Table I. Aryl Esters of Dithiocarbamic Acids 3

entry	compd.	X^- in 2	solvent, 70 °C	reactn time, h	yield,[a,b] this work	yield,[a,b] lit.	mp, °C	lit. mp, °C	IR (KBr), cm^{-1}	^1H NMR ($CDCl_3$), ppm
1	**3a**	Cl^-	*t*-BuOH	5	86	32,[6] 26[7]	93–94	94–95[6]	1508, 1385, 1261, 754, 689	3.54 (s, 6 H), 7.52 (s, 2 H)
2	**3a**	OAc^-	*t*-BuOH	4	74					
3	**3a**	Cl^-	*t*-BuOH	4	72					
4	**3a**	Br^-	*t*-BuOH	4	46					
5	**3a**	I^-	*t*-BuOH	4	17					
6	**3b**	Cl^-	*t*-BuOH	10	56	17[6]	45–46	46[6]	1495, 1423, 1275, 750, 689	1.34 (m, 6 H), 3.95 (m, 4 H), 7.50 (s, 5 H)
7	**3c**	Cl^-	*t*-BuOH	5	81	16[6]	116–117	116–117[6]	1430, 1232, 749, 685	1.74 (s, 6 H), 3.80–4.40 (br, 4 H), 7.51 (s, 5 H)
8	**3d**	Cl^-	*t*-BuOH	5	84		68–69		1478, 1399, 1254, 750, 740, 696, 690	3.40 (s, 3 H), 5.22 (s, 2 H), 7.37 (s, 5 H), 7.52 (s, 5 H)
9	**3e**	Cl^-	*t*-BuOH	4	57		148–150	104–106[14]	3220, 1558, 1348, 765, 756, 698, 689	7.20–7.33 (m, 10 H), 8.18 (s, 1 H)
10	**3f**	I^-	*t*-BuOH	10	70	26[6]	111–112	111–112[6]	1511, 1380, 1255, 810	2.40 (s, 3 H), 3.53 (s, 6 H), 7.32 (m, 4 H)
11	**3g**	Br^-	*t*-BuOH	15	63	30[6]	75–76	77–78[6]	1492, 1275, 811	1.33 (m, 6 H), 2.43 (s, 3 H), 3.95 (m, 4 H), 7.34 (m, 4 H)
12	**3h**	I^-	*t*-BuOH	12	66	36[6]	118–119	118–119[6]	1485, 1248, 812	1.74 (s, 6 H), 2.42 (s, 3 H), 4.00–4.30 (br, 4 H), 7.32 (m, 4 H)
13	**3i**	Br^-	*t*-BuOH	18	71		65–66		1490, 1399, 1250, 806, 746, 701	2.38 (s, 3 H), 3.38 (s, 3 H), 5.22 (d, 2 H), 7.36 (m, 9 H)
14	**3j**	I^-	*t*-BuOH	18	76		92–93	105–108[15]	1504, 1385, 1258, 832	3.54 (s, 6 H), 3.87 (s, 3 H), 7.20 (q, 4 H)
15	**3k**	I^-	*t*-BuOH	18	68		102–103		1504, 1255, 832	1.73 (s, 6 H), 3.87 (s, 3 H), 3.90–4.30 (br, 4 H), 7.20 (q, 4 H)
16	**3l**	Cl^-	CH_3CN	13	58		101–103	102–103[4]	1511, 1380, 1242, 850	3.56 (s, 6 H), 7.30 (m, 4 H)
17	**3m**	Cl^-	CH_3CN	13	63		90–92	94–96[15]	1476, 1244, 1009, 820, 750	1.73 (s, 6 H), 4.00–4.30 (br, 4 H), 7.30 (m, 4 H)
18	**3n**	Cl^-	CH_3CN	3	63		139–141		1540, 1526, 1389, 1358, 1254, 809 732	3.50 (s, 6 H), 7.70–8.30 (m, 4 H)
19	**3o**	Cl^-	CH_3CN	4	56		150–152		3225, 1560, 1535, 1351, 1248, 810, 752, 730, 698	7.33 (m, 9 H), 8.13 (s, 1 H)

[a] Isolated yield of analytically pure product. [b] Satisfactory microanalyses obtained: C, ±0.29; H, ±0.13; N, ±0.03.

Experimental Section

All melting points are uncorrected. NMR spectra were recorded at 60 MHz on a Varian EM-360 spectrometer with Me_4Si in $CDCl_3$ as the internal standard. IR spectra were recorded on a PE-683 spectrometer.

General Procedure for the Preparation of 3. To a stirred solution of 1 (5 mmol) in 2-methyl-2-propanol or acetonitrile (15 mL) at 70 °C was slowly added 5 mmol of the appropriate iodonium salt 2.[11,13] Stirring was continued until the inorganic salts precipitated and the reaction mixture was clear (Table I). After removal of the solvent, 10 mL of water was added, and the resulting mixture was extracted with methylene chloride (3 × 10 mL). The combined organic layers were washed with water (10 mL) and dried over anhydrous $MgSO_4$. After removal of the solvent, hexane was added to the residue, and the product was allowed to crystallize in a refrigerator overnight. The crude product was collected and recrystallized from benzene/hexane. Products were identified by comparison of experimental values with literature values and by ^1H NMR and IR spectroscopy (Table I).

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Activation of Platinum Catalysts with Oxygen To Enhance Hydrosilylation of Unactivated Alkyl-, Dialkyl-, and Trialkylsilanes with 1-Alkenes. Synthesis of Tetraalkylsilanes

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Introduction

We were interested in the one-step synthesis of tetraalkylsilanes in the C_{25}–C_{32} range via hydrosilylation of 1-alkenes with alkylsilanes. The reaction of methylsilane

Table I. Relative Reactivities of Trialkylsilanes in Hydrosilylation of 1-Octene[a]

	$H_2PtCl_6{\cdot}6H_2O$[b]	$RhCl(PPh_3)_3$[c]
$CH_3Si(C_8H_{17})_2H$	2.9	3.9
Et_3SiH	1.0[d]	1.0[d]
$(C_8H_{17})_3SiH$	0.8	0.7

[a] Reactivity per mol, based on R_4Si formed; values rounded off to the nearest tenth. [b] Feed: Et_3SiH (5.9 mmol), $CH_3Si(C_8H_{17})_2H$ (4.9 mmol), $(C_8H_{17})_3SiH$ (4.8 mmol), 1-octene (8.9 mmol), n-$C_{16}H_{34}$ (2.5 mmol, internal standard), $H_2PtCl_6{\cdot}6H_2O$ (1×10^{-2} mmol), toluene (10 mL). Conditions: 85 °C, 15 min, under N_2; R^3SiH conversion ~14%. [c] Feed: same as above; $RhCl(PPh_3)_3$ (2.2×10^{-3} mmol). Conditions: 100 °C, 20 min, under N_2; R_3SiH conversion, ~40%. [d] Assumed standard.

with 1-octene, for example, was expected to proceed in steps to yield methyltrioctylsilane (eq 4).

$$CH_3SiH_3 + C_6H_{13}CH{=}CH_2 \xrightarrow{k_1} CH_3Si(C_8H_{17})H_2 \tag{1}$$

$$CH_3Si(C_8H_{17})H_2 + C_6H_{13}CH{=}CH_2 \xrightarrow{k_2} CH_3Si(C_8H_{17})_2H \tag{2}$$

$$CH_3Si(C_8H_{17})_2H + C_6H_{13}CH{=}CH_2 \xrightarrow{k_3} CH_3Si(C_8H_{17})_3 \tag{3}$$

$$CH_3SiH_3 + 3C_6H_{13}CH{=}CH_2 \rightarrow CH_3Si(C_8H_{17})_3 \tag{4}$$

A search of the literature showed that much data was available on the reaction of trialkylsilanes, usually trimethyl- or triethylsilanes, with 1-alkenes (eq 3)[1] and little on the reaction of dialkylsilanes (eq 2).[1,2] Less information was available on the reaction of alkylsilanes with 1-alkenes (eq 1, 4),[1] although this reaction is potentially of commercial interest. Speier et al.[3] reacted n-amylsilane with 1-octene under free radical conditions and obtained amyloctylsilane (60%). Koroleva and Reikhsfel'd[4] studied the kinetics of chloroplatinic acid catalyzed addition of alkyl- and arylsilanes to various alkenes. The reactivity sequence followed the order $ClPhSiH_3 > PhSiH_3 > C_6H_{11}SiH_3 > n\text{-}BuSiH_3 > i\text{-}AmSiH_3$ and that of alkenes $MePhCH{=}CH_2 > PhCH{=}CH_2 > ClPhCH{=}CH_2 > Me_3CCH{=}CH_2 > n\text{-}BuCH{=}CH_2$. Only in the case of (chlorophenyl)silane and phenylsilane did addition to 1-hexene or 3,3-dimethyl-1-butene occur at all three Si–H bonds. In all other reactions the additions were limited to only two stages. In the reaction of n-butylsilane with 1-hexene, the relative ratio of rate constants k_1/k_2 was 47/1, and that of isopentylsilane with 1-hexene was 10/1 at 180 °C. The relative magnitude of rate constants $k_1 > k_2 \gg k_3$ was in line with the expected steric hindrance. While it was reasonable to explain the failure of arylsilanes to react completely with styrenes on the basis of steric hindrance, the lack of reactivity of alkylsilanes with 1-alkenes cannot be explained on this basis since trialkylsilanes are known to readily add to 1-alkenes.[1]

In this paper, we report on the reaction of n-hexylsilane, a representative of alkylsilanes, with 1-alkenes to form tetraalkylsilanes selectively by using commercial platinum catalysts.

Results and Discussion

Relative Reactivities. The relative reactivities of methyldioctylsilane, triethylsilane, and trioctylsilane toward 1-octene were determined by a competitive procedure in the presence of chloroplatinic acid, and compared to those obtained with Wilkinson's catalyst (Table I). All three trialkylsilanes reacted smoothly with 1-octene with the range of reactiviites being less than five; thus, steric hindrance per se was not the dominant factor controlling the course of reaction. Other reasons must be responsible for the failure of alkylsilanes to react completely with 1-alkenes in the reported paper.[4] One possible reason is deactivation of the catalyst to metallic form.[5] The order of reactivities with platinum or rhodium catalysts followed the sequence $MeSi(C_8H_{17})_2H > Et_3SiH \sim (C_8H_{17})_3SiH$.

Reaction of Alkylsilanes ($RSiH_3$). The addition of n-hexylsilane to 1-alkenes was studied by using platinum catalysts (Table II).[6] For example, reaction of hexylsilane with 1-octene gave hexyloctylsilane as the dominant product, but the reaction could not be taken much above 50% silane conversion. Minor products were identified as hexyldioctylsilane and n-octane from a competing hydrogenation reaction. Addition of an activated silane, methyldichlorosilane, to the product mixture, which readily reacts with 1-octene under identical conditions, gave no further reaction. The catalyst was completely inactive.

It was discovered by chance that addition of fresh catalyst to a reaction mixture which was left standing exposed to air overnight (20 °C) led to formation of tetraalkylsilane upon heating. Further investigation showed that oxygen in air had a drastic effect on the course of reaction. Activation by oxygen has been reported for rhodium[7-9] and ruthenium complexes,[10] but the results with platinum are not very apparent. Some oxygen is required to effect hydrogenation of alkenes and aromatics with platinum,[11] a reaction often compared to hydrosilylation,[5] since no hydrogenation occurs in absolutely oxygen-free atmosphere. Green et al.[12] reacted triethylsilane with 1-hexene in the presence of chloroplatinic acid and air, but when their reaction mixture turned brown, a phenomenon usually associated with the formation of colloidal dispersions of Pt(0),[1] the use of air was discontinued. The reaction of triethoxysilane with 1-olefins in the presence of chloroplatinic acid apparently required oxygen as a cocatalyst,[13] but this effect seems never to have been discussed in detail in the literature.

When the oxygen content in our work was low, little hydrosilylation occurred. In the case of Pt/C, for example, the small extent of reaction could be attributed to the oxide or superoxide impurities on the surface due to localized oxidations. When oxygen atoms in the catalyst were consumed in the formation of siloxanes or water, the catalyst lost its hydrosilylation activity. Recently, Benkeser and Yeh[14] studied the exchange of tetraalkylsilane in the presence of chloroplatinic acid and concluded that the active catalyst was the Pt(II) species which when reduced to Pt(0) became inactive as a catalyst for the exchange reaction. The use of PtO_2 in present work led to a rapid hydrosilylation, but as the platinum was reduced to metallic form, the hydrosilylation rate diminished, and isomerization of the alkene increased.[12]

Finally, saturation of spent catalyst with air prior to heating (~2 min), led to a drastic enhancement of hydrosilylation activity. The amount of oxygen needed to achieve the desired effect is believed to be in the catalytic range, sufficient to activate the

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Table II. Hydrosilylation of 1-Alkenes with *n*-Hexylsilane Using Platinum Catalysts[a]

			product composition, % (GLC)				
temp, °C (time, h)	catal	1-alkene	$C_6H_{13}SiH_3$	$C_6H_{13}SiRH_2$	$C_6H_{13}SiR_2H$	$C_6H_{13}SiR_3$	
115[b] (1)	A	G	39	55	6		
117[c] (1)			24	69	7		
90[d] (0.5)	B	F	60	37	3		
90[e] (0.5)			39	58	3		
102[f] (0.5)	C	F,G	12	78	10		$C_6H_{13}Si(C_8)_3$ 16 $C_6H_{13}Si(C_8)_2C_{10}$ 40 $C_6H_{13}SiC_8(C_{10})_2$ 34 $C_6H_{13}Si(C_{10})_3$ 10
105[g] (0.5)							
95[h] (0.5)	D	G	67	31	2		
95[i] (2)			46	49	5		
92[j] (1)	D	F	56	39	5		
100[k] (1)						100	
85[l] (1)	D	F	34	66			
98[m] (1)						100	
106[n] (1)	D	G				100	
80[o] (0.25)	D	G	16	74	10		
98[p] (0.5)					73	27	
(0.75)					22	78	
95[q] (0.5)						100	
80[r] (0.2)	E	G		62	38		
100 (1.5)					47	53	
100[s] (1)					20	80	

[a] All runs, unless otherwise stated, were purged with nitrogen prior to heating and run under nitrogen. Catalysts used included 5% Pt/C (A), $PtCl_2(PPh_3)_2$ (B), $PtCl_2(CH_3CN)_2$ (C), $H_2PtCl_6 \cdot 6H_2O$ (D), and PtO_2 (E). 1-Alkenes reacted included 1-octene (F) and 1-decene (G). [b] Reactants: 1-decene, 10 g; $C_6H_{13}SiH_3$, 1.5 g; A, 0.0044 g; $PhCH_3$, 5 mL; N_2 purge, 15 min. [c] Added fresh A at room temperature, 0.033 g; N_2 purge, 15 min. [d] Reactants: 1-octene, 10 g; $C_6H_{13}SiH_3$, 1.5 g; B, 0.0056 g; $PhCH_3$, 5 mL; N_2 purge, 15 min. [e] Added fresh B at room temperature, 0.003 g; N_2 purge, 15 min. [f] Reactants: 1-octene, 10 g; 1-decene, 10 g; $C_6H_{13}SiH_3$, 1.5 g; C, 0.09 g; $PhCH_3$, 8 mL; N purge, 15 min. [g] Product *f* after exposure to air (room temperature, 16 h); added fresh C, 0.031 g; N_2 purge, 15 min. [h] Reactants: 1-decene, 10 g; $C_6H_{13}SiH_3$, 1.5 g; D, 0.025 g; $PhCH_3$, 5 mL; N_2 purge, 15 min. [i] Added fresh D at room temperature, 0.021 g; N_2 purge, 15 min. [j] Reactants: 1-octene, 10 g; $C_6H_{13}SiH_3$, 1.4 g; D, 0.062 g; $PhCH_3$, 6 mL; N_2 purge, 15 min. [k] Product *j* after exposure to air (room temperature, 8.5 h); fresh D added, 0.025 g; N_2 purge, 15 min. [l] Reactants: 1-Octene, 10 g; $C_6H_{13}SiH_3$, 1.0 g; D, 0.011 g; no N_2 purge. [m] Cooled *l* to room temperature, purged with air for 2 min; no N_2 purge. [n] Reactants: 1-decene, 10 g; $C_6H_{13}SiH_3$, 1.0 g; D, 0.042 g; mixture purged with air at 55 °C for 1 min; no N_2 purge. [o] Reactants: 1-decene, 10 g; $C_6H_{13}SiH_3$, 1.0 g; D, 0.032 g; no N_2 purge. [p] Product *o* after air purge at room temperature for 0.25 min; no N_2 purge. [q] Product *p* after air purge at room temperature for 0.25 min; no N_2 purge. [r] Reactants: 1-decene, 6.7 g; $C_6H_{13}SiH_3$, 0.7 g; E, 0.006 g; N_2 purge, 5 min. [s] Product *r* purged with air at room temperature for 0.5 min; no N_2 purge.

Table III. Hydrosilylation of Mixed Alkenes with Mixed Dialkylsilanes Using Supported Platinum Catalyst[a]

	composition of products, % (GLC)								
temp, °C (time, h)	$MeSi(C_8)H_2$	MeSi-$(C_{10})H_2$	$MeSi(C_8)_2H$	$MeSi(C_8)$-$(C_{10})H$	$MeSi(C_{10})_2H$	$MeSi(C_8)_3$	MeSi-$(C_8)_2(C_{10})$	MeSi-$(C_8)(C_{10})_2$	$MeSi(C_{10})_3$
130 (1)	25	12	32	26	5				
130 (3)	20	9	36	29	6				
130 (1)[b]	10	5	43	35	7				
130 (5)[b]	9	4	45	35	7				
130 (1)[c]			3	3	tr	36	41	15	2
130 (2)[c]						38	44	15	3

[a] Reactants: 1-octene (510 g), 1-decene (210 g), $MeSi(C_8)H_2$ (130 g), $MeSi(C_{10})H_2$ (60 g), 5% Pt/C (1 g), under N_2; yield, 83%; bp 173–195 °C (0.2 mm). [b] Reaction mixture was cooled, and additional 5% Pt/C (1 g) was added. [c] Reaction mixture was cooled and filtered. About $^1/_2$ of catalyst was saturated with air in *n*-octane for 10 min and returned to the mixture for continued reaction under N_2.

catalyst. Large quantities of oxygen, such as those present when carrying out reactions at elevated temperatures with complete exposure to air, should be avoided. Under the above conditions oxygen can become the reactant and lead to formation of high-boiling siloxanes. It follows that if catalyst activation with air is required, this procedure is best performed under conditions that minimize formation of byproducts.

The addition of hexylsilane to several crystals of chloroplatinic acid (20 °C, N_2) led to an immediate evolution of hydrogen which lasted for several hours. When evolution of hydrogen ceased, the solution was amber colored, the catalyst turned black, and condensation products of silane were detected in the dimer and trimer regions by GLC. A similar run in air produced about five times as much product, giving components in the dimer (27%), trimer (32%), tetramer (24%), and pentamer (17%) regions. The addition of hexylsilane to Wilkinson's catalyst (in air or N_2) also led to a rapid evolution of hydrogen and gave some of the same condensation products that were formed with chloroplatinic acid. Measurement of hydrogen produced in one experiment reached over 100 mol/mol of catalyst, indicating the reaction to be catalytic with respect to the noble metal. Unlike chloroplatinic acid, the Wilkinson's catalyst failed to effect hydrosilylation of 1-octene with hexylsilane, although it presented no difficulty with dialkyl- and trialkylsilanes.

Reaction of Dialkylsilanes (R_2SiH_2). The reaction of diethylsilane or dibutylsilane with 1-octene or 1-nonene (H_2PtCl_6, 160–180 °C)[2] was used to prepare trialkylsilanes in 20–30% yield. In the present work, a mixture of methyloctylsilane and methyldecylsilane was reacted with a mixture of 1-octene and 1-decene by using a supported catalyst (5% Pt/C, Table III). As in the case of hexylsilane, the reaction did not proceed very far, even after adding a second batch of catalyst. After activation of the catalyst with oxygen, the reaction was brought to completion, yielding four tetraalkylsilanes.

Reaction of Trialkylsilanes (R_3SiH). The reaction of triethylsilane with 1-alkenes, catalyzed by chloroplatinic acid, gave ~20% yield of tetraalkylsilanes.[1] The low yield apparently led Washburne[15] to report that trialkylsilanes react best under free radical conditions. Our experience has been that trialkylsilanes such as methyldioctylsilane[16] and triethylsilane will react with

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1-alkenes in the presence of platinum catalysts to afford high yields of tetraalkylsilanes, but the procedure requires a high ratio of Pt/R_3SiH ($\sim 10^{-3}$ mol/mol). Lower ratios of platinum to silane can be used, but the catalyst will require frequent activation with air. At a platinum/silane ratio of 1.3×10^{-3} (mol/mol, 40 °C), Millan et al.[17] reacted triethylsilane with 1-hexene to yield 75% of triethylhexylsilane in less than 40 min.

Green et al.[12] reported new diplatinum catalysts which are active for hydrosilylation at room temperature and more resistant to deactivation than chloroplatinic acid. Whether these catalysts will be effective with monoalkylsilanes is not known.

Recent work indicated that reduction of platinum complexes or platinum metal to Pt(0) does not necessarily result in catalyst deactivation, but depending on the colloidal nature of Pt(0), it can actually become a more active catalyst for hydrosilylation reaction.[18]

Conclusion. Platinum catalysts are widely used in hydrosilylation of alkenes. The reaction requires only a small amount of catalyst and is ideally suited for halogen- or alkoxy-activated silanes and electron-rich alkenes. With relatively unactivated monoalkyl-, dialkyl-, and trialkylsilanes and 1-alkenes, the reaction affords only low yields of hydrosilylation products and is accompanied by side reactions and catalyst deactivation. It was discovered that treatment of platinum catalyst with oxygen restored its hydrosilylation activity and allowed all simple alkylsilanes to be converted to tetraalkylsilanes. In many of the runs, the unreacted alkenes were isomerized up to ~25%, mostly during the later stage of hydrosilylation. The isomerization appears to be promoted by Pt(0) complexes[12] and efforts must be made to maintain the catalyst in the active form by reactivation.

Experimental Section

All reactions, unless otherwise indicated, were carried out at atmospheric pressure in standard laboratory glassware under nitrogen. Chromatographic analyses were performed on a Hewlett-Packard 5880A (FID) chromatograph, using a 25-m, 2% OV-101, fused silica capillary column, programmed from 50 to 300 °C at 8 deg/min. The ^1H NMR spectra were recorded on a Varian T-60 spectrometer, usually in carbon tetrachloride or acetone-d_6. The chemical shifts are in δ units (ppm) relative to Me_4Si (s = singlet, d = doublet, t = triplet, m = multiplet). The IR spectra were recorded on a Perkin-Elmer Model 597 spectrometer. GC/MS data were obtained on a Finnigan 4510 system with an electron impact source at 70 eV. All platinum catalysts were obtained from commercial sources. The following procedure is representative of the reaction of silanes with 1-alkenes (see footnotes of Tables II and III for details).

Reaction of *n*-Hexylsilane with 1-Octene. A 100-mL, three-necked, round-bottomed flask, fitted with a condenser connected to a nitrogen source, a stirrer, thermometer, and a serum cap, was charged with 1-octene (10.0 g, 89 mmol), *n*-hexylsilane (1.4 g, 12.1 mmol), and chloroplatinic acid hexahydrate (0.004 g, 7.7×10^{-3} mmol). After being purged with nitrogen (15 min), the mixture was heated to 95 °C. After 1 h, the reaction stopped at about 50% silane conversion. The mixture was cooled to 25 °C, and compressed air was bubbled vigorously through the mixture for 1 min. The mixture was again heated to 95 °C (under N_2) for 1 h. Analysis (GLC) showed that silane completely reacted to give hexyltrioctylsilane: bp 180–185 °C (~0.5 mmHg) (73%); NMR δ 1.32 (s, 44 H, CH_2), 0.92 (distorted t, 12 H, CH_3), 0.47 (br m, 8 H, CH_2Si); mass spectrum, *m/e* (relative intensity) 452 (0) [P^+], 367 (10) [$(P - C_6H_{13})^+$], 339 (35) [$(P - C_8H_{17})^+$], 256 (14), 255 (61) [$(C_8H_{17})_2SiH^+$], 228 (15), 227 (78) [$(C_8H_{17})(C_6H_{13})SiH^+$], 143 (100), 115 (40), 113 (28), 101 (15), 99 (79), 87 (17), 85 (58), 83 (15), 73 (36), 71 (28), 59 (34), 43 (21), 32 (21), 28 (72); IR (absence of Si–O, Si–H bonds).

Registry No. $C_6H_{13}Si(C_8)_3$, 109528-78-1; Et_3SiH, 617-86-7; $RhCl(PPh_3)_2$, 14694-95-2; $MeSi(C_8)_3$, 3510-72-3; $Et_3Si(C_8)$, 10175-53-8; $Si(C_8)_4$, 3429-74-1; $C_6H_{13}Si(C_{10})H_2$, 109528-79-2; $C_6H_{13}Si(C_{10})_2H$, 109552-35-4; $C_6H_{13}Si(C_8)H_2$, 109528-80-5; $C_6H_{13}Si(C_8)_2H$, 109528-81-6; $C_6H_{13}Si(C_8)_2(C_{10})$, 109528-82-7; $C_6H_{13}Si(C_8)(C_{10})_2$, 109528-83-8; $C_6H_{13}Si(C_{10})_3$, 109528-84-9; $MeSi(C_{10})H_2$, 109528-85-0; $MeSi(C_8)_2(C_{10})$, 83094-48-8; $MeSi(C_8)(C_{10})_2$, 83584-71-8; $MeSi(C_{10})_3$, 18769-78-3; $C_6H_{13}SiH_3$, 1072-14-6; $MeSi(C_8)_2H$, 51502-63-7; $HSi(C_8)_3$, 18765-09-8; Pt, 7440-06-4; $PtCl_2(PPh_3)_2$, 10199-34-5; $PtCl_2(CH_3CN)_2$, 13869-38-0; PtO_2, 11129-89-8; $MeSi(C_8)H_2$, 80204-10-0; F, 111-66-0; G, 872-05-9; chloroplatinic acid hexahydrate, 18497-13-7.

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Stereoselective (*E*)-Olefin Formation by Wittig-Type Olefination of Aldehydes with Allylic Tributylphosphorus Ylides Derived from Allylic Nitro Compounds

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The Wittig reaction has been widely recognized as a practical method for olefination of aldehydes and ketones.[1] Concurrently, much attention has been paid on the mechanistic details of this reaction to account for the stereochemical results strongly depending on the type of ylides and the reaction conditions.[1,2]

Allylic triphenylphosphorus ylides, available from allylic halides, triphenylphosphine (PPh_3), and base, have been used as valuable reagents to produce conjugated dienes and polyenes by reacting with saturated and conjugated aldehydes, respectively.[1] Recently it has been revealed that allylic alcohols and their derivatives react directly with PPh_3 through the mediation of palladium(0) complex to afford allylic phosphorus ylides or phosphonium salts, which are subsequently utilized for olefination of aldehydes.[3] These reactions apparently involve the intermediary of π-allylpalladium complexes which are formed by the oxidative addition of allylic substrates to a palladium(0) complex, followed by the attack of PPh_3 on the π-allyl complexes.[4] In these olefination reactions, no appreciable stereoselectivity with respect to a newly formed double bond was observed, as is usual with allylic triphenylphosphorus ylides.[1a,3] To our knowledge, little is known about the stereochemistry of the Wittig reactions effected with allylic trialkylphosphorus ylides.[1]

Here we report that allylic nitro compounds, prepared from nitromethane and ketones,[5] undergo the Pd(0)-cat-

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