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Hydrosilylation Chemistry and Catalysis with *cis*-$PtCl_2(PhCH{=}CH_2)_2$

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The precursor *cis*-$PtCl_2(PhCH{=}CH_2)_2$ is shown to catalyze (i) the hydrosilylation of various terminal olefins and acetylenes, (ii) the reduction of carbonyl functions with silanes in the presence of pyridine or aniline as cocatalyst, and (iii) the formation of $R^1{}_3SiOR^2$ from $R^1{}_3SiH$ and R^2OH. The hydrosilylation of styrene is shown to proceed via reduction of $PtCl_2(PhCH{=}CH_2)_2$ to $Pt(PhCH{=}CH_2)_3$ with concomitant formation of 2 equiv of R_3SiCl and 1 equiv of $PhCH_2CH_3$. Extensive ^{195}Pt measurements together with ^{13}C studies on complexed styrene selectively enriched at the β-carbon support the formation of the Pt(0) complex. The precursor *cis*-$PtCl_2(PhCH{=}CH_2)_2$ is suggested to arise from the trans isomer which is identified by ^{195}Pt NMR and its reaction chemistry.

Introduction

The homogeneously catalyzed hydrosilylation of olefins (eq 1) remains a reaction of interest both synthetically[1a,b] and mechanistically.[2] We have recently been interested

$$R_3Si{-}H + R^1CH{=}CH_2 \rightarrow R_3SiCH_2CH_2R^1 \qquad (1)$$

in platinum complexes as catalysts and specifically *cis*-$PtCl_2(PhCH{=}CH_2)_2$ (1) as catalyst precursor. This complex is readily available in good yield[3] although it exists in several isomeric forms. As we discussed the hydrosilylation of styrene with Et_3SiH in our earlier report on 1, we considered it important to evaluate the versatility of this and related catalysts with respect to (i) hydrosilylation as a function of the silane, (ii) hydrosilylation of various terminal olefins and acetylenes, (iii) hydrosilylation of some organic carbonyl derivatives, and (iv) other reactions of silanes, e.g., synthesis of alkoxysilanes R^3SiOR^1. Further, as early studies by Stone and coworkers[4] and recently by Chandra et al.[5a] and Matsumoto et al.[5b] suggested that platinum(0) compounds may be involved in hydrosilylation chemistry, we considered that the hydrosilylation of styrene with triethylsilane[3] (eq 2)

$$PhCH{=}CH_2 + Et_3SiH \xrightarrow[PtCl_2(PhCH=CH_2)_2]{} PhCH_2CH_2SiEt_3 \qquad (2)$$

might be accompanied by the formation of $Pt(PhCH{=}CH_2)_n$. We report here the in situ generation of $Pt(PhCH{=}CH_2)_3$ combined with extensive catalytic results that suggest 1 to be a flexible catalyst precursor.

Results and Discussion

A. Catalysis Using *cis*-$PtCl_2(PhCH{=}CH_2)_2$ (1). In view of the extensive literature[6] on hydrosilylation we have begun to evaluate the breadth of our new precursor, 1, and a summary of our efforts in this direction is shown in Tables I–IV. Although the tables contain a substantial amount of data the most salient points can be summarized in 1–5.

1. **Reactions with Various Silanes.** Complex 1 efficiently catalyzes the hydrosilylation of styrene with several different silanes—as do the complexes $Bu_4N[PtCl_3(PhCH{=}CH_2)]$ (2) and $K[PtCl_3(CH_2{=}CH_2)]$ (3). We note that 2 is sometimes more selective. The silanes $(PhCH_2)_3SiH$ and Ph_3SiH react relatively slowly and not at all, respectively, so that, in the former case, other pathways become competitive. The appearance of *trans*-$PhCH{=}CHSiEt_3$ has been noted previously,[3,7] and we assume that the analogous *trans*-$PhCH{=}CHSi(CH_2Ph)_3$ complex is generated in a similar fashion. The lack of catalytic reactivity with Ph_3SiH is deceptive as this reagent does indeed react with 1 as we shall show.

2. **Reactions of Olefins and Acetylenes.** Complex 1 also smoothly hydrosilylates the following olefins at room temperature: $CH_2{=}CHOCH_2CH_3$, $CH_2{=}CHSiMe_3$, 1-hexene, indene, and $PhC(CH_3){=}CH_2$. The reaction with 2-vinylpyridine is sluggish (54% after 30 h) presumably due to complexation of the platinum by nitrogen (although there is no compelling evidence for this assumption as $\delta(^{195}Pt)$ in situ at −3353 is not very different from those of 1, $\delta(^{195}Pt)$ −3169, −3290, and −3310[3]). Indene reacts relatively slowly as well (85% after 2 h) when compared to ethyl vinyl ether (81% after 20 min).

We note, for 1-hexene, that there is only a few percent of isomerization to internal olefins; obviously, the hydrosilylation is faster than the isomerization. Harrod and Chalk have suggested that isomerization of 1-hexene may require a cocatalyst.[8]

The acetylenes $HC{\equiv}C$-*n*-Pr and $HC{\equiv}CPh$ react smoothly with $PhMe_2SiH$ in the presence of 1 to afford *trans*-olefin products. In view of the good yields it would seem that the hydrosilylation of the product olefin is slower than that of the starting acetylene.

3. **Reduction of Organic Carbonyl Functions.** Complex 1 alone does not catalyze the reduction of acetophenone using $MeCl_2SiH$ (see eq 3 and entry 12, Table III); however, addition of a cocatalyst, e.g., a pyridine,

$$PhCOCH_3 + MeCl_2SiH \xrightarrow[1]{} PhCH(CH_3)OSiCl_2Me \qquad (3)$$

aniline, or aliphatic nitrogen ligand enhances the activity significantly such that reduction readily occurs at room temperature over a period of hours. We find no obvious correlation of yield with the pyridine basicity. As aniline

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Table I. Hydrosilylation of Styrene with Various Silanes[a]

silane	cat.	time, min	product, % $PhCH_2CH_2SiCl_2Me$	product, % $PhCH(CH_3)$-CH_2SiCl_2Me
1. $MeCl_2SiH$	*cis*-$PtCl_2(PhCH{=}CH_2)_2$	5	60	40
	$(Bu_4N)[PtCl_3(PhCH{=}CH_2)]$	13	96	n.o.
	$K[PtCl_3(CH_2{=}CH_2)]$	3	63	37

silane	cat.	time, min	product, % $PhCH_2CH_2SiClMe_2$	product, % $PhCH(CH_3)$-$SiClMe_2$
2. Me_2ClSiH	*cis*-$PtCl_2(PhCH{=}CH_2)_2$	5	78	15
	$(Bu_4N)[PtCl_3(PhCH{=}CH_2)]$	9	33	n.o.
		240	93	n.o.
	$K[PtCl_3(CH_2{=}CH_2)]$	7	no reaction	
		75	82	17

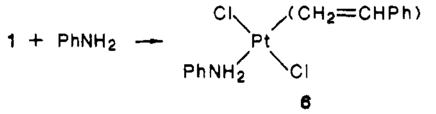
silane	cat.	time, min	product, % $PhCH_2CH_2SiMeEt_2$
3. Et_2MeSiH[b]	*cis*-$PtCl_2(PhCH{=}CH_2)_2$	5	84
		60	91
	$(Bu_4N)[PtCl_3(PhCH{=}CH_2)$	5	70
		60	89
	$K[PtCl_3(CH_2{=}CH_2)]$	5	83
		60	89
	$PtCl_2$(1,5-COD)	60	89

silane	cat.	time, min	product, % $PhCH_2CH_2SiMe_2Ph$	product, % $PhCH(CH_3)SiMe_2Ph$
4. Ph_2MeSiH	*cis*-$PtCl_2(PhCH{=}CH_2)_2$	10	93	3
		60	95	3
	$(Bu_4N)[PtCl_3(PhCH{=}CH_2)]$	10	78	2
		60	94	2
	$K[PtCl_3(CH_2{=}CH_2)]$	10	91	4
		60	96	2
	$PtCl_2$(1,5-COD)	10	87	2
		60	93	2

silane	cat.	time, h	product (%)
5. $(PhCH_2)_3SiH$	*cis*-$PtCl_2(PhCH{=}CH_2)_2$	114	$PhCH_2CH_2Si(CH_2Ph)_3$ (11) $PhCH(CH_3)Si(CH_2Ph)_3$ (1) *trans*-$PhCH{=}CHSi(CH_2Ph)_3$ (41) $PhCH_2CH_3$ (42)
	$(Bu_4N)[PtCl_3(PhCH{=}CH_2)]$	114	$PhCH_2CH_2Si(CH_2Ph)_3$ (13) $PhCH(CH_3)Si(CH_2Ph)_3$ (2) *trans*-$PhCH{=}CHSi(CH_2Ph)_3$ (40) $PhCH_2CH_3$ (41)
6. Ph_3SiH	*cis*-$PtCl_2(PhCH{=}CH_2)_2$		no reaction

[a] Reactions under N_2 atmosphere at room temperature. Styrene/silane = 1:1; catalyst/styrene = 1:2300; n.o. = not observed. Ratio of products determined by ^1H integration, ±1%. [b] Only linear products observed.

proved to be an effective cocatalyst and since we were uncertain whether it was coordinated, we considered the reaction of this ligand with 1 in two solvents. A CH_2Cl_2 solution of 1 and aniline yields the styrene complex 6 as shown in eq 4. The trans geometry of 6 is supported by



(4)

6

the single ν(Pt–Cl) stretch at 335 cm^{-1} and the coordination of both aniline and $PhCH{=}CH_2$ by ^1H, ^{13}C, and ^{195}Pt NMR studies as well as a satisfactory microanalysis. Since [^{15}N]aniline was available from previous studies,[9] we prepared an ^{15}N-enriched isotopomer of 6 (95 atom % ^{15}N) and measured its ^{15}N and ^{195}Pt characteristics: $\delta(^{195}Pt)$ −2831 ($^1J(^{195}Pt,^{15}N)$ = 244 Hz). With this background we now considered a solution of 1 and $Ph^{15}NH_2$ in acetophenone. ^{195}Pt NMR spectroscopy shows $\delta(^{195}Pt)$ at −2813 ($^1J(^{195}Pt,^{15}N)$ = 239 Hz) which we take to represent complex 6; therefore, it seems likely that the nitrogen is coordinated in the early stages of the catalysis. We note that 1 also reacts with both benzonitrile and *p*-methoxybenzonitrile to give isolable *cis*-$PtCl_2$(nitrile)$(PhCH{=}CH_2)$ complexes, $\delta(^{195}Pt)$ −2709 and −2688, respectively (see Experimental Section) but that nitriles are poor cocatalysts (see Table III), so that initial coordination of aniline, or nitrile etc., need not reflect its role later in the reaction.

4. Alcoholysis. At room temperature 1 induces the alcoholysis of the silanes Et_3SiH and $PhMe_2SiH$ as shown in eq 5. The reaction is strongly exothermic and can be

$$PhMe_2SiH + ROH \xrightarrow[1]{} H_2 + PhMe_2SiOR \qquad (5)$$

$$R = Me, Et, i\text{-}Pr, \text{cyclohexyl}$$

carried out at lower temperature. (successful with Et_3SiH and CH_3OH at −18 °C). This type of reaction is known[10] and is often carried out in the presence of a base so as to deprotonate the alcohol. Since our conditions are mild and

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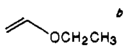
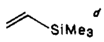
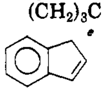
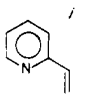
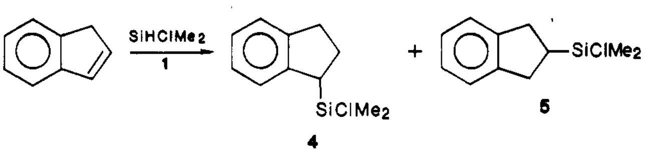
Table II. Hydrosilylation of Some Olefins and Acetylenes Using *cis*-$PtCl_2(PhCH{=}CH_2)_2$ as Catalyst[a]

silane	olefin (acetylene)	product(s)
1. $PhMe_2SiH$	 [b]	$PhMe_2SiCH_2CH_2OCH_2CH_3$ (81%)
2. $PhMe_2SiH$	 [d]	$Ph_3SiCH_2CH_2SiMe_3$ (100%)
3. $PhMe_2SiH$	$CH_2{=}CH(CH_2)_3CH_3$[d]	$PhMe_2Si(CH_2)_5CH_3$ (94%)
4. $PhMe_2SiH$	 [e]	α-silylated (85%)
5a. $PhMe_2SiH$	$CH_2{=}C(CH_3)Ph$[f]	$PhCH(CH_3)CH_2SiPhMe_2$ (ca. 13%)
5b. $MeCl_2SiH$	$CH_2{=}C(CH_3)Ph$[g]	$PhCH(CH_3)CH_2SiCl_2Me$ (ca. 100%)
6. $PhMe_2SiH$	$HC{\equiv}C$-*n*-Pr[h]	*trans*-$PhMe_2SiCH{=}CH$-*n*-Pr (74%) $CH_2{=}C(SiMe_2Ph)$-*n*-Pr (19%)
7a. $PhMe_2SiH$	$HC{\equiv}CPh$[g]	*trans*-$PhMe_2SiCH{=}CHPh$ (72%) $CH_2{=}C(SiMe_2Ph)Ph$ (28%)
7b. Et_3SiH	$HC{\equiv}CPh$[i]	*trans*-$Et_3SiCH{=}CHPh$ (72%) $CH_2{=}C(SiEt_3)Ph$ (14%)
8. Et_3SiH	 [j]	α-silylated (54%) β-silylated (14%)

[a] Reactions were carried out without solvent at room temperature. Unless otherwise specified the ratio of olefin to catalyst was 2300:1. [b] After 20 min. Using $PtCl_2$ affords 93% of the product after the same time. Reaction strongly exothermic. [c] After 20 min. The result was obtained by using $PtCl_2$. [d] After 20 min. Ca. 4% 2-hexene was detected. Using a catalyst olefin ratio of 7600 gives qualitatively identical results after 30 min, as does the use of $PtCl_2$ (2300:1). [e] After 2 h. [f] After 15 min. [g] After 45 min. [h] After 30 min. There are at least two additional products based on ^{1}H and ^{29}Si NMR. [i] After 30 h. [j] Slow reaction data for a 7-day reaction: 24% vinylpyridine remains; ca. 6% 2-ethylpyridine observed.

require no base, the use of 1 may prove advantageous for substrates that are sensitive to either temperature or base.

5. Product Distribution and Structure Proof. Although there is a marked preference for the silicon fragment to end on the terminal carbon, the product distribution shown in Tables I and II is not always readily rationalized. The observed difference between Et_3SiH (ca. 70–75% $PhCH_2CH_2SiEt_3$[3]) and Et_2MeSiH (ca. 90% $PhCH_2CH_2SiMeEt_2$) is mystifying, and we have no explanation for this observation. In almost all cases, the proof of structure for the silanes was readily accomplished via ^{1}H, ^{13}C, and ^{29}Si NMR (see Experimental Section and Tables V–VII). However, for the α-silylindane 4, the product of the hydrosilylation of indene with Me_2ClSiH (eq 6), the two methyl groups are nonequivalent so that



4
5
(6)

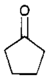
naive symmetry considerations, i.e., two sp^3 ^{13}C signals in a 2:1 ratio in 5 vs three resonances for 4, were insufficient to establish the structure. The unequivocal identification of the $Me_2ClSiCH$ proton at δ 2.83, as a doublet of doublets (via a ^{1}H–^{13}C correlation), suffices for the correct assignment, since the corresending proton in 5 is part of a more complex spin system.

B. $Pt(PhCH{=}CH_2)_3$ and Some of Its Chemistry. In view of the various reports[4,5] suggesting or implicating zerovalent complexes in hydrosilylation chemistry, we have attempted to reduce 1 with stoichiometric quantities of either Et_3SiH or Ph_3SiH. As mentioned above the former affords hydrosilylation products whereas the latter does not. We find that 1 equiv of 1 reacts with 2 equiv of *either* of these silanes to give $Pt(PhCH{=}CH_2)_3$ (7) as shown in eq 7. The equivalent of ethylbenzene was proven by ^{1}H

$$1 + 2R_3SiH \xrightarrow[PhCH=CH_2]{} \underset{\mathbf{7}}{Pt(PhCH{=}CH_2)_3} + PhCH_2CH_3 + 2R_3SiCl \quad (7)$$

NMR and explains why 2 equiv of silane are consumed;

Table III. Hydrosilylation of Carbonyl Groups with $MeCl_2SiH$ Using *cis*-$PtCl_2(PhCH{=}CH_2)_2$ and a Cocatalyst[a]

substrate	time, h	cocat.	product (%)
1. $PhCOCH_3$	38	pyridine	$PhCH(CH_3)OSiCl_2Me$ (72)
2. $PhCOCH_3$	41[b]	2-ethylpyridine	$PhCH(CH_3)OSiCl_2Me$ (80)
3. $PhCOCH_3$	41[b]	4-methylpyridine	$PhCH(CH_3)OSiCl_2Me$ (83)
4. $PhCOCH_3$	41	4-hydroxypyridine	$PhCH(CH_3)OSiCl_2Me$ (75)
5. $PhCOCH_3$	38	4-acetylpyridine	$PhCH(CH_3)OSiCl_2Me$ (61)
6. $PhCOCH_3$	26[b]	4-aminopyridine	$PhCH(CH_3)OSiCl_2Me$ (81)
7. $PhCOCH_3$	17[b]	4-methylaniline	$PhCH(CH_3)OSiCl_2Me$ (83)
8. $PhCOCH_3$	26[b]	1,2-phenylenediamine	$PhCH(CH_3)OSiCl_2Me$ (79)
9. $PhCOCH_3$	41[b]	piperidine	$PhCH(CH_3)OSiCl_2Me$ (79)
10. $PhCOCH_3$	26	NEt_3	$PhCH(CH_3)OSiCl_2Me$ (80)
11a. $PhCOCH_3$	32[b]	aniline	$PhCH(CH_3)OSiCl_2Me$ (84)
11b. $PhCOCH_3$	12	$PtCl_2(PhCH{=}CH_2)$(aniline)[c,d]	$PhCH(CH_3)OSiCl_2Me$ (98)
11c. $PhCOCH_3$	7	$PtCl_2(PhCH{=}CH_2)$(aniline)[c]	$PhCH(CH_3)OSiCl_2Me$ (68)
12. $PhCOCH_3$	26	none	$PhCH(CH_3)OSiCl_2Me$ (4)
13. $PhCOCH_3$	28	CH_3CN	$PhCH(CH_3)OSiCl_2Me$ (5)
14. $PhCOCH_3$	28	*p*-methoxybenzonitrile	$PhCH(CH_3)OSiCl_2Me$ (5)
15. $PhCOCH_3$	26	PPh_3	$PhCH(CH_3)OSiCl_2Me$ (51)
16. $PhCOCH_3$	32[b]	$AsPh_3$	$PhCH(CH_3)OSiCl_2Me$ (75)
17. $PhCOCH_3$	32[b]	$SbPh_3$	$PhCH(CH_3)OSiCl_2Me$ (89)
18. $PhCHO$	28	4-aminopyridine	$PhCH_2OSiCl_2Me$ (59)
	28[b]	4-aminopyridine	$(CH_2)_4CHOSiMeCl_2$ (84)
20. CH_3COCH_3	28[b]	4-aminopyridine	$(CH_3)_2CHOSiMeCl_2$ (88)
21. $CH_3COCH_2CH_3$	28	4-aminopyridine	$CH_3CH_2CH(CH_3)OSiMeCl_2$ (80)
22. CH_3CO-*i*-Bu	32[b]	4-aminopyridine	i-$BuCH(CH_3)OSiMeCl_2$ (69)

[a] In a blind run without catalyst, we observe "loss" of $MeCl_2SiH$ (bp 20 °C (352 Torr)) as a function of time: 20% after 7 h; 37% after 28 h. Ratio of substrate to Pt complex = 2000:1; room temperature using the reactants as solvent; *cis*-$PtCl_2(PhCH{=}CH_2)_2$/cocatalyst = 1:1. [b] No remaining $MeCl_2SiH$. [c] Isolated catalyst. [d] Silane/olefin = 1:5, thereby assuring that enough silane was present for complete reaction. See footnote *a*.

Table IV. Catalytic Preparation of R_3SiOR' Using *cis*-$PtCl_2(PhCH{=}CH_2)_2$[a]

	$R_3SiH + R'OH \rightarrow H_2 + R_3SiOR'$		
silane	alcohol	reactn time, h	yield,[b] %
$PhMe_2SiH$	MeOH	1	80
	EtOH	1[c]	85
	i-PrOH	3	100
	cyclohexanol	3	100
Et_3SiH	MeOH	0.33	100
	EtOH	0.33	100
	i-PrOH	3	100
	cyclohexanol	3	100

[a] Room temperature; ratio of catalyst to alcohol = 30 000:1 unless otherwise specified. [b] As determined by ^1H NMR integration. [c] EtOH/catalyst = 15 000.

Table V. Spectroscopic Data[a] for the Hydrosilylation of Styrene with Various Silanes

^1H	^{13}C	^{29}Si
$PhCH_2CH_2SiCl_2Me$[b]		
0.72 (CH_3, $^2J(Si,H) = 73$)	5.38 (CH_3)	31.88
1.50 (CH_2)[c]	22.63 (CH_2)[e]	
2.86 (CH_2)[d]	28.63 (CH_2)[e]	
$PhCH(CH_3)SiCl_2Me$		
0.66 (CH_3)[f]	3.34 (CH_3)[f]	29.43
1.65 (CH_3, $^3J(H,H) = 7.7$)	14.31 (CH_3)	
2.75 (CH)	33.96 (CH)	
$PhCH_2CH_2SiClMe_2$[b]		
0.42 (CH_3, $^2J(Si,H) = 6.8$)	1.77 (CH_3)	31.02
1.21 (CH_2)[c]	20.99 (CH_2)[e]	
2.77 (CH_2)[d]	29.25 (CH_2)[e]	
$PhCH(CH_3)SiClMe_2$		
0.42 (CH_3)[f,g]	0.44 (CH_3)[f]	29.89
0.44 (CH_3)[f,g]	0.58 (CH_3)[f]	
1.55 (CH_3, $^3J(H,H) = 7.5$)	14.57 (CH_3)	
2.53 (CH)	31.75 (CH_3)	
$PhCH_2CH_2SiMeEt_2$[b]		
0.03 (CH_3,[f] $^2J(Si,H) = 5.8$)	−6.15 (CH_3)[f]	5.42
0.59 (CH_2,[h] $^3J(H,H) = 8.0$)	5.07 (CH_2)[h]	
0.94 (CH_2)[c]	7.47 (CH_3)	
1.01 (CH_3, $^3J(H,H) = 8.0$)	15.29 (CH_2)[c]	
2.68 (CH_2)[d]	30.11 (CH_2)[d]	
$PhCH_2CH_2SiMe_2Ph$[b]		
0.37 (CH_3, $^2J(Si,H) = 6.3$)	−3.01 (CH_3)[i]	−3.17
1.21 (CH_2)[c]	17.78 (CH_2)[c]	
2.72 (CH_2)[d]	30.04 (CH_2)[d]	
trans-$PhCH{=}CHSi(CH_2Ph)_3$		
2.32 (CH_2)		
6.35[e] ($CH{=}$, $^3J(H,H) = 19.4$)		
6.80[e] ($CH{=}$)		
$PhCH_2CH_2Si(CH_2Ph)_3$		
2.26 (CH_2)[j]		
0.92 (CH_2)[c]		
2.46 (CH_2)[d]		

[a] Chemical shifts in ppm, relative to TMS; coupling constants in Hz; $CDCl_3$ solutions; ^{29}Si measurements made on solutions containing 10^{-2} M $Cr(acac)_3$. [b] Satisfactory mass spectrum and microanalysis. [c] β-Carbon to ring. [d] α-Carbon to ring. [e] Not assigned. [f] $SiCH_3$. [g] Nonequivalent $SiMe_2$ groups. [h] $SiCH_2$. [i] $^1J(Si,C) = 52$ Hz. Same value found for $^1J(SiCH_2)$. [j] $Si(CH_2Ph)_3$.

the presence of R_3SiCl was shown by careful integration of the ^{29}Si spectrum. (For reliable integrals, the ^{29}Si measurements are made in the presence of $Cr(acac)_3$. The R_3SiCl is available commercially so that the product which arises is certain.) Complex 7 may also be obtained starting from $PtBr_2(PhCH{=}CH_2)_2$, so that there is no question of halogen in the coordination sphere.

Regretably, 7 is not stable in the absence of excess styrene, in contrast to $Pt(CH_2{=}CH_2)_3$.[11] Slow removal of stryene in vacuo leads to a change in the solution color from yellow to brown and the eventual deposition of platinum metal.

As we were unable to isolate 7 as a solid, we have prepared several derivatives with phosphorus ligands and these are shown in eq 8 and 9. The presence of R_3SiCl (eq 7) is troublesome as this is a potential reagent for zerovalent phosphine complexes of platinum.[12] The chlorosilane is conveniently removed by washing with aqueous NH_3 and then passing the product solution through a ca. 3.5 cm long column containing basic alumina. If the solution still contains R_3SiCl when a tertiary phosphine is added, an oxidation to Pt(II) follows as shown in eq 10,

$$Pt(PhCH{=}CH_2)_3 + 2\text{diphos} \xrightarrow[-PhCH{=}CH_2]{} Pt(\text{diphos})_2 \tag{8}$$

$$Pt(PhCH{=}CH_2)_3 + \text{excess } P(OEt)_3 \xrightarrow[-PhCH{=}CH_2]{} Pt\{P(OEt)_3\}_4 \tag{9}$$

$$Pt(PhCH{=}CH_2)_3 + 2\text{diphos} \xrightarrow[-PhCH{=}CH_2 \\ 2Ph_3SiCl]{} [Pt(\text{diphos})_2]Cl_2 \tag{10}$$

and we have prepared the dication $[Pt(diphos)_2]Cl_2$, independently, to be certain of its identity. The silicon-containing component of eq 10 is believed to be $Ph_3Si-SiPh_3$. The transformation from $Pt(diphos)_2$ to $Pt(diphos)_2^{2+}$ in the presence of R_3SiCl can be followed by both ^{31}P and ^{195}Pt NMR spectroscopy. $Pt(diphos)_2$ ($\delta(^{31}P)$ 31.20 ($^1J(Pt,P) = 3726$ Hz); $\delta(^{195}Pt)$ −5351) has been reported by Clark et al.,[13] whereas $Pt\{P(OEt)_3\}_4$ ($\delta(^{31}P)$ 127.82 ($^1J(Pt,P) = 5369$ Hz); $\delta(^{195}Pt) = -5751$) stems from this laboratory.[14]

In view of the mild conditions necessary to prepare 7, we considered its reaction with 1,5-COD, in the hopes of an alternative preparation for $Pt(1,5\text{-}COD)_2$. Complex 7 reacts with an excess of 1,5-COD to give a new Pt(0) complex, perhaps $Pt(PhCH{=}CH_2)(1,5\text{-}COD)$; however, we find no evidence for $Pt(1,5\text{-}COD)_2$. Reversing matters, $Pt(1,5\text{-}COD)_2$ reacts with excess $PhCH{=}CH_2$ to give 7 quantitatively, as shown by ^{195}Pt NMR, and this brings us to the NMR characterization of $Pt(PhCH{=}CH_2)_3$.

Attempts to isolate this new Pt(0) complex via addition of solvents such as pentane (in which 7 is soluble), methanol, or ether proved fruitless so that the composition was determined by using ^{195}Pt, ^{13}C, and ^1H NMR spectroscopy in situ. The complex exists as two isomers in approximately 1.5:1 ratio with platinum chemical shifts at δ −5904 and −5886 (toluene-d_8/styrene (1:10), at 263 K). (We assume that these isomers arise as a consequence of different orientations for the phenyl rings with respect to one another.) These shifts are somewhat solvent- (and temperature-) dependent, and we show these data in the Experimental Section. It is worth noting that the δ values for the two isomers have different temperature dependences and can "cross" when the temperature is lowered. The position of these signals is at relatively high field $Pt(1,5\text{-}COD)_2$ has δ −4634 (CD_2Cl_2/CH_2Cl_2 at 223 K)), in keeping with the zero oxidation state. The number of

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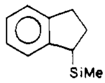
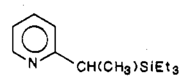
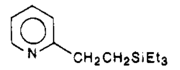
(11) Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1977, 271.

(12) Ciriano, M.; Green, M.; Gregson, D.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc. Dalton Trans.* **1979**, 1294. Eaborn, C.; Ratcliff, B.; Pidcock, A. *J. Organomet. Chem.* **1974**, *65*, 181. Chatt, J.; Eaborn, C.; Kapoor, P. N. *J. Chem. Soc. A* **1970**, 881.

(13) Clark, H. C.; Hampden-Smith, M.; Rüegger, H., submitted for publication in *J. Am. Chem. Soc.*

(14) Pregosin, P. S.; Sze, S. N. *Helv. Chim. Acta* **1977**, *60*, 1371.

Table VI. Spectroscopic Data[a] for the Silanes Derived from Various Olefins

^1H	^{13}C	^{29}Si
$CH_3CH_2OCH_2CH_2SiMe_2Ph$		
0.35 (CH_3,^{b} ^2J(Si,H) = 6.4)	−2.79 (CH_3)^{b}	−4.67
1.23 (CH_3)	15.14 (CH_3)	
1.25 (CH_2)^{c}	17.31 (CH_2)^{c}	
3.46 (CH_2)^{d}	65.38 (CH_2)^{f}	
3.54 (CH_2)^{e}	67.24 (CH_2)^{f}	
$Me_3SiCH_2CH_2SiMe_2Ph$		
0.05 (3CH_3,^{g} ^2J(Si,H) = 6.3)	−2.01 (CH_3)^{g}	−1.87^{f}
0.34 (2CH_3)	−3.56 (CH_3)	−2.72^{f}
0.48 (CH_2)^{f}	8.02 (CH_2)	
0.73 (CH_2)^{f}	8.99 (CH_2)	
$CH_3(CH_2)_5SiMe_2Ph$		
0.36 (CH_3, ^2J(Si,H) = 6.4)	−2.80 (CH_3)^{b}	−3.47
0.85 (CH_2)^{c}	14.31 (CH_3)	
0.97 (CH_3)	15.94 (CH_2)	
	22.81 (CH_2)	
1.39 (4CH_2)	24.05 (CH_2)	
	31.76 (CH_2)	
	33.46 (CH_2)	
		
0.42 (CH_3)^{h}	0.19 (CH_3)^{h}	28.69
0.46 (CH_3)^{h}	0.42 (CH_3)^{h}	
2.23 (CH)	26.92 (CH_2)	
2.40 (CH)	32.64 (CH_2)	
2.83 (CHSi)	36.41 (CH)	
2.98 (2CH)^{i}		
$PhCH(CH_3)CH_2SiCl_2Me$		
0.45 (CH_3)^{b}	6.01 (CH_3)^{b}	31.31
1.44 (CH_3)	25.74 (CH_3)	
1.63 (CH_2)	32.01 (CH_2)	
3.20 (CH)	35.57 (CH)	
$PhCH(CH_3)CH_2SiMe_2Ph$		
0.45 (CH_3)^{b,h}		−4.06
0.47 (CH_3)^{b,h}		
1.29 (CH_2)		
1.36 (CH_3)		
2.98 (CH)		
trans-$CH_3CH_2CH_2CH{=}CHSiMe_2Ph$		
0.45 (CH_3)^{b}	−2.22 (CH_3)^{b}	−12.16
1.04 (CH_3)	13.84 (CH_3)	
1.57 (CH_2)	22.00 (CH_2)	
2.23 ($CH_2CH{=}$)	39.09 ($CH_2CH{=}$)	
5.89 ($CH{=}$)^{j}		
6.26 ($CH{=}$)^{k}		
$CH_2{=}C(CH_2CH_2CH_3)SiMe_2Ph$		
0.50 (CH_3)^{b}	−2.69 (CH_3)^{b}	−8.97
0.97 (CH_3)	14.06 (CH_3)	
5.54 ($CH_2{=}$, ^2J(H,H) = 1.5)	22.21 (CH_2)	
5.81	38.45 ($CH_2CH{=}$)	
	126.06 ($CH_2{=}$)	
	150.32 ($C{=}CH_2$)	
trans-$PhCH{=}CHSiMe_2Ph$		
0.54 (CH_3)		−10.44
6.70 ($CH{=}$, ^3J(H,H) =19.1)		
7.06 ($CH{=}$)		
$CH_2{=}CPh(SiMe_2Ph)$		
0.52 (CH_3)		−8.39
5.78 ($CH{=}$, ^2J(H,H) = 2.9)		
6.11 ($CH{=}$)		
		
0.54 (CH_2,^{c} ^3J(H,H) = 8.0)	2.24 (CH_2)^{c}	8.40
0.88 (CH_3)^{b}	7.43 (CH_3)^{b}	
1.43 (CH_3, ^3J(H,H) = 7.5)	14.40 (CH_3)	
2.57 (CH)	30.14 (CH)	
		
0.57 (CH_2)^{c}	3.32 (CH_2)^{c}	6.88
ca. 0.9 (CH_2)^{l}	7.47 (CH_3)	
0.96 (CH_3)	11.98 (CH_2)	
2.79 (CH_2)^{m}	32.71 (CH_2)^{m}	

[a] Chemical shifts in ppm relative to TMS; coupling constants in Hz; $CDCl_3$ solutions. Data for aromatic protons (carbons) not given although these were recorded. ^{29}Si measured in the presence of 10^{-2} M $Cr(acac)_3$. [b] $SiCH_3$. [c] $SiCH_2$. [d] CH_2CH_3. [e] OCH_2OCH_3. [f] Not assigned. [g] $SiMe_3$. [h] Nonequivalent CH_3 groups, not assigned. [i] Assumed to be benzylic protons. [j] $SiCH{=}$, $^3J(H,H)_{trans}$ = 18.4, ^4J(H,H) = 1.5 Hz. [k] $CCH{=}$, $^3J(H,H)_{trans}$ = 18.4, ^3J(H,H) = 6.2 Hz. [l] CH_2CH_2. [m] CH_2 α to pyridine.

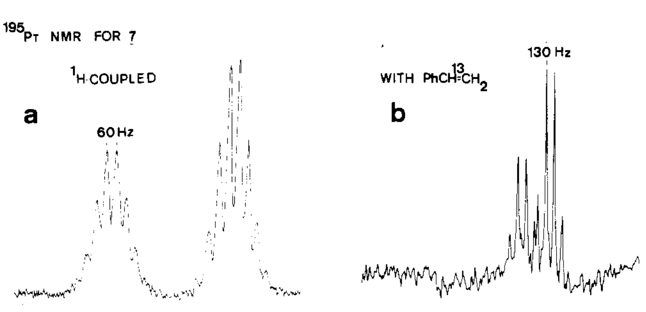


Figure 1. ^{195}Pt NMR for $Pt(PhCH{=}CH_2)_3$: (a) ^1H-coupled spectrum; (b) ^1H-decoupled with enriched $PhCH{=}^{13}CH_2$, showing ^1J(Pt,C).

coordinated styrene molecules was determined via (a) a *proton-coupled* ^{195}Pt spectrum from which multiplicities were obtained (see Figure 1) and (b) ^{13}C multiplicity in the ^{195}Pt spectrum from a sample prepared enriched with ^{13}C at the β-carbon, i.e., $PhCH{=}^{13}CH_2$. We note that in his review paper, Speier[2] suggests an eventual reduction of H_2PtCl_6 "...very probably to the zerovalent state. Every effort to prove the structure of the soluble complex was frustrated", so that we may consider the recognition of 7 in situ as nontrivial and a confirmation of the value of ^{195}Pt NMR spectroscopy.

Complex 7 catalyzes the hydrosilylation of $PhCH{=}CH_2$ with Et_3SiH and indeed affords a slightly faster reaction under comparable conditions.

C. ^{195}Pt NMR Studies on *trans*-$PtCl_2(PhCH{=}CH_2)_2$ and $PtCl_2$(solvent)($PhCH{=}CH_2$). Although we have utilized 1 extensively, it was clear from our earlier efforts[3] that it is only a convenient and less soluble form of catalyst precursor. Stirring $PtCl_2$ in styrene *slowly* affords 1 in good yield; however, a ^{195}Pt measurement *immediately* after the $PtCl_2$ dissolves reveals a signal at δ −2609 as the *only* visible complex (the isomers of 1 appear at ca. −3100). Two possibilities for this material, 8, are *trans*-$PtCl_2(PhCH{=}CH_2)_2$ and $PtCl_2(H_2O)(PhCH{=}CH_2)$. ($H_2O$ is ubiquitous.) Chatt and Wilkins,[15] in a careful preparative study, have isolated a complex to which they assign the structure *trans*-$PtCl_2(C_2H_4)_2$; however, the material is unstable above −6 °C. Despite the instability of this geometric isomer, we favor the structure *trans*-$PtCl_2(PhCH{=}CH_2)_2$ for the following reasons (i) Complex 8 is the only complex formed in the presence of styrene as solvent. (ii) Addition of 2 equiv of $PhCH{=}CH_2$ to the dimer $[Pt(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2$ in CD_2Cl_2 immediately

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(15) Chatt, J.; Wilkins, R. G. *J. Chem. Soc.* **1952**, 2622.

Table VII. Spectroscopic Data for the Alkoxysilanes $ROSiCl_2Me$ (Ketone Reduction), $ROSiMe_2Ph$, and $ROSiEt_3$ (Alcoholysis)[a]

R	$\delta(^1H)$	^{13}C	^{29}Si
	1. $ROSiCl_2Me$		
$PhCH(CH_3)$[b]	0.78 (CH_3,[c] $^2J(Si,H) = 9.0$)	5.04 (CH_3)[c]	−11.60
	1.58 (CH_3, $^3J(H,H) = 6.4$)	25.61 (CH_3)	
	5.30 (CH)	73.66 (CH)	
$PhCH_2$	0.86 (CH_3)	4.36 (CH_3)	−9.22
	5.00 (CH_2)	66.17 (CH_2)	
cyclopentyl	0.76 (CH_3, $^2J(Si,H) = 9.0$)	4.38 (CH_3)	−12.76
	4.67 (CH)	23.10 (CH_2)	
		34.99 (CH_2)	
		77.48 (CH)	
$(CH_3)_2CH$	0.77 (CH_3,[c] $^2J(Si,H) = 9.0$)	4.99 (CH_3)[c]	−13.10
	1.27 (CH_3, $^3J(H,H) = 6.2$)	24.93 (CH_3)	
	4.44 (CH)	68.68 (CH)	
$CH_3CHCH_2CH_3$	0.77 (CH_3,[c] $^2J(Si,H) = 9.0$)	5.00 (CH_3)[c]	−13.05
	0.91 (CH_3,[d] $^3J(H,H) = 7.4$)	9.84 (CH_3)[d]	
	1.25 (CH_3)[e]	22.43 (CH_3)[e]	
	4.18 (CH)	31.54 (CH_2)	
		73.59 (CH)	
CH_3CHCH_2CH-$(CH_3)_2$	0.78 (CH_3,[c] $^2J(Si,H) = 9.0$)		
	0.91 (CH_3)[h]		
	0.92 (CH_3)[h]		
	1.27 (CH_3)		
	1.23, 1.53 (CH)[i]		
	1.70 (CH)		
	2. $ROSiMe_2Ph$		
CH_3	0.41 (CH_3)[c]	−2.33 (CH_3)[c]	9.25
	3.47 (CH_3)	50.64 (CH_3)	
CH_3CH_2	0.41 (CH_3)[c]	−1.74 (CH_3)[c]	6.87
	1.21 (CH_3)	18.42 (CH_3)	
	3.70 (CH_2)	56.68 (CH_2)	
$(CH_3)_2CH$	0.40 (CH_3)[c]	−1.07 (CH_3)[c]	4.40
	1.16 (CH_3)	25.74 (CH_3)	
	4.01 (CH)	65.33 (CH)	
cyclohexyl	0.40 (CH_3)	−0.98 (CH_3)	4.13
	3.62 (CH)	24.27 (CH_2)	
		25.54 (CH_2)	
		35.86 (CH_2)	
		71.29 (CH)	
	3. $ROSiEt_3$		
CH_3	0.59 (CH_2, $^3J(H,H) = 8.0$)	4.06 (CH_2)	20.45
	0.94 (CH_3)[f]	6.66 (CH_3)	
	3.44 (CH_3)	50.64 (CH_3)	
CH_3CH_2	0.58 (CH_2)[g]	4.44 (CH_2)[g]	18.31
	0.94 (CH_3)	6.70 (CH_3)[f]	
	1.17 (CH_3)	18.61 (CH_3)	
	3.67 (CH_2)	58.38 (CH_2)	
$(CH_3)_2CH$	0.59 (CH_2)	4.84 (CH_2)[g]	16.43
	0.96 (CH_3)[f]	6.81 (CH_3)[f]	
	1.16 (CH_3)	25.88 (CH_3)	
	3.99 (CH)	66.97 (CH)	
cyclohexyl	0.59 (CH_2)[g]	4.96 (CH_2)[g]	16.26
	0.96 (CH_3)	6.85 (CH_3)	
	3.56 (CH)	24.45 (CH_2)	
		25.66 (CH_2)	
		36.15 (CH_2)	
		70.90 (CH)	

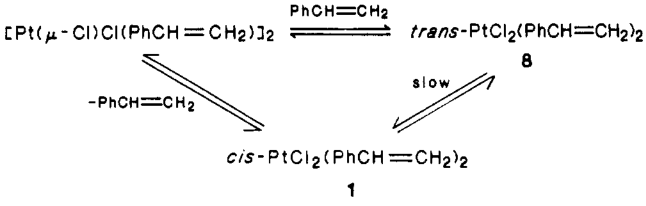
[a] Chemical shifts in ppm relative to TMS; coupling constants in Hz; $CDCl_3$ solutions; ^{29}Si measured in presence of 10^{-2} M $Cr(acac)_3$. [b] Mass spectrum shows molecule ion at *m/e* 235. [c] CH_3 on Si. [d] $\mathit{CH_3}CH_2$. [e] $\mathit{CH_3}CH$. [f] $SiCH_2\mathit{CH_3}$. [g] $Si\mathit{CH_2}CH_3$. [h] Nonequivalent CH_3. [i] Nonequivalent CH_2.

forms mostly 8. Addition of 26 equiv forms 8 exclusively. If this solution stands for 24 h, all of the isomers of 1 form in solution. (iii) The IR of 8 in styrene shows a single band in the Pt–Cl region at 332 cm^{-1} ($PtCl_2$ dissolved in *p*-methylstyrene shows an analogous signal at 338 cm^{-1}). IR spectra for a series of *trans*-$PtCl_2L_2$ complexes have been reported[16] and show this vibration between 326 and 343 cm^{-1}. Analogous cis complexes reveal two bands, and we show some data for these based on our measurements in Table VIII. Moreover, as H_2O is a notably poor ligand for Pt(II) and as 8 forms quickly when styrene is added, we reject the aquo complex.

Table VIII. Pt–Cl IR Spectroscopic Data

complex	ν(Pt–Cl), cm^{-1}	
cis-$[PtCl_2(PhCH{=}CH_2)_2]$	330	365
cis-$[PtCl_2(p\text{-}MeC_6H_4CH{=}CH_2)_2]$	332	367
cis-$[PtCl_2(COD)]$	316	337
cis-$[PtCl_2(PhCH{=}CH_2)(PhCN)]$	325	360
cis-$[PtCl_2(PhCH{=}CH_2)(p\text{-}MeOC_6H_4CN)]$	324	360
trans-$[PtCl_2(PhCH{=}CH_2)(PhNH_2)]$	335	
cis-$[PtCl_2(PhNH_2)_2]$	339	372
cis-$[PtCl_2(PPh_3)_2]$	306	332
cis-$[PtCl_2\{P(OPh)_3\}_2]$	293	319

Scheme I



One can also consider a possible five-coordinate complex, e.g., $PtCl_2(PhCH{=}CH_2)_3$. We eliminated this composition as follows: starting from a known concentration of the dimer $[Pt(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2$, one can add modest amounts of styrene—we chose first 0.2 and then in a second experiment 0.5 equiv per platinum—and, with the assumption that all the metal is complexed, the position of the equilibrium can be determined from

$$[Pt(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2 \xrightleftharpoons{PhCH=CH_2} 8 \qquad (11)$$

the integrals in the platinum NMR spectrum.[17] The ratio of 8/(dimer) depends on the number of coordinated styrene molecules, and we find good agreement for two coordinated olefins. In this methodology it is not strictly necessary to assume that all of the styrene complexes, provided that 8 is relatively stable.[18] In principle multiplicity data from either a proton-coupled or a ^{13}C-enriched ^{195}Pt spectrum should suffice to determine the number of styrenes; however, 8 is very dynamic with $\Delta\nu_{1/2}$ in the metal spectrum of ca. 300 Hz at −90 °C, and although we have measured its ^{13}C spectrum with coordinated $PhCH{=}^{13}CH_2$, there is no clear multiplicity observable.

As we have already shown[3] that 1 converts to the dimer in solution, we can summarize our solution results for these few complexes as shown in the scheme. In keeping with our observations for 1 and 8, we note that Chatt and Wilkins suggested[15] that the *cis*-$PtCl_2(C_2H_4)_2$ should be more stable than the trans isomer.

Our decision against an aquo complex for 8 was based on the reaction chemistry. Nevertheless, having noted that 1 reacts with PhCN and aniline, we considered generating some solvent-stabilized materials by simply dissolving the dimer in a variety of oxygen donors (eq 12). For MeOH there is a single ^{195}Pt resonance at δ −2697 (in EtOH, δ

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(16) Adams, D. M. *Metal-Ligand and Related Vibrations*; Edward Arnold Ltd.: London, 1967. Ferraro, J. R. *Low-Frequency and Related Vibrations*; Plenum: New York, 1971.

(17) ^{195}Pt T_1 values are relatively short, see: Pregosin, P. S. *Annual Reports on NMR Spectroscopy*; Academic: London, 1986; Vol. 17, p 285.

(18) Assuming we measure all the *platinum* in our ^{195}Pt spectrum, knowing the total concentration of platinum, the ratio of the ^{195}Pt integrals, (dimer)/(unknown), and the total styrene concentration, one can eliminate three coordinated styrenes as a possibility without assuming all the styrene to be co ordinated. However, this approach is not valid if the equilibrium in the equation lies to the left.

$$[\mathrm{Pt}(\mu\text{-Cl})\mathrm{Cl}(\mathrm{PhCH{=}CH_2})]_2 + \text{solvent} \rightleftharpoons 2\mathrm{PtCl_2}(\text{solvent})(\mathrm{PhCH{=}CH_2}) \quad (12)$$

−2644). In MeOH/acetone (3:1), the signal moves downfield slightly to δ −2634. In acetone we find three signals with the major component at δ −2616 and two smaller resonances at δ −2592 and −2141. In THF there are two absorptions at δ −2644 and −2142. In chloroform or methylene chloride we find no evidence for a solvent complex. For THF and acetone solutions, where there are several signals, one might argue for cis and trans isomers of the type PtCl$_2$(solvent)(PhCH=CH$_2$), with trans at low field and cis at high field; however, we do not feel that there is enough data for a definite assignment. In ethanol the product shows two Pt–Cl stretching vibrations at 324 and 330 cm^{-1}, suggesting a cis molecule. An honest appraisal of all these solvent experiments leads to the conclusion that, apart from the fact that these solvents do react with the dimer, little can be said about the structures in situ.

Before closing this section, we would like to comment on the dimer ^{195}Pt signals, which fall at δ −2317, −2331, −2334, and 2427 in CH$_2$Cl$_2$/CD$_2$Cl$_2$. Previously, we considered all four absorptions to belong to the various possible isomers of [Pt(μ-Cl)Cl(PhCH=CH$_2$)]$_2$, e.g., sym-trans, sym-cis, and possible styrene orientation isomers. At −90 °C the signal at δ −2427 grows with increasing dilution to a point where the remaining three resonances are barely visible. As it seems unlikely that isomers arising from rotation and/or symmetry would be so concentration dependent, there is always the possibility of assigning the δ −2427 resonance to either an aquo or a solvent complex.

D. Comment. The ease with which Pt(PhCH=CH$_2$)$_3$ (7) is generated in situ combined with its catalytic activity suggests it is yet another intermediate in the platinum-catalyzed hydrosilylation of styrene. The lack of reactivity observed for 1 plus Ph$_3$SiH is not related to the inability to reduce 1 to 7 but must stem from a slow reaction further on in the cycle. In view of the observed dependence of the hydrosilylation rate on the choice of silane, it is difficult to generalize about relative rates of subsequent steps; however, for MeCl$_2$SiH and styrene, with 1 the catalyst, we have observed several ^{1}H hydride resonances by cooling a reaction solution below −90 °C. This suggests that the oxidative addition of the silane to the (presumed) Pt(0) complex 7 is facile and that, at least in this case, the slow step is either an insertion or a reductive elimination reaction. We are currently evaluating deuterium isotope effect data and will elaborate on these in a later paper.

Experimental Section

NMR spectra were measured on a Bruker WM-250 spectrometer (^{1}H at 250, ^{13}C at 63, ^{195}Pt at 53, and ^{29}Si at 50 MHz, respectively). For the ^{195}Pt NMR spectroscopy we estimate that chemical shifts are ±1 ppm. This is not based on the computer digitization but rather on the known solvent and temperature dependence of this nucleus (see ref 16). Chemical shifts are relative to external Na$_2$PtCl$_6$. Infrared data were obtained from CsCl pellets by using either a Perkin-Elmer series 1430 or 883 spectrometer. Silanes were either commercially available or prepared as described previously.[3,19] All reagents were distilled shortly before use. Complex 1 was prepared as given in ref 3. No solvents were used unless noted. All the runs with silanes were performed under nitrogen. The catalytic reactions are frequently exothermic so that, for volatile silanes, although the ratio of olefin (acetylene) to silane was chosen as 1:1, it was often found that the reaction "stopped" after ca. 95% of the olefin was consumed. No attempt was made to thermostat the reactions. Where essentially all of the olefin was consumed, the reaction solution was either green or brown in color, suggesting decomposition of the catalyst via metal deposition. The ratio of catalyst to reagent is provided in footnote *a* of Tables I–IV.

Hydrosilylation of PhMe$_2$SiH and Other Silanes with Various Olefins. The catalyst was dissolved in the alkene or stirred in the alkene for 45 min after which time the silane was added. All the reactions were carried out under nitrogen and those for EtOCH=CH$_2$, Me$_3$SiCH=CH$_2$, 1-hexene, PhCH(CH$_3$)=CH$_2$, and HC≡C-*n*-Pr were markedly exothermic. Products were monitored periodically via ^{1}H NMR. Commercial indene contains up to 2% benzonitrile so that the indene was first distilled and then chromatographed over silica gel with pentane as eluent and then distilled a second time. The products of the vinylpyridine hydrosilylation were separated via fractional distillation at 10 Torr followed by two chromatographic separations. The first (silica gel; pentane/ethanol, 10:1) afforded a pure sample of the branched isomer. The second run (silica gel; hexane/ethanol, 15:1) served to separate remaining small quantities of the branched from the linear isomer.

Ketone Reduction. The catalyst and cocatalyst were stirred in the ketone for 15 min to afford a clear yellow solution, after which time an equivalent of MeCl$_2$SiH was added. The product PhCH(CH$_3$)OSiCl$_2$Me was distilled under N$_2$.

Alcoholysis. Complex 1 was suspended in the degassed alcohol and the previously degassed silane added. There followed an immediate vigorous evolution of gas, and the yellow solution became brown in color. These reactions are extremely fast (the reaction with CH$_3$OH at −18 °C is finished shortly after mixing), and we interpret the color change to imply the reaction is essentially finished and the catalyst decomposed.

Synthesis of *cis*-PtCl$_2$(PhCN)(PhCH=CH$_2$). *cis*-PtCl$_2$(PhCH=CH$_2$)$_2$ (93.3 mg, 197 μmol) was added as a solid to a solution of PhCN (20.2 mg, 197 μmol) in 5 mL of CH$_2$Cl$_2$ and the resulting solution allowed to stand for 18 h. The orange suspension that resulted was filtered and the filtrate concentrated. The material that remains was treated with 7 mL of CH$_2$Cl$_2$/toluene (1:1) followed by 10 mL of pentane. After 2 days of standing at ca. −78 °C the yellow solid that resulted was filtered, washed with 10 mL of pentane, and then dried in vacuo to afford 76.1 mg (82%) of product. Anal. Calcd for C$_{15}$H$_{13}$Cl$_2$NPt: C, 38.07; H, 2.77; N, 2.96; C, 14.98. Found: C, 38.22; H, 2.86; N, 2.07; Cl, 15.30. ^{1}H NMR (CDCl$_3$, 250 MHz): δ 4.78 (H^B, ^2J(Pt,H) = 69 Hz, ^3J(H^A,H^B) = 8.1 Hz), 5.01 (H^C, ^2J(Pt,H) = 59 Hz, ^3J(H^A,H^C) = 14.3 Hz), 6.63 (H^A, ^3J(H^A,H^B = 8.1, ^3J(H^A,H^C) = 14.3 Hz). H^B is cis to H^A and geminal to H^C. ^{195}Pt NMR: δ −2709. ^{13}C NMR: δ 62.98 (C$^\beta$, ^1J(Pt,C) = 178 Hz), 94.06 (C$^\alpha$, ^1J(Pt,C) = 134 Hz).

The *p*-methoxybenzonitrile was prepared in an analogous fashion.

Synthesis of *trans*-PtCl$_2$(PhNH$_2$)(PhCH=CH$_2$). Aniline (19.2 μL, 211 μmol) was added to a solution of *cis*-PtCl$_2$(PhCH=CH$_2$)$_2$ (100 mg, 211 μmol) in 20 mL of CH$_2$Cl$_2$. The resulting solution was allowed to stand for 16 h and then filtered. The filtrate was concentrated and then diluted to 3 mL with CH$_2$Cl$_2$. Dropwise addition of 20 mL of pentane followed by standing for 17 h at −25 °C afforded a yellow solid that was collected by filtration and washed with pentane to afford after drying 79 mg (81%) of product. Anal. Calcd for C$_{14}$H$_{15}$Cl$_2$NPt: C, 36.30; H, 3.26; N, 3.02. Found: C, 35.83; H, 3.45; Cl, 2.77. ^{1}H NMR (CDCl$_3$, 250 MHz): δ 4.37 (H^B, ^2J(Pt,H) = 713, ^3J(H^A,H^B) = 8.4 Hz), 5.11 (H^C, ^2J(Pt,H) = 61, ^3J(H^A,H^C) = 14.5 Hz), 6.58 (H^A, ^2J(Pt,H) = 72.8, ^3J(H^A,H^B) = 14.5, ^3J(H^A,H^C) = 8.3 Hz); ^{13}C NMR (CDCl$_3$, −20 °C): δ 62.45 (CH$_2$), 95.30 (CH), aromatic carbons at δ 121.13, 125.82, 128.62, 129.18, 129.47, 134.70, 137.98. ^{195}Pt NMR (CD$_2$Cl$_2$/CH$_2$Cl$_2$ (1:4), −20 °C) δ −2831 (^{15}N enriched, ^1J(Pt,N) = 245 Hz). ^{15}N NMR (CD$_2$Cl$_2$/CH$_2$Cl$_2$, 1:4, −20 °C): δ 30.1 (relative to NH$_3$, ^1J(Pt,N) = 244 Hz). IR: ν(Pt–Cl) 335 cm^{-1}.

Preparation of Pt(diphos)$_2$. A suspension of 1 (50 mg, 1.05 × 10^{-4} mol) in 2 mL PhCH=CH$_2$ was treated with Ph$_3$SiH (55 mg, 2.11 × 10^{-4} mol) for 15 min at room temperature. The resulting solution was then poured through an Alumina column (Woelm B, activity I; 7 cm long × 20 mm wide) with 15 mL of styrene as eluent. The first 3 mL of colorless liquid was treated with diphos (84 mg, 2.11 × 10^{-4} mol) with the result that the solution became yellow in color. A ^{31}P NMR spectrum showed

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(19) Reynolds, H. H.; Bigelow, L. A.; Crans, C. A. *J. Am. Chem. Soc.* **1929**, *51*, 3067.

$Pt(diphos)_2$ as the only complex in solution.

Generation of $Pt(PhCH=CH_2)_3$. A suspension of 1 (50 mg, 105 μmol) in 2 mL of styrene was treated with Ph_3SiH (55 mg, 211 μmol). Stirring for 30 min affords a clear yellow solution. ^{195}Pt NMR spectroscopy shows $Pt(PhCH=CH_2)_3$ both under N_2 and in air. The synthesis can be accomplished under N_2 by using $MeCl_2SiH$ as reducing agent.

The Pt(0) styrene is separated from silane as follows: 2 mL of the styrene solution was stirred together with 2 mL of H_2O and 0.5 ml concentrated NH_3 for ca. 75 min. If the phases do not separate cleanly, an additional 2 mL of water may be added. The styrene phase was separated and stirred with another 2 mL of H_2O for 20 min. Separation of the styrene phase was followed by placing it on a 5-mm wide column containing 3.5 cm of basic Alox (activity I). After the solution was collected, the column was washed with 1.5 mL of styrene and this eluate added to the first fraction. Omitting the NH_3 treatment results in reduced yields and requires a longer column, ca. 7 cm with 2.5 cm diameter. $[Pt(PhCH=CH_2)_3]$ (isomers A and B): ^{195}Pt NMR (δ, CD_2Cl_2/styrene (15:1), 263 K) −5892 (A), −5873 (B); ^{195}Pt NMR (δ, CD_2Cl_2/styrene (50:1), 193 K) −5921 (A), −5958 (B); ^{195}Pt NMR (δ, toluene-d_8/styrene (1:10), 263 K), −5904 (A), −5886 (B); ^{195}Pt NMR (δ, toluene-d_8/styrene (7:1), 263 K) −5902 (A), −5882 (B); ^{195}Pt NMR (δ, toluene-d_8/styrene (7:1), 223 K) −5930 (A), −5958 (B).

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Registry No. 1, 106862-48-0; 2, 106799-82-0; 3, 12012-50-9; 6, 59982-20-6; 7, 113948-64-4; 8, 59982-22-8; $PtCl_2$(1,5-COD), 12080-32-9; *cis*-$[PtCl_2(PhCN)(PhCH=CH_2)]$, 113948-65-5; *cis*-$[PtCl_2(PhCH=CH_2)(p\text{-}MeOC_6H_4CN)]$, 113948-66-6; $Pt(diphos)_2$, 25398-76-9; *cis*-$[PtCl_2(p\text{-}MeC_6H_4CH=CH_2)_2]$, 113948-67-7; *cis*-$[PtCl_2(PhNH_2)_2]$, 41637-08-5; *cis*-$[PtCl_2(PPh_3)_2]$, 15604-36-1; *cis*-$[PtCl_2\{P(OPh)_3\}_2]$, 30053-58-8; $PhCH=CH_2$, 100-42-5; $CH_2=CHOEt$, 109-92-2; $CH_2=CHSiMe_3$, 754-05-2; $CH_2=CH(CH_2)_3CH_3$, 592-41-6; $CH_2=C(CH_3)Ph$, 300-57-2; $HC\equiv CPr$, 627-19-0; $HC\equiv CPh$, 536-74-3; $MeCl_2SiH$, 75-54-7; Me_2ClSiH, 1066-35-9; Et_2MeSiH, 760-32-7; Ph_2MeSiH, 776-76-1; $(PhCH_2)_3SiH$, 1747-92-8; Ph_3SiH, 789-25-3; $PhMe_2SiH$, 766-77-8; Et_3SiH, 617-86-7; $PhCH_2CH_2SiCl_2Me$, 772-65-6; $PhCH(CH_3)CH_2SiCl_2Me$, 13617-28-2; $PhCH_2CH_2SiClMe_2$, 17146-08-6; $PhCH(CH_3)SiClMe_2$, 65118-86-7; $PhCH_2CH_2SiMeEt_2$, 76111-01-8; $PhCH_2CH_2SiMe_2Ph$, 62257-76-5; $PhCH(CH_3)SiMe_2Ph$, 65231-38-1; $PhCH_2CH_2Si(CH_2Ph)_3$, 113948-54-2; $PhCH(CH_3)Si(CH_2Ph)_3$, 113948-55-3; *trans*-$PhCH=CHSi(CH_2Ph)_3$, 113948-56-4; $PhCH_2CH_3$, 100-41-4; $PhMe_2SiCH_2CH_2OEt$, 113948-57-5; $Ph_3SiCH_2CH_2SiMe_3$, 102105-77-1; $PhMe_2Si(CH_2)_5CH_3$, 65118-84-5; *trans*-$PhMe_2SiCH=CHPr$, 113948-58-6; $CH_2=C(SiMe_2Ph)Pr$, 113948-59-7; *trans*-$PhMe_2SiCH=CHPh$, 64788-85-8; $CH_2=C(SiMe_2Ph)Ph$, 63935-90-0; *trans*-$Et_3SiCH=CHPh$, 21209-32-5; $CH_2=C(SiEt_3)Ph$, 42478-41-1; $PhCOCH_3$, 98-86-2; PhCHO, 100-52-7; CH_3COCH_3, 67-64-1; $CH_3COCH_2CH_3$, 78-93-3; CH_3CO-*i*-Bu, 108-10-1; NEt_3, 121-44-8; $PhNH_2$, 62-53-3; PPh_3, 603-35-0; $AsPh_3$, 603-32-7; $SbPh_3$, 603-36-1; $PhCH(CH_3)OSiCl_2Me$, 60199-01-1; $PhCH_2OSiCl_2Me$, 113948-61-1; $(CH_2)_4CHOSiMe_2Cl$, 113948-62-2; $(CH_3)_2CHOSiMeCl_2$, 999-89-3; $CH_3CH_2CH(CH_3)OSiMeCl_2$, 1825-79-2; *i*-$BuCH(CH_3)OSiMeCl_2$, 113948-63-3; $PhMe_2SiOMe$, 17881-88-8; $PhMe_2SiOEt$, 1825-58-7; $PhMe_2SiOCH(CH_3)_2$, 17988-21-5; $PhMe_2SiOCH(CH_2)_5$, 65335-82-2; Et_3SiOMe, 2117-34-2; Et_3SiOEt, 597-67-1; $Et_3SiOCH(CH_3)_2$, 1571-45-5; $Et_3SiOCH(CH_2)_5$, 4419-18-5; indene, 95-13-6; 2-vinylpyridine, 100-69-6; 1-(dimethylphenylsilyl)indan, 41273-54-5; 1-triethylsilyl-1-(2-pyridinyl)ethane, 113948-60-0; 1-triethylsilyl-2-(2-pyridinyl)ethane, 17082-72-3; cyclopentanone, 120-92-3; pyridine, 110-86-1; 2-ethylpyridine, 100-71-0; 4-methylpyridine, 108-89-4; 4-hydroxypyridine, 626-64-2; 4-acetylpyridine, 1122-54-9; 4-aminopyridine, 504-24-5; 4-methylbenzenamine, 106-49-0; 1,2-phenylenediamine, 95-54-5; piperidine, 110-86-1.

Isolation and X-ray Crystal Structures of the Homoleptic, σ-Bonded, Transition-Metal Aryl Complexes $[(LiEt_2O)_4VPh_6]$ and $[(LiEt_2O)_3CrPh_6]$

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The isolation and X-ray crystal structures of the homoleptic, σ-bonded, transition-metal aryl complexes $[(LiEt_2O)_4VPh_6]$ (1) and $[(LiEt_2O)_3CrPh_6]$ (2) are reported. In both compounds the transition metal is surrounded by six, octahedrally disposed, phenyl groups. In 1, four ether-solvated Li^+ ions cap alternate faces of the VC_6 octahedron, giving rise to a tetrahedral array of four Li^+ ions with V at the center. In 2, one of the $(LiEt_2O)$ moieties is absent so that the $CrLi_3$ group is in an array of C_{3v} symmetry. Both complexes feature long M–C bonds and fairly short M–Li distances, suggesting the possibility of significant M–Li interaction. Crystal data, with Mo Kα (λ = 0.710 69 Å) radiation, at 130 K are as follows: 1, a = 12.790 (3) Å, b = 14.352 (4) Å, c = 13.117 (3) Å, β = 95.06 (2)°, Z = 2, space group $P2_1$, R = 0.036; 2, a = 12.010 (3) Å, b = 19.148 (8) Å, c = 20.410 (7) Å, α = 113.91 (2)°, β = 95.51 (3)°, γ = 90.32 (3)°, Z = 4, space group $P\bar{1}$, R = 0.049.

Introduction

The σ-bonded metal alkyls and aryls constitute a major class of transition-metal organometallics.[1,2] An interesting but barely known sub-class of these compounds involves low-oxidation state (<+2), electron-rich, polyphenyl derivatives, which contain no π-acceptor ligands and are generally obtained as complexes with ether-solvated alkali-metal ions. A notable feature of these compounds is the possibility of a σ-acceptor interaction of the lithium ions with the central transition-metal atom as suggested by Taube.[3] Such interactions have been reported in a

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