tube. The mixture was shaken for about 5 min, during which period evolution of ethylene occurred, and then set aside for about 30 min before being placed in the spectrometer.

The complex *cis*-[Pt(C≡CPh)($SnPh_3$)(PPh_3)$_2$] was obtained after treatment of [Pt(C_2H_4)(PPh_3)$_2$] (0.37 g) in toluene (10 cm^3) with a slight excess of PhC≡C-$SnPh_3$ (0.23 g). The solution was stirred for 2 h at room temperature. Hexane (20 cm^3) was added to give the product as yellow crystals (63%), m.p. 208°C, ν(C≡C) 2100 cm^{-1} (Analysis found: C, 62.5; H, 4.9. $C_{60}H_{50}P_2PtSn$ calcd.: C, 63.6; H, 4.3%).

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