ORGANOMETALLICS

Volume 7, Number 10, October 1988

A Multinuclear NMR Study of Asymmetrically Coordinated η^3-Allyls in [PtCl(η^3-allyl)(phosphine)] and [Pt(phenyl)(η^3-allyl)(phosphine)] Complexes

Howard C. Clark,*,† Mark J. Hampden-Smith,‡ and Heinz Ruegger§

Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

Received August 18, 1986

The title complexes were prepared and fully characterized by multinuclear (^{1}H, ^{31}P, ^{13}C, ^{195}Pt) NMR methods. The ^{1}H NMR resonances of the allyl groups were unequivocally assigned by using a combination of one- and two-dimensional NMR spectroscopic techniques. The spectroscopic data have been interpreted in terms of contributions of asymmetric η^1–η^2-allyl bonding modes to the more familiar symmetrical η^3-allyl arrangement. The relative orientation and extent of the asymmetric η^1–η^2-bonding were shown to be markedly dependent upon the nature of the other ligands coordinated to platinum. On prolonged standing in chloroform solution, the title complexes rearranged to give the known complexes $[X(R_3P)Pt(\mu\text{-}Cl)]_2$ and *trans*-$XClPt(PR_3)_2$ (X = Cl, Ph). Conversion of the allyl moiety to propene gas was shown by ^{1}H NMR and gas chromatographic analysis.

Introduction

Complexes containing η^3-allyl ligands play a crucial role in the nickel-catalyzed cyclooligomerization of dienes. Nickel phosphine or phosphite catalysts in particular are used for the dimerization of butadiene.[1] Important intermediates and precursors of the reductive coupling in such processes are complexes containing metal–π-allyl and metal–σ-alkyl bonds. Platinum–allyl complexes can be expected to have a higher stability compared to their palladium and nickel analogues and to provide additional spectroscopic information due to interaction with the NMR-active ^{195}Pt isotope. Moreover, a survey of the existing literature revealed that information about platinum alkyl–allyl complexes is generally restricted to platinacycles[2] and that the only aryl–allyl compounds reported contain polyhalogenated phenyls.[3] Here we wish to report on the chemical and spectroscopic properties of the complexes Pt(Ph)(η^3-C_3H_5)(L) (L = tertiary phosphine) obtained from the reaction of the analogous chloro compounds and organotin reagents.

Experimental Section

Materials. The complexes [PtCl(η^3-C_3H_5)(L)] (L = PMe_2Ph, **1a**; L = $PMePh_2$, **1b**; L = P(4-$FC_6H_4)_3$, **1c**; L = PCy_3, **1d**; L = PPh_2(*sec*-$CH_2CHMeEt$), **1e**) were prepared from $[PtCl(\eta^1\text{-}\mu\text{-}C_3H_5)]_4$ and the corresponding phosphines (obtained from Strem Chemicals) according to the literature.[4,5] The compounds [PtCl(η^3-C_3H_4R)(PCy_3)] (R = Me, **1g**; R = Ph, **1h**) were obtained from [PtCl(η^1-C_3H_4R)(COD)] and PCy_3 according to the reported[7] method. $SnMe_3Ph$ was prepared from $SnMe_3Cl$ (Aldrich Chemical Co.) and PhMgBr in ether and purified by distillation.

Generally, reactions were carried out under an atmosphere of dry nitrogen, and solvents were dried and redistilled before use.

Physical Measurements. The nuclear magnetic resonance spectra were recorded as follows: ^{1}H NMR on a Bruker WH-400 or AC-250, the raw data were generally processed by using resolution enhancement techniques; ^{13}C and ^{31}P NMR on a Bruker WH-400, AM-250, or AC-250; ^{195}Pt NMR on a Bruker CXP-200 or WH-400. Two-dimensional NMR spectra were recorded by using the Bruker programs COSY, NOESY, XHCORR, and JRES with appropriate digitalization in F_1 and F_2 and optimized window functions.

Elemental analyses were obtained from Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada.

† Present address: Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3.

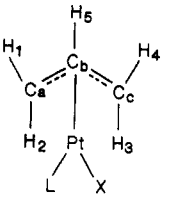
‡ Department of Chemistry, Indiana University, Bloomington, IN 47401.

§ Spectrospin AG, Industriestrasse 26, 8117 Fakkabder, Zürich, Switzerland.

(1) Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Academic: New York, 1975; Vol. 2.
(2) Barker, G. K.; Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1839.
(3) Numata, S.; Okawara, R.; Kurosawa, H. *Inorg. Chem.* **1977**, *90*, 8234.
(4) Mann, B. E.; Shaw, B. L.; Shaw, G. *J. Chem. Soc. A* **1971**, 3536.
(5) Carturan, G.; Scrivanti, A.; Longato, B.; Morandini, F. *J. Organomet. Chem.* **1979**, *172*, 91.
(6) Carturan, G.; Belluco, U.; DelPra, A.; Zanotti, G. *Inorg. Chim. Acta* **1979**, *33*, 155.
(7) Boag, N. M.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1208.

0276-7333/88/2307-2085$01.50/0

Table I. NMR Data for Complexes $[Pt(\eta^3\text{-}C_3H_5)Cl(L)]^a$



L	parameter	H_1 dq	H_2 dd	H_3 dd	H_4 ddd	H_5 m
PMe_3	δ	3.28	2.14	2.88	4.25	4.73
	J_{H-H}	J_{1-5} = 6.5	J_{2-5} = 11.2	J_{3-5} = 13.5	J_{4-5} = 6.0	
		J_{1-4} = 2.2	J_{1-2} = 1.7			
	J_{H-P}	2.2		9.3	5.0	
	J_{H-Pt}	21	83	30		
PCy_3	δ	3.13	2.00	2.83	4.23	4.70
	J_{H-H}	J_{1-5} = 6.4	J_{2-5} = 10.9	J_{3-5} = 13.2	J_{4-5} = 6.6	
	J_{H-P}	2.0		8.3	5.1	
	N_{H-Pt}	20	81	29		64
PMe_2Ph	δ	3.15	2.13	2.93	4.31	4.78
	J_{H-H}	J_{1-5} = 6.5	J_{2-5} = 11.3	J_{3-5} = 13.2	J_{4-5} = 7.4	
		J_{1-4} = 2.3	J_{1-2} = 2.6			
	J_{H-P}	2.3		9.5	5.1	
	J_{H-Pt}	21	82	30		66
$PMePh_2$	δ	2.98	2.13	2.97	4.35	4.84
	J_{H-H}	*b*	J_{2-5} = 10.2	J_{3-5} = 12.8	J_{4-5} = 6.0	
	J_{H-P}			9.0	5.0	
	J_{H-Pt}		80	30		67
$P(4\text{-}FC_6H_4)_3$	δ	2.84	2.28	3.10	4.44	4.98
	J_{H-H}	J_{1-5} = 6.5	J_{2-5} = 11.2	J_{3-5} = 13.3	J_{4-5} = 7.3	
		J_{1-4} = 2.1	J_{1-2} = 2.4	J_{3-4} = 1.2	J_{2-4} = 0.7	
	J_{H-P}	2.2		9.6	5.3	1.4
	J_{H-Pt}	23	79	29		69
$P(Ph_2R)^c$	δ	2.96	1.98	2.80	4.26	4.43
	J_{H-H}		J_{2-5} = 11.0			

[a] In $CDCl_3$ solutions at room temperature; spectra referenced to tetramethylalane (TMS): coupling constants in Hz. [b] Obscured by H_3. [c] R* = *sec*-$CH_2CHMeEt$

Preparation of the Complexes $[PtCl(\eta^3\text{-}C_3H_5)(L)]$ (L = PMe_2Ph, PPh_2Me, $P(4\text{-}FC_6H_4)_3$, PCy_3, PPh_3, PPh_2(*sec*-$CH_2CHMeEt$). These complexes were prepared according to the literature method[5] and characterized by NMR spectroscopy. NMR parameters not included in Tables I and II are as follows.

$[PtCl(\eta^3\text{-}C_3H_5)(PMe_2Ph)]$ (1a). ^1H NMR (δ): PMe_2, 1.93/1.89, J_{H-P} = 10.2, J_{H-Pt} = 38.8 Hz; PPh, 7.65 (m) and 7.42 (m). ^{13}C NMR (δ): PMe_2, 14.6, 14.4, J_{H-P} = 36 Hz; PPh, C_o, 130.6, J_{C-P} = 10.8 Hz; C_m, 128.6, J_{C-P} = 8.0 Hz; C_p, 130.4.

$[PtCl(\eta^3\text{-}C_3H_5)(PMePh_2)]$ (1b). ^1H NMR (δ): PMe, 2.20, J_{H-P} = 10.1, J_{H-Pt} = 35.9 Hz; PPh, 7.57 (m), 7.42 (m). ^{13}C NMR (δ): PMe, 12.9, J_{C-P} = 35.8, J_{C-Pt} = 27 Hz; PPh, C_o, 132.2, J_{C-P} = 10.8 Hz; C_m, 128.5, J_{C-P} = 7.3 Hz; C_p, 130.5.

$[PtCl(\eta^3\text{-}C_3H_5)(P(4\text{-}FC_6H_4)_3)]$ (1c). ^1H NMR (δ): $P(4\text{-}FC_6H_4)_3$, H_o, 7.44, J_{H-P} = 11.6, J_{F-H} = 5.3 Hz; H_m, 7.19, J_{H-P} = 1.0, J_{F-H} = 8.6 Hz; ^{13}C NMR: C_α, 127.3 J_{C-P} = 57 Hz; C_o, 136.0, J_{C-P} = 7.0 Hz; C_m, 115.9, J_{C-P} = 11.7, J_{F-C} = 18.4 Hz; C_p, 164.2, J_{F-C} = 253 Hz.

$[PtCl(\eta^3\text{-}C_3H_5)(PCy_3)]$ (1d). ^1H NMR (δ): H_α, 2.33, J_{H-P} = 10.9, $^3J_{H-H}$ = 12.4, 2.4 Hz; $H_{\beta e}$, 1.92; $H_{\beta a}$, 1.48; $H_{\gamma e}$, 1.80; $H_{\gamma a}$, 1.26; $H_{\delta e}$, 1.72; $H_{\delta a}$, 1.25. ^{13}C NMR (δ): C_α, 34.4, J_{C-P} = 27.4, J_{C-Pt} = 38.7 Hz; C_β, 29.9, 30.0; C_γ, 27.7, J_{C-P} = 10.5 Hz; C_δ, 26.6.

$[PtCl(\eta^3\text{-}C_3H_5)(PPh_2$(*sec*-$CH_2CHMeEt))]$ (1e). ^1H NMR (δ, P–CH_aH_b–CH_c–$(CH_d{}^3)(CH_eH_fCH_g{}^3)$; two diastereomeric complexes 1e and 1e′): H_a, H_b, 2.7 (m); H_c, H_c', 2.0 (m); H_d, H_d', 1.05 (d) (6.6), 1.00 (d) (6.6); H_e, H_e', 1.55 (m); H_f, H_f', 1.30 (m); H_g, H_g', 0.84, 0.83 (t) (7.3); PPh_2, 7.70 (m); 7.25 (m). ^{13}C NMR (δ, P–$C_aH^2C_bH(C_cH^3)(C_dH^2$–$C_eH^3)$): C_a, C_a', 33.8, 33.9, J_{C-P} = 30, 32 Hz; C_b, C_b', 31.4; C_c, C_c', 21.1, 21.0, J_{C-P} = 7 Hz; C_d, C_d', 31.6, J_{C-P} = 9 Hz; C_e, C_e', 11.4, PPh_2, C_o, 133.2; C_m 128.5; C_p, 130.4.

$[PtCl(\eta^3\text{-}C_3H_5)(PMe_3)]$ (1f). To a suspension of *sym-trans*-$[Pt_2Cl_4(PMe_3)_2]$ (684 mg, 1.00 mmol) in ether was added allylmagnesium chloride (1.90 mmol) at 0 °C. Stirring for 1 h was followed by filtration and hydrolyzation with an aqueous saturated solution of NH_4Cl. The organic phase was separated and dried ($MgSO_4$). The volume of the solution was reduced to 1 mL, and pentane (4 mL) was added. Cooling to −70 °C afforded the product as a white powder. Yield: 55%. ^1H NMR (δ): PMe_3, 1.62, J_{H-P} = 10.5, J_{H-Pt} = 39.6 Hz.

Table II. ^{13}C, ^{31}P, and ^{195}Pt NMR Data for Complexes $[Pt(\eta^3\text{-}C_3H_5)Cl(L)]^a$

L	parameter	C_a	C_b	C_c	P	Pt
PCy_3	δ	39.2	106.5	69.8	35.7	
	J_{X-P}			28.5		
	J_{X-Pt}	275	41	40	4272	
PMe_2Ph	δ	42.6	107.9	67.8	−2.4	−4842
	J_{X-P}			33.2		
	J_{X-Pt}	255	43	48	4285	
$PMePh_2$	δ	45.3	108.2	67.9	10.6	−4834
	J_{X-P}			33.2		
	J_{X-Pt}	252	44	48	4340	
$P(4\text{-}FC_6H_4)_3$	δ	48.3	109.5	69.4[b]	21.2[c]	−4799
	J_{X-P}		1.0	32.9		
	J_{X-Pt}	249.6	45.6	54.8	4499	
$P(Ph_2R^*)$	δ	45.5	107.0	67.1	18.1	
	J_{X-P}			33		
	J_{X-Pt}	243	48	55	4315	

[a] In $CDCl_3$ solutions at room temperature referenced to TMS (^{13}C), H_3PO_4 (^{31}P), and Na_2PtCl_6 (^{195}Pt). J values in Hz. [b] J_{C-H} = 163.7 Hz. [c] J_{P-F} = 2.7 Hz.

$[PtCl(\eta^3\text{-}C_3H_4Me)(PCy_3)]$ (1g). This compound was prepared similarly to the bromo derivative.[7] ^{31}P NMR (δ): 37.9, J_{P-Pt} = 4540 Hz. ^1H NMR (δ): H_1, 2.89, J_{15} = 6.4, J_{12} = 3.0, J_{H-Pt} = 18 Hz; H_2, obscured; H_3, 3.54, J_{35} = 13.0, J_{3Me} = 6.5, J_{H-P} = 6.5 Hz; H_5, 4.46, J_{H-Pt} = 60 Hz; Me, 1.86, J_{H-P} = 6 Hz; PCy_3, H_α, 2.31; $H_{\beta e}$, 1.92; $H_{\beta a}$, 1.47; $H_{\gamma e}$, 1.80; $H_{\gamma a}$, 1.26; $H_{\delta e}$, 1.72; $H_{\delta a}$, 1.26.

$PtCl(\eta^3\text{-}C_3H_4Ph)(PCy_3)$ (1h) was prepared according to the literature.[7] The ^1H NMR data were not reported previously. ^{31}P NMR (δ): 37.3, J_{P-Pt} = 4482 Hz (lit.[7] 37.0, J_{P-Pt} = 4458 Hz). ^1H NMR (δ): H_1, 3.04, J_{15} = 6.4, J_{12} = 2.3, J_{H-Pt} = 20 Hz; H_2, 2.04,

Table III. ^1H, ^{31}P, and ^{195}Pt NMR Data for Complexes $[Pt(\eta^3\text{-}C_3H_5)Ph(L)]$[a]

L	parameter	H_1 dd	H_2 d	H_3 ddd	H_4 ddt	H_5	H_o d	H_m t	H_p t	P s	Pt d
PMe_2Ph	δ	3.57	2.40	2.24	3.70	4.65	7.34	7.01	6.85	-9.3	-5097
	J_{H-H}	J_{1-5} = 7.5	J_{2-5} = 13.1	J_{3-5} = 12.7	J_{4-5} = 7.7						
		J_{1-4} = 2.0		J_{3-4} = 2.6							
	J_{H-P}			10.0	5.2	0.8					
	J_{X-Pt}		40.7	62.8	16.5	42.0	66.4	11.1		3797	
$P(4\text{-}C_6H_4F)_3$	δ	3.46	2.52	2.39	3.76	4.85	7.02	6.82	6.74	21.1[b]	-5069
	J_{H-H}	J_{1-5} = 7.4	J_{2-5} = 13.2	J_{3-5} = 13	J_{4-5} = 7.2						
		J_{1-4} = 2.8		J_{3-4} = 2.8							
	J_{H-P}	0.7		10.3	5.2						
	J_{X-Pt}		39.1	64.8	17.2	40.0	65.8	11.0		3929	
$PMePh_2$	δ									6.4	-5093
	J_{X-Pt}									3832	
PCy_3	δ									28.7	
	J_{X-Pt}									3785	

[a] J values in Hz. [b] J_{P-F} = 2.7.

Table IV. ^{13}C NMR Data for $[Pt(\eta^3\text{-}C_3H_5)(Ph)(P(4\text{-}FC_6H_4)_3)]$

parameter	C_a	C_b	C_c	C_i	C_o	C_m	C_p	C_i	C_o	C_m	C_p
δ	60.5	112.9	54.3	149.9	138.7	127.2	121.7	128.8	135.7	115.4	163.9
J_{C-P}, Hz	...	3.07	40.0	9.8	1.7	...	...	53.7	13.8	11.6	2.5
J_{C-Pt}, Hz	18.0	12.2	152.3		32.1	74.8	14.0	35.0	22.3		
J_{C-F}, Hz								3.6	8.5	21.0	252.0

J_{25} = 10.3, J_{H-Pt} = 78 Hz; 4.42, J_{35} = 12.5, J_{H-P} = 8.2, J_{H-Pt} = 26 Hz; H_5, 5.07, J_{H-Pt} = 60 Hz; H_o, 7.39 (d); H_m, 7.33 (t); H_p, 7.18 (t); PCy_3, H_α, 2.33; $H_{\beta e}$, 1.94; $H_{\beta a}$, 1.47; $H_{\gamma e}$, 1.80; $H_{\gamma a}$, 1.26; $H_{\gamma e}$, 1.72; $H_{\delta a}$, 1.26.

Preparation of the Complexes $[Pt(Ph)(\eta^3\text{-}C_3H_5)(L)]$ (L = PMe_2Ph, $PMePh_2$, $P(4\text{-}FC_6H_4)_3$). $[Pt(Ph)(\eta^3\text{-}C_3H_5)(P(4\text{-}FC_6H_4)_3)]$ (2c). To a solution of $[Pt(Cl)(\eta^3\text{-}C_3H_5)(P(4\text{-}FC_6H_4)_3)]$ (94 mg, 0.16 mmol) in CH_2Cl_2 (2 mL) was added a solution of $SnMe_3Ph$ (80 mg, 0.32 mmol) in CH_2Cl_2 (1 mL), and the mixture was stirred in the dark for 17 h. Then the volatiles were removed in vacuo leaving a pale brown oil residue which was washed with two 1-mL portions of hexanes to give white solid (38 mg). The hexane washings were combined, the solvent was evaporated, and the residue was washed with 1 mL of cold cyclopentane to yield a further 36 mg of white solid **2c**. These solids were recrystallized from a mixture of dichloromethane and *n*-pentane at low temperature. Yield: 73.5%. Anal. Calcd for **2c**, $C_{27}H_{22}F_3PPt$: C, 51.51; H, 3.52. Found: C, 51.33; H, 3.73. ^1H NMR (δ): ($4\text{-}FC_6H_4$), H_o, 7.27 (m), J_{H-P} = 10.8, J_{H_o-F} = 5.7 Hz; H_m, 7.00 (m), J_{H-P} = 1.2, J_{H_m-F} = 8.8 Hz.

The compounds $[Pt(Ph)(\eta^3\text{-}C_3H_5)(PMe_2Ph)]$ (**2a**) and $[Pt(Ph)(\eta^3\text{-}C_3H_5)(PMePh_2)]$ (**2b**) were prepared in an analogous manner. NMR (δ): PMe_2, 1.72, 1.64, J_{H-P} = 9.7, J_{H-Pt} = 37.3, 38.2 Hz; PPh, 7.5 (m), 7.3 (m).

Reaction of $[PtCl(\eta^3\text{-}C_3H_5)(L)]$ (L = PMe_2Ph, $PMePh_2$, PCy_3) with $SnMe_3Ph$ (Long Reaction Times). L = PMe_2Ph. A solution of $[PtCl(\eta^3\text{-}C_3H_5)(PMe_2Ph)]$ (0.10 mmol) and $SnMe_3Ph$ (0.12 mmol) in 0.6 mL of $CDCl_3$ was sealed in a 5-mm NMR tube. Complete conversion to $[Pt(Ph)(\eta^3\text{-}C_3H_5)(PMe_2Ph)]$ (**2a**) occurred in 2 h, and the formation of $SnMe_3Cl$ (^1H NMR (δ): Me, 0.66, $J_{^{119}Sn-H}$ = 57.7 Hz) was observed. Small amounts of impurities were observed after 2 days. Reexamination of the solution after 1 month showed complete disappearance of **2a** and the formation of three phosphorus-containing compounds.

The NMR tube was then opened and hexane (3 mL) added to the solution resulting in the precipitation of an off-white material which consisted of a mixture of *sym-trans/cis*-$[Pt_2(Ph)_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (**3a**). ^1H NMR (δ): (A), PMe_2, 1.47, J_{H-P} = 11.2 Hz; PPh, 7.42 (m), 7.70 (m); PtPh, H_o, 7.15, H_m, 6.83, H_p, 6.75; (B), PMe_2, 1.52, J_{H-P} = 11.2 Hz; PPh, 7.42 (m), 7.76 (m); PtPh, H_o, 7.11. ^{31}P NMR (δ): (A), -13.1, J_{P-Pt} = 4880 Hz; (B), -13.3, J_{P-Pt} = 4900 Hz. The mother liquor was pumped to dryness in vacuo and the residue reexamined spectroscopically. The NMR parameters of the third compound are identical with those of *trans*-$[PtCl(Ph)(PMe_2Ph)_2]$ (**5a**). ^{31}P NMR (δ): -5.0, J_{P-Pt} = 2869 Hz. ^1H NMR (δ): PMe_2, 1.51, $^2J_{P-H} + {}^4J_{P-H}$ = 6.9 Hz; PPh, 7.37 (m), 7.60 (m); PtPh, H_o, 6.99, J_{H-Pt} = 60 Hz.

L = $PMePh_2$: The reaction was carried out analogously to that of **2a** and $SnMe_3Ph$. Fractional crystallization gave a mixture of *sym-trans/cis*-$[Pt_2(Ph)_2(\mu\text{-}Cl)_2(PMePh_2)_2]$ (**3b**). ^1H NMR (δ): PMe, 1.54, 1.56, J_{H-P} = 11, 10.8 Hz; PPh_2, H_o, 7.62 (dd), J_{H-P} = 11.9 Hz; H_m, H_p, 7.36 (m); PtPh, H_o, 7.11, 7.10; H_m, H_p, 6.7 (m). After workup, the mother liquor was found to contain *trans*-$[PtCl(Ph)(PMePh_2)_2]$ (**5b**). ^1H NMR (δ): PMe, 1.73, $^2J_{P-H} + {}^4J_{P-H}$ = 7.2, J_{P-Pt} = 32.6 Hz; PPh, 7.58 (m), 7.31 (m); PtPh, H_o, 6.81; H_m, 6.44; H_p, 6.51.

L = PCy_3. A solution of $[PtCl(\eta^3\text{-}C_3H_5)(PCy_3)]$ (0.10 mmol) and $SnMe_3Ph$ (0.50 mmol) in 0.6 mL of $CDCl_3$ was placed in a 5-mm NMR tube. The progress of the reaction was periodically monitored by ^{31}P (and ^1H) NMR spectroscopy. After 2 days, 20% conversion to $[Pt(Ph)(\eta^3\text{-}C_3H_5)(PCy_3)]$ (**2d**) was observed. The structure was assigned by comparison of its phosphorus NMR parameters (^{31}P NMR (δ): 28.7, J_{P-Pt} = 3785 Hz) with those given for **2a–c**. This is supported by the appearance of new resonances in the allylic region of the ^1H NMR spectrum. The intensity of this ^{31}P signal decreased in the following weeks, and an increase for the compound *sym-trans*-$[Pt_2(Ph)_2(\mu\text{-}Cl)_2(PCy_3)_2]$ (**3c**), was observed ^{31}P NMR (δ): 18.4, J_{P-Pt} = 4758 Hz.

The Decomposition of Analytically Pure $[Pt(Ph)(\eta^3\text{-}C_3H_5)(P(4\text{-}FC_6H_4)_3)]$ in $CDCl_3$ Solution. $[Pt(Ph)(\eta^3\text{-}C_3H_5)(P(4\text{-}FC_6H_4)_3)]$ (35 mg) was dissolved in $CDCl_3$ (0.4 mL) in an NMR tube under argon and then sealed. This solution darkens slowly with time, and after 2 months the following organometallic products are observed by ^{31}P NMR spectroscopy (data in Table III): (a) $[Pt(Ph)(\eta^3\text{-}C_3H_5)(P(4\text{-}FC_6H_4)_3]$, 65%; (b) $[PtCl(\eta^3\text{-}C_3H_5)(P(4\text{-}FC_6H_4)_3)]$, 12%; (c) $[PtCl(Ph)(P(4\text{-}FC_6H_4)_3)_2]$, 10%; and (d) $[PtCl(Ph)(P(4\text{-}FC_6H_4)_3)]_2$, 13%. The purely organic decomposition products are identified by ^1H and partly by ^{13}C NMR spectroscopy. They are particularly easily distinguished from the organometallic components by their much longer T_1 values. These are between 20 and 35 s for propene as compared to 1–2 s for the protons of the allyl group in $[Pt(Ph)(\eta^3\text{-}C_3H_5)\text{-}(P(4\text{-}FC_6H_4)_3)]$. The following products are identified as arising from decomposition.

1-Propene. ^1H NMR (δ): $H_{1(Z)}$, 5.02, ddq, $^2J_{H_{1(Z)}-H_{1(E)}}$ = 2.2, $^3J_{H_{1(Z)}-H_2}$ = 17.0, $^4J_{H_{1(Z)}-H_3}$ = 1.7 Hz; $H_{1(E)}$, 4.92, ddq, $^3J_{H_{1(E)}-H_2}$ = 10.0, $^4J_{H_{1(E)}-H_3}$ = 1.5 Hz; H_2, 5.82, ddq, $^3J_{H_2-H_3}$ = 6.5 Hz; H_3, 1.71, ddd. ^{13}C NMR (δ): C_3, 19.3, other resonances obscured.

Benzene. ^1H NMR (δ): 7.35, s.

Reaction of $[PtCl(\eta^3\text{-}C_3H_5)(PMePh_2)]$ with $SnMe_4$. To a solution of $[PtCl(\eta^3\text{-}C_3H_5)(PMePh_2)]$ (0.10 mmol) in $CDCl_3$ (0.6 mL) was added $SnMe_4$ (0.40 mmol). The mixture was kept in the dark for 2 weeks and then examined by ^1H NMR spectroscopy. On the basis of their ^1H NMR parameters, the following compounds were identified. **$[Pt(Me)(\eta^3\text{-}C_3H_5)(PMePh_2)]$ (6).** ^1H NMR (δ): allyl, H_1, 3.37 (dd), J_{15} = 7, J_{14} = 2 Hz; H_2, 2.02 (d), J_{25} = 13 Hz; H_3, obscured; H_4, 3.55 (ddt), J_{45} = 7, J_{34} = 2, J_{H-P} = 5 Hz; H_5, 4.50 (m). ***sym-cis/trans*-$[Pt(Me)_2(\mu\text{-}Cl)_2$-**

($PMePh_2$)$_2$] (7). ^{1}H NMR (δ): PMe, 2.00, 1.94, J_{H-P} = 11 Hz; PtMe, (A), 0.40 (d), J_{H-P} = 4, J_{H-Pt} = 75 Hz; (B), 0.50 (d), J_{H-P} = 3, J_{H-Pt} = 77 Hz. ***trans*-[PtCl(Me)($PMePh_2$)$_2$] (8).** ^{1}H NMR (δ): PMe, 2.18 (t); PtMe, −0.06 (t), J_{H-P} = 7, J_{H-Pt} = 81 Hz (Lit.[15] PMe, 2.22; PtMe, −0.02, J_{H-P} = 6.9, J_{H-Pt} = 80.8 Hz).

Preparation of Ph_4As[$PtCl_2(\eta^3$-$C_3H_5)$] (9). Ph_4AsCl (42 mg, 0.10 mmol) was added to a suspension of $[PtCl(allyl)]_4$ (27 mg, 0.025 mmol) in 10 mL of CH_2Cl_2, and the mixture was magnetically stirred for 15 h. A small amount of a white solid was removed by filtration, and the filtrate was concentrated to a volume of 2 mL under reduced pressure. Ether was then added carefully, and pale yellow needles formed that were separated from the mother liquor by decantation. The crystals were washed with ether and dried in air. Yield: 40 mg (58%). ^{1}H NMR (δ, $CDCl_3$): allyl, H_1 = H_4, 3.61 (d), J_{15} = 6.0, J_{H-Pt} = 32 Hz; H_2 = H_3, 1.76, J_{25} = 10.5, J_{H-Pt} = 78 Hz, H_5, 4.17 (tt), J_{H-Pt} = 86; $AsPh_4^+$, 7.68 (2 H), 7.85 (3 H). ^{1}H NMR (δ CD_2Cl_2): $AsPh_4^+$, H_o, 7.64; H_m, 7.79; H_p, 7.90. ^{13}C NMR (δ): Allyl, C_a = C_c, 42.4, {269}; C_b, 90.0; $AsPh_4^+$, C_α, 120.4; C_o, C_m, 133.0, 131.5; C_p, 134.9.

Preparation of Complexes [Pt(η^3-C_3H_5)(L)$_2$]BF_4 (L = P(4-FC_6H_4)$_3$, $PMePh_2$). [Pt(η^3-C_3H_5)(P(4-FC_6H_4)$_3$)$_2$]]BF_4 (10a). A solution of P(4-FC_6H_4)$_3$ (63 mg, 0.20 mmol) in CH_2Cl_2 (5 mL) was added to a suspension of $[PtCl(allyl)]_4$ (27 mg, 0.025 mmol) in CH_2Cl_2 (10 mL). This mixture was stirred for 2 h after which the solvent was removed in vacuo. The [Pt(C_3H_5)(P(4-FC_6H_4)$_3$)$_2$Cl] formed was redissolved in acetone (10 mL) and treated with $NaBF_4$ (33 mg, 0.30 mmol) for 12 h. After removal of the solvent in vacuo, the residue was extracted with CH_2Cl_2 (2 × 2 mL) and filtered. Addition of heptane gave a colorless powder. Yield: 78 mg (82%). ^{1}H NMR (δ): allyl, H_1 = H_4, 3.81, J_{15} = 6.3 Hz; H_2 = H_3, 3.23, J_{25} = 12.6, J_{H-P} = 8.1, J_{H-Pt} = 36 Hz; H_5, 5.72; (4-FC_6H_4), H_o, 7.34; H_m, 7.08. ^{31}P NMR (δ): 15.2, J_{P-Pt} = 4025 Hz.

[Pt(η^3-C_3H_5)($PMePh_2$)$_2$]BF_4 (10b). This complex was prepared analogously to **10a**. ^{1}H NMR (δ): allyl, H_1 = H_4, 3.85, J_{15} = 6.8 Hz; H_2 = H_3, 3.03, J_{25} = 12.7, J_{H-P} = 7.8, J_{P-Pt} = 40 Hz; H_5, 5.34, J_{P-Pt} = 54 Hz; PMe, 1.97, J_{H-P} = 9.5, J_{H-Pt} = 36.9 Hz; PPh_2, H_o, 7.40; H_m, 7.34; H_p, 7.27. ^{31}P NMR (δ): 0.0, J_{P-Pt} = 3949 Hz.

Results and Discussion

I. Synthesis and Reactivity. The starting materials [PtCl(η^3-C_3H_5)(L)] (L = PMe_2Ph, $PMePh_2$, P(4-FC_6H_4)$_3$, PCy_3, PPh_2(*sec*-$CH_2CHMeEt$)) were synthesized according to published methods[4,5] whereas the complex [PtCl(η^3-C_3H_5)(PMe_3)] was obtained from the dimeric *sym-trans*-[$Pt_2Cl_4(PMe_3)_2$] and allylmagnesium chloride in ether. They were fully characterized by multinuclear NMR methods (^{1}H, ^{13}C, ^{31}P, and ^{195}Pt) and by comparison with data in the literature.[4-7] These revealed, however, that although the *general* features of the ^{1}H NMR spectra agreed well with the literature reports, detailed assignment showed some discrepancies. We therefore reevaluated the spectroscopic properties of these compounds, including the parameters presented in Tables I and II, and we discuss them later in detail.

Addition of $SnMe_3Ph$ to solutions of these chloro complexes converted them to the corresponding phenyl derivatives according to eq 1. The newly formed platinum

$$\underset{\mathbf{1}}{[PtCl(\eta^3\text{-}C_3H_5)(L)]} + SnMe_3Ph \rightarrow \underset{\mathbf{2}}{[Pt(Ph)(\eta^3\text{-}C_3H_5)(L)]} + SnMe_3Cl \quad (1)$$

L = PMe_2Ph (**a**), $PMePh_2$ (**b**), P(4-FC_6H_4)$_3$ (**c**), PCy_3 (**d**)

complexes **2a–c** were isolated as colorless or off-white air-stable materials. They were fully characterized by elemental analyses and multinuclear (^{1}H, ^{13}C, ^{31}P, and ^{195}Pt) NMR spectroscopy. The ^{1}H NMR spectra exhibit a solution of the expected ABCDEX spin system consistent with a static η^3-allyl group in an asymmetric coordination mode. Evidence for a platinum–phenyl group σ-bond is derived from the observed coupling of the ortho and meta protons with the platinum-195 isotope of ~64 and ~11 Hz, respectively. Coordination of a single phosphine is apparent from the observation of a doublet in the ^{195}Pt NMR spectra. The NMR data of the new phenyl–allyl compounds are summarized in Table III, and a detailed discussion of the spectroscopic parameters is given later. The second reaction product is identified as $SnMe_3Cl$ from its ^{1}H NMR spectrum [δ 0.66 (J^{119}_{Sn-H} = 57.7 Hz)], identical with the values obtained from an authentic sample (Aldrich).

The course of the reaction can be monitored easily by ^{31}P and ^{1}H NMR spectroscopy. On following the progress of the reactions in CH_2Cl_2 solutions at room temperature with ^{31}P NMR spectroscopy, only signals due to the starting materials (**1a–c**) and the products [Pt(Ph)(η^3-C_3H_5)(L)] (**2a–c**) could be observed: no intermediates could be detected. Qualitatively, the rate of the reaction decreased with increasing size of the phosphine. We found that for L = PMe_2Ph the reaction is complete in approximately 2 h, whereas for L = PCy_3 even after 4 days, conversion of [PtCl(η^3-C_3H_5)(PCy_3)] to [Pt(Ph)(η^3-C_3H_5)(PCy_3)] was incomplete. Furthermore, it is evident that a consecutive reaction takes place with a similar rate. The ^{31}P NMR parameters of this secondary product [δ 18.5 (J_{Pt-P} = 4758 Hz)] suggested that the phosphine is positioned trans to a ligand with a weak trans influence such as an olefin or a bridging chloride. The latter possibility suggests a known class of compounds *sym-cis/trans*-[$Pt_2(Ph)_2(\mu\text{-}Cl)_2(PR_3)_2$]. The reported[8] ^{31}P NMR parameters for these compounds are similar. However, the other possibility cannot be fully excluded, and a complex of the type [Pt(Ph)(η^1-μ-C_3H_5)(L)]$_2$ has also to be considered. In the nickel triad, platinum shows the highest tendency to form σ-allyl-bonded species and complexes such as [PtCl(η^1-μ-C_3H_5)]$_4$,[9] [Pt(acac)(η^1-μ-C_3H_5)]$_2$,[10] and [PtCl(η^1-μ-C_3H_5)(py)]$_2$[7] with bridging allyl groups are well-known. In theory, it should be possible to distinguish between these two possibilities by ^{1}H NMR spectroscopy. However, the ^{1}H NMR spectrum is complicated by the mixture of **1d**, **2d**, the unknown platinum compound, and different organotin species, as well as the cyclohexyl protons which cover a good part of the spectrum. We therefore studied similar complexes with different phosphine ligands.

II. Secondary Products in the Reaction of [PtCl(η^3-C_3H_5)(L)] with $SnMe_3Ph$. Mixtures of [PtCl(η^3-C_3H_5)(L)] (L = PMe_2Ph, $PMePh_2$, or P(4-FC_6H_4)$_3$) and $SnMe_3Ph$ in $CDCl_3$ were sealed in NMR tubes and kept up to 2 months. ^{1}H NMR spectra were recorded periodically and showed complete conversion to [PtPh(η^3-C_3H_5)(L)] and $SnMe_3Cl$ in less than 1 day. The signals due to these compounds decreased slowly in the following month and the solutions darkened considerably during this period. New resonances due to PtPh and PMe groups and to a σ-allyl species were evident. The compounds *sym-trans/cis*-[$Pt_2(Ph)(\mu\text{-}Cl)_2)(L)_2$] (**3**) and *trans*-[PtCl(Ph)-$(L)_2$] (L = PMe_2Ph, $PMePh_2$) could be identified after the solutions were worked up. Table V gives the NMR characteristics of the secondary reaction products along with some reference data from the literature. The possible reaction pathways are summarized in Scheme I. Quali-

(8) Eaborn, G.; Odell, K. J.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1978**, 1288.
(9) Raper, G.; McDonald, W. S. *J. Chem. Soc., Chem. Commun.* **1970**, 655.
(10) McDonald, W. S.; Mann, B. E.; Raper, G.; Shaw, B. L.; Shaw, G. *J. Chem. Soc., Chem. Commun.* **1969**, 1254.

Table V. NMR Parameters of the Secondary Products

L	$\delta(H_o)$	J_{H_o-P}, Hz	J_{H_o-Pt}, Hz	$\delta(H_m)$	$\delta(H_p)$	δ(Me)	$J_{H_{Me}-P}$, Hz	$J_{H_{Me}-Pt}$, Hz	δ(P)	J_{P-Pt}, Hz
					sym-trans/cis-$[Pt_2(Ph)_2(\mu\text{-}Cl)_2(L)_2]$					
PMe_2Ph	7.15			6.83	6.75	1.47	11.2	*d*	−13.1	4880
	7.11					1.52	11.2	*d*	−13.3	4900
$PMePh_2$	7.11					1.54	10.8	*d*	0.0[a]	4940
	7.10					1.56	11.0	*d*	0.1[a]	4993
PCy_3									18.4	4758
									16.7[b]	4761
$P(4\text{-}C_6H_4F)_3$									8.9[e]	4737
					trans-$[PtCl(Ph)(L)_2]$					
PMe_2Ph	6.99		60			1.51	6.9	*d*	−5.0	2869
$PMePh_2$	6.81			6.44	6.51	1.73	7.2	32.6	8.7[b,c]	3010
$P(4\text{-}C_6H_4F)_3$									22.8	3174
					sym-trans/cis-$[Pt_2(Me)_2(\mu\text{-}Cl)_2(L)_2]$					
$PMePh_2$	0.40	4.0	75			2.00	11.0	*d*		
	0.50	3.0	77			1.94	11.0	*d*		
PMe_2Ph	0.39[f]	3.6	84			1.64	11.4	51		
					trans-$[PtCl(Me)(L)_2]$					
$PMePh_2$	−0.06	7.0	81	2.18						
	−0.02[g]	6.9	81			2.22			13.55	3028

[a] Reference 11. [b] Reference 12. [c] Reference 13. [d] Platinum satellites very broad due to chemical shift anisotropy contribution to the relaxation of ^{195}Pt.[16] [e] J_{P-F} = 2.3 Hz. [f] Reference 14. [g] Reference 15.

Table VI. Selected NMR Data[a] for Symmetrical Allyl Complexes $[Pt(\eta^3\text{-}C_3H_5)(L)_2]$

L	$J_{Pt-H_{anti}}$	$J_{Pt-H_{syn}}$	$J_{H_a-H_{anti}}$	$J_{H_a-H_{syn}}$	$J_{C_\alpha-Pt}$	$J_{C_\beta-Pt}$	ref
$^1/_2\eta^5\text{-}C_5H_5$	110	62	9	4	382	90	19
$^1/_2\eta^3\text{-}C_3H_5$	81	20.5	12	7	225.2	61.1	35
	78	27	10.5		226.0	54.5	35
Cl	78	32	10.5	6.0			this work
py	71	24	11	7	221	81	
PMe_2Ph	40	n.o.[a]	12.7	6.8			this work
$^1/_2COD$	33		14	7	144	45	36

[a] In J values in Hz.

tatively it was found that compound $[Pt(Ph)(\eta^3\text{-}C_3H_5)(P(4\text{-}FC_6H_4)_3)]$ is the most stable in the series and that the stability decreased in the order $P(4\text{-}FC_6H_4)_3 > PMePh_2 > PMe_2Ph$.

Scheme I

$$[Pt(Ph)(\eta^3\text{-}C_3H_5)(L)] \xrightarrow{i} {}^1/_2[Pt(Ph)(\mu\text{-}Cl)(L)]_2 + ii$$

$$[Pt(Ph)(\eta^1\text{-}C_3H_5)(L)_2] \xrightarrow{i} \textit{trans}\text{-}[PtCl(Ph)(L)_2] + ii$$

$$L = PMe_2Ph,\ PMePh_2,\ PCy_3$$

(i) $SnMe_3Cl/CDCl_3$;

(ii) unknown organotin compounds and propene

The chloride in the secondary reaction products may be derived from the solvent (chloroform) or trimethylchlorostannane; organometallic compounds are known to react with CCl_4 and $CHCl_3$ by an electron-transfer mechanism producing chloro complexes.[17] The electron-rich allyl complexes could be suitable electron donors for such processes.

The formation of bis(phosphine) complexes indicates the intermediate presence of free phosphine, probably as a result of decomposition (brownish solutions) to platinum. It is well-known that dimeric complexes of the type *sym-cis/trans*-$[Pt_2(R)_2(\mu\text{-}Cl)_2(PR_3)_2]$ react instantaneously with suitable ligands, L, such as phosphines to produce complexes of the general formula $[PtCl(R)(PR_3)(L)]$.[8,18] Formation of the compounds *trans*-$[PtCl(Ph)(L)_2]$ from the dimeric complexes **3** is therefore easily explained. However, in an alternative route, the σ-allyl complex **4** may be formed by the reaction of **2** with free phosphine. An analogous reaction using substituted phenyl compounds has been shown[3] to occur readily and to lead to the isolation of stable products of formula **4**. Indeed, in the ^1H NMR spectra we do observe the formation of an allylic group, but *without* the expected platinum-195 satellites that would be characteristic of a platinum-σ-allylic moiety.[3,19-21] Additionally, we find no ^{31}P resonance that would correspond to a complex of type **4**. On the basis of these observations, the allyl is therefore likely to be part of the unknown organotin compound.

In a separate experiment, analytically pure **2c** was dissolved in $CDCl_3$ and allowed to stand at room temperature for about 1 month. NMR spectroscopic analysis of the solution after this time showed that decomposition had occurred even in the absence of organotin compounds. The source of chloride in *sym-cis/trans*-[Pt(Cl)Ph(P(C_6H_4F-

(11) Cross, R. J.; McLennan, A. J. *J. Organomet. Chem.* **1983**, *255*, 133.
(12) Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* **1981**, *20*, 3607.
(13) Anderson, G. K.; Clark, H. C.; Davies, J. A. *Organometallics* **1982**, *1*, 64.
(14) Puddephatt, R. J.; Thompson, P. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1219.
(15) Bennett, M. A.; Chee, H.-k.; Robertson, G. B. *Inorg. Chem.* **1979**, *18*, 1061.
(16) Lalleman, J.; Soulie, J.; Chottard, J. *J. Chem. Soc., Chem. Commun.* **1980**, 436.
(17) Kochi, J. K. *Organometallic Mechanisms and Catalysts*; Academic: New York, 1978.
(18) Clark, H. C.; Ferguson, G.; Jain, V. K.; Parvez, M. *Inorg. Chem.* **1985**, *24*, 1478.
(19) Boad, N. M.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1220.
(20) Hene, B.; Jolly, P. W.; Salz, R.; Stobbe, S.; Wilke, G.; Benn, R.; Mynott, R.; Seevogel, K.; Goddard, R.; Kruer, C. *J. Organomet. Chem.* **1980**, *191*, 449.
(21) Carturan, G.; Scrivanti, A.; Belluco, U. *Inorg. Chim. Acta* **1977**, *21*, 103.

$4)_3]_2$ is therefore the solvent. Also, the fate of the allyl moiety was found to be *propene* by ^1H and ^{13}C NMR (see Experimental Section) and gas chromatographic analysis. Furthermore, since the propene formed is *not* deuteriated, then the proton acquired by the η^3-allyl group does not originate from the solvent. It is also likely that propene is formed in the presence of the organotin compounds.

III. The Reaction of [PtCl(η^3-C_3H_5)(PMePh$_2$)] with SnMe$_4$. From the reactions of [PtCl(η^3-C_3H_5)(L)] with $SnMe_3Ph$ above, we can conclude that (i) a phenyl group is transposed from tin to platinum much more easily than a methyl group, resulting in the exclusive formation of the phenyl derivatives (there is a stoichiometric excess of Me in $SnMe_3Ph$); (ii) longer reaction periods result in formation of secondary products of type **3** and **4**.

With these ideas in mind, it is not surprising to learn that the reaction of [PtCl(η^3-C_3H_5)(PMePh$_2$)] with $SnMe_4$ results in a complicated mixture of products. In the ^1H NMR spectrum we can clearly identify the resonances of the η^3-C_3H_5 group of the complex [Pt(Me)(η^3-C_3H_5)(PMePh$_2$)], which compare well with those of [Pt(η^1-C_3H_5)(η^3-C_3H_5)(PMe$_3$)].[20] The NMR data of the secondary reaction products are included in Table III. The structures *sym-trans/cis*-[Pt$_2$(Me)$_2$(μ-Cl)$_2$(PMePh$_2$)$_2$] and *trans*-[PtCl(Me)(PMePh$_2$)$_2$] were deduced from the spectroscopic properties and by comparison with data reported.

From the distribution of products in this reaction, it may be seen that the compounds $SnMe_4$ and $SnMe_3Ph$ react analogously with **1b** although at considerably different rates.

IV. Spectroscopic Properties. The heavy nuclei spectra of the compounds **1** and **2** analyze straightforwardly. The multinuclear NMR data are summarized in Tables II and III, and we begin the discussion by considering the platinum NMR spectra.

^{195}Pt NMR. The doublet multiplicity in the platinum NMR spectra show that a single phosphine is coordinated to platinum. The chemical shifts of both classes of compounds are found at rather high field and reflect a very high electron density at the metal, typical of η^3-allyl compounds.[22]

^{31}P NMR. Comparison of the coupling constants $J_{^{31}P-^{195}Pt}$ between [PtCl(η^3-C_3H_5)(L)] and [Pt(Ph)(η^3-C_3H_5)(L)] shows a decrease of ca. 500 Hz. This is in contrast to expectations based on the known cis influence of a phenyl group compared to a chloride. For example, substitution of a chloride in *trans*-[PtCl$_2$(PPh$_3$)$_2$] with phenyl to give *trans*-[PtCl(Ph)(PPh$_3$)$_2$][13] results in an increase of J_{P-Pt} from 2633 to 3152 Hz. Similarly, in the pair *trans*-[PtCl(SnCl$_3$)(PPh$_3$)$_2$][23] and *trans*-[PtPh(SnCl$_3$)(PPh$_3$)$_2$],[13] the coupling constants J_{P-Pt} are 2338 and 2837 Hz, respectively, and in the dimers *sym-trans*-[Pt$_2$Cl$_4$(PMe$_2$Ph)$_2$][24] and *sym-trans*-[Pt$_2$Cl$_2$(Ph)$_2$(PMe$_2$Ph)$_2$][11] are 3900 and 4940 Hz, respectively.

^{13}C NMR. The interpretation of the ^{13}C NMR spectra is straightforward. The central carbon (C_b) is identified as the resonance at lowest field in a symmetric η^3-allyl such as [PtCl$_2$(η^3-C_3H_5)]$^-$ based on relative intensity and multiplicity. No dramatic change in the chemical shift occurs for this carbon on substitution at platinum. The geometric dependence of $^2J_{P-C}$, being substantially larger for a mutual trans arrangement of the two spins, and the dependence

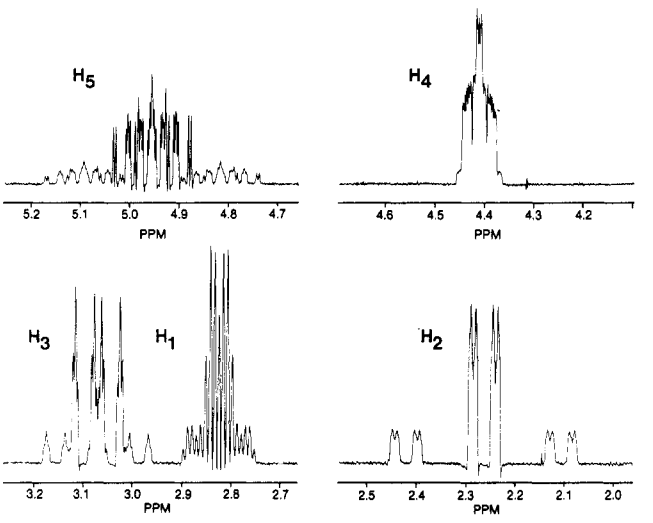
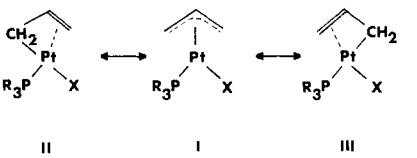


Figure 1. ^1H NMR. The allylic resonance of [PtCl(η^3-C_3H_5)(P(4-FC$_6$H$_4$)$_3$)].

Scheme I



of $^1J_{Pt-C}$ on the position of a ligand in the trans influence series allows unambiguous identification of the terminal carbons C_a and C_c. Examination of the ^{13}C NMR data in Table II shows that $^1J_{Pt-C}$ changes slightly with different phosphine ligands. Replacing the chloride with a ligand of strong trans influence such as an alkyl or aryl leads to a considerable increase, for example, this parameter measures 140 Hz in the complex [Pt(η^1-C_3H_5)(η^3-C_3H_5)(PMe$_3$)][2a] and 152.3 Hz in **2c** compared to 50 Hz in compounds **1**.

^{1}H NMR. (1) Complexes [PtCl(η^3-C_3H_5)(L)]. (a) Multiplet Fine Structure. Reconstruction or simulation of the ^1H NMR spectra of these known compounds from the data given in the literature[4-6] shows the terminal protons of the allyl as doublets (H_1 and H_2) or as doublets of doublets (H_3 and H_4) due to additional coupling with phosphorus. Inspection of a spectrum (Figure 1) reveals that this is only approximately the case for proton H_3 (dd). For all of the other resonances more complex multiplets are clearly observed. A more accurate first-order analysis of the fine structure of the bands is given on top of Table I. Helpful in the interpretation was a chemical shift correlated 2D NMR (COSY) spectrum. Off-diagonal peaks are expected for spins that are coupled through scalar coupling, and the upper half of Figure 2 shows the correlation network for [PtCl(η^3-C_3H_5)(PMe$_2$Ph)], reproduced schematically in Scheme II.

In addition to the expected and reported interaction with the central proton H_5, we find crosspeaks between the two syn protons and geminal interactions. The interpretation of the resonance attributed to H_3 excludes the observation of a resolved geminal coupling to H_4. However, it is not unusual that small unresolved couplings show up in COSY experiments; for example, *trans*-[PtH(SiH$_3$)(PCy$_3$)$_2$] shows no observable coupling between the hydride substituents on platinum and silicon,[26] but the COSY

(22) Benn, R. 68th Annual Conference Chem. Ins. Can., Kingston, 1985.
(23) Ruegger, H. Theses ETH Zurich, 1983.
(24) Kennedy, J. D.; McFarlane, W.; Puddephatt, R. J.; Thompson, P. J. *J. Chem. Soc., Dalton Trans.* **1976**, 874.
(25) Hartley, F. R. *The chemistry of platinum and palladium*; Applied Science: London, 1973.
(26) Ebsworth, E. A. V.; Marganian, V. M.; Reed, F. J. S.; Gould, R. O. *J. Chem. Soc., Dalton Trans.* **1978**, 1167.

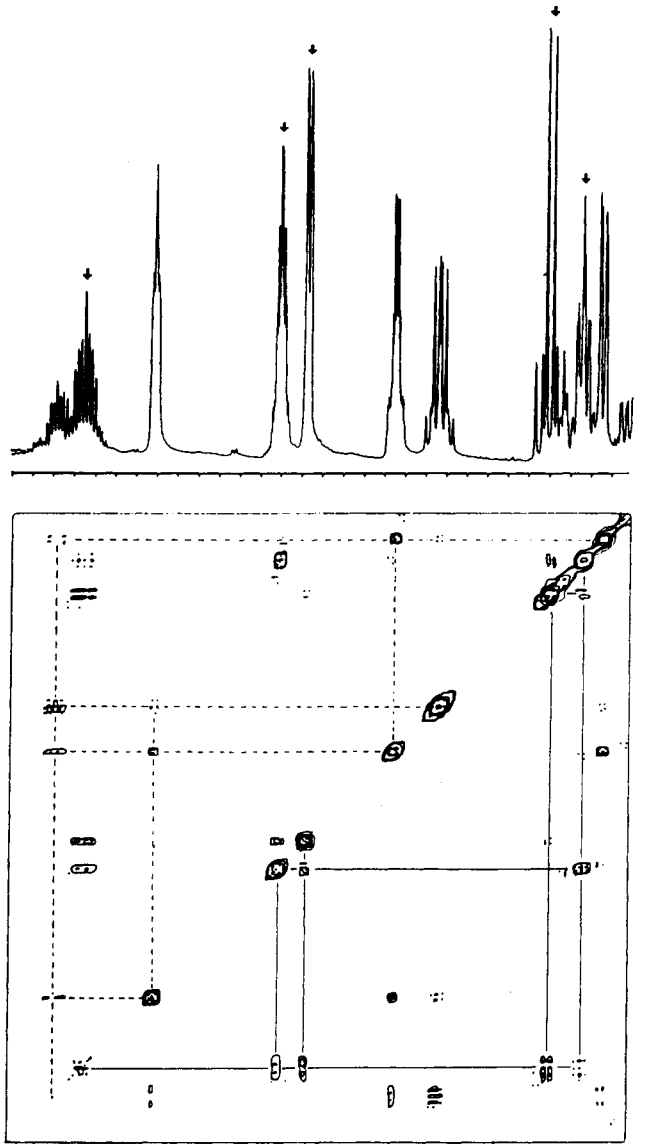


Figure 2. Allylic part of the chemical shift correlated 2D ^{1}H NMR spectrum at half reaction in [PtCl(η^3-C_3H_5)(PMe_2Ph)] + $SnMe^3Ph$ → [Pt(Ph)(η^3-C_3H_5)(PMe_2Ph)] + $SnMe_3Cl$. The upper half shows the correlations for the starting material and the lower half of the diagonal those for the product (↓).

spectrum exhibits the expected crosspeak.[27] In contrast to H_3, the other antiproton, H_2 shows an additional splitting of ~2 Hz, not previously reported. This coupling constant may be assigned either to the geminal interaction with H_1 or alternatively to heteronuclear coupling to phosphorus in the cis position. The following arguments and experiments show it to be the homonuclear coupling: (i) The resonance assigned to H_1 (observed dq) demands coupling to four spins (to H_5, H_4, and H_2 according to Scheme II and ^{31}P). (ii) Homodecoupling at the frequency of H_1 led to the collapse of the small coupling. (iii) In the 2D NMR experiment JRES homonuclear couplings evolve in the F1 domain, whereas chemical shifts and heteronuclear couplings are found from projections on to the *F*2 axis. A cross-section taken at the frequency of H_2 showed the dd multiplicity of two homonuclear couplings. It is of interest to note that in contrast to the antiprotons, both of the syn protons show a resolved coupling to phosphorus. This was previously unnoticed but follows directly from the analysis of the multiplet structure. To our knowledge the observation of a cis coupling between a terminal allyl hydrogen and phosphorus is unique. We feel that this is the result of a combination of two factors: (i) the asymmetric η^3-allyl structure resembling partly resonance form II (see later) (it is well-known[28] that in platinum alkyl compounds $^3J_{H-P}$ is almost geometry independent, having $^3J_{cis} \simeq 3J_{trans}$]; (ii) a particular conformation with respect to H_1 and P. The dependence of $^3J_{H-X}$ on the dihedral angle is well-established.[29] It is also noteworthy that a similar conformational dependence must be responsible for the difference in $^2J_{Pt-H}$ between the syn and anti protons at the same carbon atom. Interestingly, we cannot observe the cis coupling constant $^3J_{H_1-P}$ in the compounds [PtCl(η^3-C_3H_4R)(PCy_3)] (R = Me, **1g**, and R = Ph, **1h**), having the substituent R in the position 4 of the allylic moiety. This demonstrates that the effects leading to observation of this parameter are rather subtle.

(b) Assignment of Allylic Protons. The *general* features of the ^{1}H NMR spectra of the complexes [PtCl(η^3-C_3H_5)(L)] are in agreement with those previously reported. However, our assignment of the allylic protons of these compounds differ from some of these reports,[4,5] but are in accord with others.[6] We find that careful assignment of the allylic resonances is essential because dynamic processes involving the allyl group are very common in organometallic chemistry. The investigation and interpretation of the mechanism of such processes, which interchange individual protons of the allylic group, depend largely upon a proper assignment. Therefore, we will outline the principles on which our interpretations are based.

(i) **Coupling Constants—Homonuclear Coupling.** The central proton of an π-allyl interacts with the anti proton to exhibit a greater coupling constant than with a syn proton.

Platinum Coupling. For the two protons in the terminal position at the same carbon atom it is the one in the anti position that shows the greater coupling constant to platinum. The magnitude of this coupling depends on the nature of the trans ligand and is characteristic of the trans influence series.

Phosphorus Coupling. Coupling constants between two spins in a mutual trans arrangement are greater than the corresponding cis coupling constants.

(ii) Chemical Shifts. The anti protons are generally at higher field than the syn protons.

Most of these principles are common knowledge and are rarely a source of misinterpretation. However, the last point of (i) requires some comment since it resulted in a different assignment by Carturan et al. It is well-documented that $^2J_{^{31}P-X_{trans}} \gg {}^2J_{^{31}P-X_{cis}}$ (X = ^{1}H,[30] ^{13}C,[31] ^{15}N,[32] ^{29}Si,[27] ^{31}P,[33] ^{119}Sn,[37] etc.). For example, in the cationic

(27) Clark, H. C.; Hampden-Smith, M. J.; Ruegger, H., unpublished results.

(28) Clark, H. C.; Ruddick, J. D. *Inorg. Chem.* **1970**, *9*, 1226.
(29) Karpug, M. *J. Am. Chem. Soc.* **1963**, *85*, 2876.
(30) Chisholm, M. H.; Clark, H. C.; Manzer, L. E.; Stothers, J. B.; Ward, J. E. H. *J. Am. Chem. Soc.* **1973**, *95*, 8574.
(31) Motschi, H.; Pregosin, P. S. *Inorg. Chim. Acta* **1980**, *24*, 141.
(32) Koie, Y.; Shinoda, S.; Saito, Y. *Inorg. Nucl. Chem. Lett.* **1981**, *17*, 147.
(33) Ostoja Starzewski, K. A. H.; Pregosin, P. S.; Ruegger, H. *Helv. Chim. Acta* **1982**, *65*, 785.
(34) Hene, B.; Jolly, P. W.; Salz, R.; Wilke, G.; Benn, R.; Hoffmann, E. G.; Mynott, R.; Schroth, G.; Seevogel, K.; Sekutowski, J. C.; Kruger, C. *J. Organomet. Chem.* **1980**, *191*, 425.
(35) Boag, N. M.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1200.
(36) Chisholm, M. H.; Clark, H. C.; Manzer, L. E.; Stothers, J. B. *J. Chem. Soc., Chem. Commun.* **1971**, 1627.
(37) Faller, J. W.; Blankership, C.; Whitmore, B.; Sera, S. *Inorg. Chem.* **1985**, *24*, 4483.

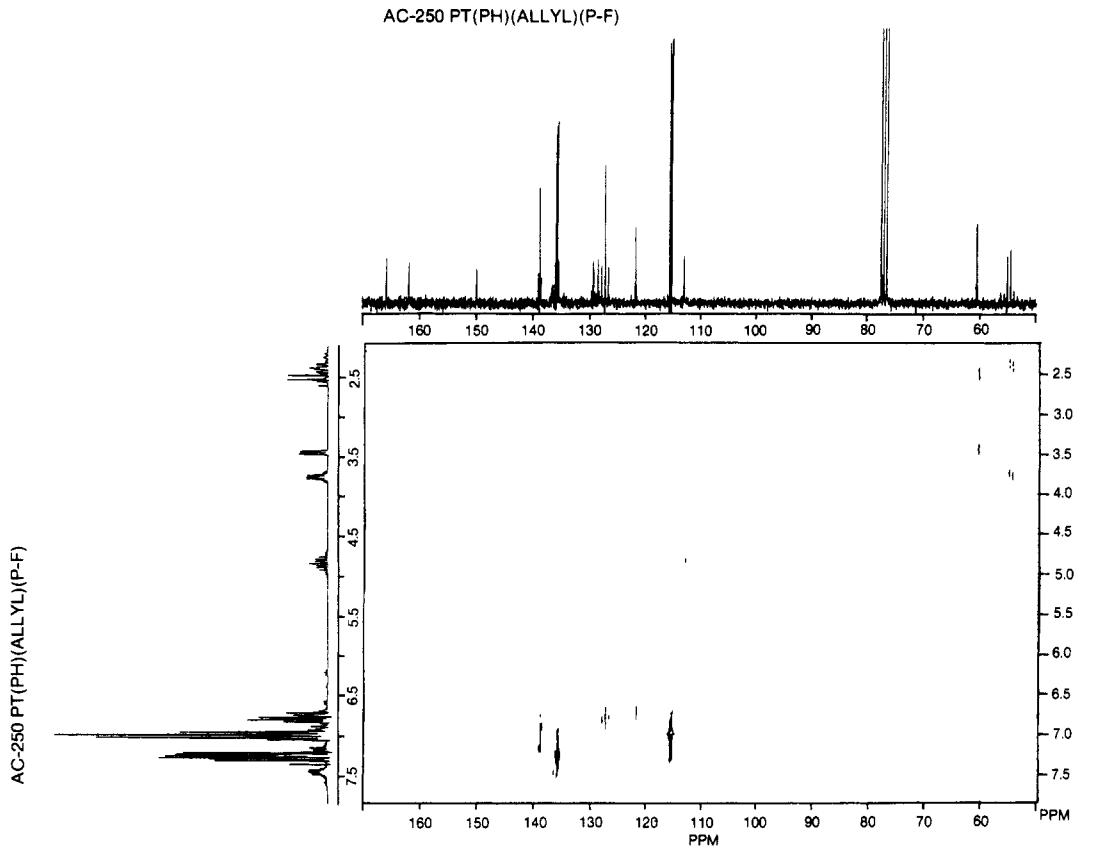


Figure 3. Heteronuclear shift correlated 2D (^{1}H–^{13}C) NMR spectrum of [Pt(Ph)(η^3-C_3H_5)(P(4-FC_6H_4)$_3$)].

hydride complex $[PtH(PEt_3)_3]^+$, $^2J_{^{31}P-^1H_{trans}}$ is found to be 159 Hz, whereas the corresponding cis coupling constant is considerably smaller (16 Hz).[30] The situation for the three-bond coupling constants $^3J_{^{31}P-^1H}$, however, is not so clear. In $[Pt(CH_3)(PMe_2Ph)_3]^+$, for example, the cis and trans coupling constants are of the same magnitude.[23]

Returning to the system under discussion [PtCl(η^3-C_3H_5)(L)], we (and others) find phosphorus couplings of ~9 and ~0 Hz for the two anti protons, respectively, making their assignment reasonably straightforward. However, for the syn protons, phosphorus interaction has been reported for one of them only. Careful examination of the multiplets revealed a phosphorus splitting for the second syn proton as well, the values of these parameters being ~5 and ~23 Hz, respectively. In such a case, an assignment based on the assumption of $J_{trans} > J_{cis}$ is not necessarily secure, and additional confirmation certainly is desirable. From the positions of chloride and phosphine in the trans influence series we expect smaller $^2J_{^{195}Pt-^1H}$ trans to phosphorus. We find this coupling to measure between ~0 and ~20 Hz. Since strong cross relaxation is expected between the protons of a geminal pair of hydrogens, then having assigned the anti protons properly, we are able to find the corresponding syn protons. A NOESY (2D NMR) spectrum of [PtCl(η^3-C_3H_5)(PCy_3)] shows the expected off-diagonal peaks due to the cross relaxation. However, care has to be taken with this experiment because slow chemical exchange (slow on the NMR time scale, well below coalescence temperature) produces similar crosspeaks representing the exchange network rather than cross relaxation.

To circumvent all these problems we recorded the heteronuclear chemical shift-correlated (^{13}C, ^{1}H) 2D NMR spectrum of [PtCl(η^3-C_3H_5)(PCy_3)]. The ^{13}C NMR spectrum analyses straightforwardly (see above), and the directly bonded protons are found unambigously from the crosspeaks.

With all these experiments we feel that the assignment of the five allylic protons is secured and that the principles (i) and (ii) can be applied to simple 1D NMR spectra leading to a correct assignment.

(2) Complexes [Pt(Ph)(η^3-C_3H_5)(L)]. The NMR parameters of the phenyl derivatives are summarized in Table III. A first-order analysis of the fine structure in the multiplets is given in the top line of this table. The principles described above and similar experiments were employed to assign the resonances of the five allylic protons. The lower part of Figure 2 shows the chemical shift correlated (COSY) 2D NMR spectrum of [Pt(Ph)(η^3-C_3H_5)(PMe_2Ph)], and Figure 3 shows the heteronuclear chemical shift correlated (^{13}C, ^{1}H) 2D NMR spectrum of [PtPh(η^3-C_3H_5)(P(4-FC_6H_4)$_3$)].

From the parameters listed in Table III, we note in particular that (a) the coupling constants J_{Pt-H} are smaller than in the complexes of type 1, in accord with the presence of two ligands with a stronger trans influence, (b) the cis coupling between phosphorus and the syn proton H_1 is not observed, and (c) contrary to the situation observed for complexes 1, the resolved geminal coupling in these phenyl compounds is found trans to the phosphine.

Spectroscopic Evidence for the Nature of Asymmetric Bonding in Allylic Systems. In a square-planar η^3-allyl complex substituted with two additional ligands of different electronic properties some asymmetry in the bonding of the allylic group may be induced. We have therefore considered the influence of asymmetric bonding modes of the η^3-allyl group in the platinum(II) complex. Two additional resonance structures (II and III) may contribute to the overall description (I). Depending on the trans influence of the ligand X, the relative contributions of II or III to I may vary. For X = Cl the bonding situation resembles II, leaving the phosphine trans to an "olefin" with a trans influence known to be weak.[25] Substitution of chloride with phenyl (X = Ph) makes contributions to

the resonance form III more important. In this case, an "σ-alkyl" is trans to the phosphine. Alkyl groups exert a strong trans influence and, as a result, a small phosphorus–platinum coupling is observed. This kind of asymmetric η^3-allyl bonding was demonstrated spectroscopically and crystallographically for $[PtCl(\eta^3\text{-}C_3H_5)P^tBu_3)]$,[6] and additional arguments supporting the idea are presented in the discussion of the ^1H NMR parameters. At one extreme, a resonance structure of such an asymmetric allyl could be formulated as a σ-alkyl–π-olefin complex (A). The expected spectroscopic properties for such A-type compounds will be compared with the experimental data of (a) complexes 1 and 2 and (b) symmetrical η^3-allyl complexes.

Coupling Constants $^2J_{Pt\text{-}H_2}$ and $^2J_{Pt\text{-}H_3}$. Previously, it has been argued[6] that the relatively high value of $^2J_{Pt\text{-}H_2}$ in compounds 1 (~80 Hz) especially when compared with $^2J_{Pt\text{-}H_3}$ supports a contribution of form A to the nature of allyl bonding. However, comparing $^2J_{Pt\text{-}H}$ in olefin complexes, which measure typically 60–70 Hz (64.5 Hz in $[PtCl_3(C_2H_4)]^-$) with alkyl compounds where this parameter lies between 50 and 80 Hz depending on the trans ligand,[37] shows that this coupling constant is not sufficiently discriminating between different platinum–carbon bonding modes. Indeed, Table IV shows that in symmetrically substituted η^3-allyl compounds $^2J_{Pt\text{-}H}$ can considerably exceed the typical values of σ-alkyl groups.

Coupling Constants $^3J_{H_5\text{-}H_2}$ and $^3J_{H_5\text{-}H_3}$. Trans coupling constants in olefins are usually larger than vicinal couplings in aliphatic compounds. Therefore, we expect to find $^3J_{H_5\text{-}H_3} > {}^3J_{H_5\text{-}H_2}$ for A. This is what we observe for compounds 1. However, the difference between the two values cannot be fully accounted for by the bonding asymmetry of the allyl group since substitution of the trans ligand by one of higher trans influence generally leads to an increase in the value of this parameter.

Geminal Couplings. Geminal couplings in olefins are usually much smaller (<4 Hz) than in aliphatic compounds (e.g. 11–14 Hz in cyclohexyl compounds). In keeping with this we expect $^2J_{H_1\text{-}H_2} > {}^2J_{H_3\text{-}H_4}$, exactly what is found for complexes 1. Interestingly, in compounds 2 the opposite is observed. The observation is consistent with a higher contribution from resonance form III to the structure of compounds 2 and the fact that the phenyl group is known to have a higher *trans* influence than phosphine ligands.

^{13}C NMR Data. As we have noted above, changing phosphine ligands in compounds 1 results only in a small change in the ^{13}C NMR chemical shifts and the $^1J_{C\text{-}Pt}$ coupling constants in the allyl moiety. Replacing the chloride ligand of **1c** with phenyl, **2c**, results in reversal of the order of carbon chemical shifts of C_a and C_c (48.3 and 69.4 ppm, respectively, for **1c** compared to 60.5 and 54.3 ppm, respectively, for **2c**). Since the observed asymmetry in chemical shifts may result from charge effects from the other substituents in these compounds, any conclusions drawn on the basis of the shift data alone are ambiguous. However, the $J_{C\text{-}Pt}$ coupling constants reinforce the trends seen in the ^{13}C chemical shift data. So for example, $J_{C\text{-}Pt}$ for C_a of **1c** is 249.6 Hz (trans to Cl) whereas for **2c** it is 18 Hz (trans to Ph) and for C_c of **1c** is 40 Hz but for **2c** is 152.3 Hz.

A similar value for $^1J_{C\text{-}Pt}$ (140 Hz) was observed in the complex $[Pt(\eta^1\text{-}C_3H_5)(\eta^3\text{-}C_3H_5)(PMe_3)]$.[2a]

Recently, the X-ray structural analysis of $[(\eta^3\text{-}2\text{-methylallyl})PdCl(PPh_3)]$ demonstrated that the two carbon–carbon distances in the allyl ligand were similar within the limits of the experiment (3σ). However, the Pd–C_3 distance (2.120 (5) Å) trans to Cl was significantly shorter than Pd–C_1 (2.211 (6) (Å), trans to PPh_3, consistent with the established order of trans influence for these ligands.

Conclusion

The complexes $[PtX(\eta^3\text{-allyl})(PR_3)]$ (X = Cl, Ph) have been prepared and studied in solution. The complexes, X = Ph, were prepared from their chloride analogues by simple metathesis using $SnMe_3Ph$. These complexes were shown to be reasonably stable in solution and have been characterized by a variety of multinuclear NMR spectroscopic methods. Particular attention was paid to the accurate assignment of the allyl proton resonances of these complexes, and confirmatory evidence for the assignments was obtained from a variety of 2D NMR techniques. Although the allyl group is normally considered as a η^3-moiety, the spectroscopic data obtained in this work are consistent with significant contributions from asymmetric η^1–η^2-allyl coordination (see Scheme II). The geometry of this mode of coordination is markedly dependent on the nature of ligands X, preferring η^1-bonding of the allyl group trans to X for ligands, X of low trans influence, and η^2-bonding of the allyl group trans to X ligands of high trans influence. Some of the spectroscopic parameters discussed above are affected by the geometric orientation of the spins involved, and a detailed study of their dependence on the particular conformational changes an allyl group may undergo would be desirable.

Registry No. **1a**, 71035-52-4; **1b**, 71035-51-3; **1c**, 115603-54-8; **1d**, 71035-50-2; **1e**, 115603-55-9; **1f**, 71035-53-5; **1g**, 115603-56-0; **1h**, 75811-55-1; **2a**, 115603-57-1; **2b**, 115603-58-2; **2c**, 115603-59-3; **3a** (trans), 115603-60-6; **3a** (cis), 115728-61-5; **3b** (trans), 89195-35-7; **3b** (cis), 89194-94-5; **3** (*trans*), 78064-15-0; **5a**, 27081-34-1; **5b**, 60772-01-2; **6**, 115603-62-8; **7** (cis), 115603-63-9; **7** (trans), 115728-62-6; **8**, 24833-61-2; **9**, 115603-65-1; **10a**, 115603-67-3; **10b**, 36607-45-1; *sym-trans*-$[Pt_2Cl_4(PMe_3)_2]$, 17522-93-9; $SnMe_3Ph$, 934-56-5; *trans*-$[PtCl(Ph)(P(4\text{-}FC_6H_4)_3)_2]$, 115603-61-7; *trans*-$[PtCl(Ph)(P(4\text{-}FC_6H_4)_3)]_2$, 115650-87-8; $SnMe_4$, 594-27-4; Ph_4AsCl, 60805-89-2; $[PtCl(allyl)]_4$, 32216-28-7; $P(4\text{-}FC_6H_4)_3$, 18437-78-0; $PMePh_2$, 1486-28-8; ^{195}Pt, 14191-88-9; allylmagnesium chloride, 2622-05-1.