Peterson Olefination Reactions of C-Silylated Phosphoranimines: Synthesis of *P*-Vinyl-Substituted Phosphazene Precursors[1]

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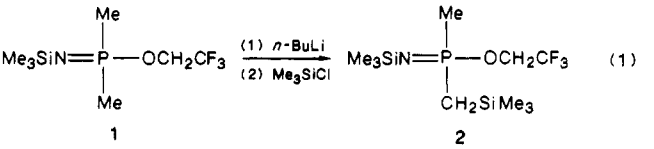
A series of *P*-vinyl-substituted phosphazene precursors have been prepared by the application of the Peterson olefination reaction to the C-silylated phosphoranimines $Me_3SiN{=}P(Me)(X)(CH_2SiMe_3)$ (**2**, X = OCH_2CF_3; **8**, X = OPh). Deprotonation of **2** by treatment with *n*-BuLi, followed by addition of aldehydes, and quenching with Me_3SiCl afforded the phosphoranimine derivatives $Me_3SiN{=}P(Me)(OCH_2CF_3)$-CH=CHR [**3**, R = Ph; **4**, R = *p*-$Me_2NC_6H_4$; **5**, R = *t*-Bu; **6**, R = C_6F_5; **7**, R = CH=CHMe], which contain substituted vinyl groups. Similarly, the *P*-phenoxy compound **8** was converted to the acetaldehyde derivative $Me_3SiN{=}P(Me)(OPh)CH{=}CHMe$ (**9**). The anion derived from **2** underwent similar reactions with ketones to give phosphoranimines bearing trisubstituted vinyl groups, $Me_3SiN{=}P(Me)(OCH_2CF_3)CH{=}CRR'$ [**10**, R = Ph, R′ = Me; **11**, R = Ph, R′ = *n*-Pr; **12**, R = Ph, R′ = CF_3; **13**, R = Me, R′ = CH=CHPh; **14**, R = R′ = $CH{=}CMe_2$; **15**, R, R′ = $C_{12}H_8$ (fluorene)]. These new phosphoranimines **3–7** and **9–15**, which were obtained as distillable liquids in yields of 65–80%, are fully characterized by NMR (^1H, ^{13}C, and ^{31}P) spectroscopy and elemental analyses.

Introduction

The condensation polymerization of appropriate *N*-silylphosphoranimine precursors (e.g. **1**) is an important synthetic route to a relatively new class of inorganic polymers, the poly(alkyl/arylphosphazenes), $[R_2PN]_n$, in which all of the substituents are attached to phosphorus via P–C bonds.[2] Much of the current work on this polymer system is directed toward methods of introducing various functional groups into both the precursors[3] and the preformed polymers.[4] For example, precursors bearing *P*-vinyl substituents are of interest for the eventual preparation of poly(alkyl/arylphosphazenes) that can be subsequently cross-linked to provide useful elastomers. Recently, we have prepared and characterized a series of allyl,[3b] butenyl,[3c] and vinyl[5] substituted phosphoranimines, $Me_3SiN{=}P(R)(OCH_2CF_3)[(CH_2)_nCH{=}CH_2]$ (R = Me, Ph; *n* = 0, 1, 2). These compounds, all of which contain a *terminal* $-CH{=}CH_2$ group, however, undergo thermal cross-linking *during* the condensation polymerization of the *N*-silylphosphoranimine to yield *insoluble* polymeric products that are difficult to characterize.

In an effort to circumvent this problem and thus obtain precursors to *soluble*, *uncross-linked* polymers with pendant vinyl groups, we have turned our attention to the use of substituted vinyl groups (e.g., –CH=CHPh). Access to such compounds is provided by the C-silylated derivatives (e.g., **2**) which are easily prepared by deprotonation/substitution reactions (eq 1) of the parent dimethyl-

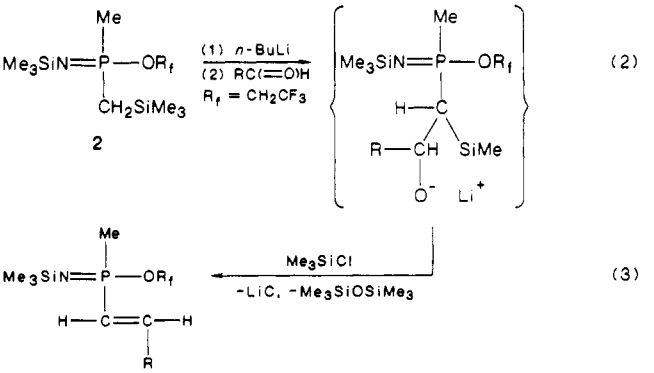


(1)

phosphoranimine **1**.[3a] We report here the synthesis and detailed NMR characterization of a wide variety of vinyl-substituted *N*-silylphosphoranimines via the application of the Peterson olefination reaction[6] to the *C*-silylphosphoranimine **2**.

Results and Discussion

Compound **2** was selected as the primary starting material in this work since we had previously observed that a second deprotonation/silylation reaction readily occurred at the silylmethylene site to afford the bis(trimethylsilyl)methyl derivative $Me_3SiN{=}P(Me)(OCH_2CF_3)[CH(SiMe_3)_2]$.[3a] The facility of this process indicated that **2** would be a good substrate for the Peterson olefination reaction. Indeed, deprotonation of **2** by treatment with *n*-BuLi at –78 °C followed by addition of aldehydes (eq 2) leads ultimately to the isolation of the expected *P*-vinylphosphoranimines **3–7**. Chlorotrimethylsilane was added (eq 3) after the aldehyde in order to quench the



(2)

(3)

3: R = Ph
4: R = *p*-$Me_2NC_6H_4$
5: R = *t*-Bu
6: R = C_6F_5
7: R = CH=CHMe

$LiOSiMe_3$ and prevent it from possibly attacking the Si—N=P—O linkage. In this manner, compounds **3–7**

(1) Taken in part from: Scheide, G. M. Ph.D. Dissertation, Texas Christian University, Fort Worth, TX, 1988.

(2) (a) Neilson, R. H.; Wislan-Neilson, P. *Chem. Rev.* **1988**, *88*, 541. (b) Neilson, R. H.; Hani, R.; Wisian-Neilson, P.; Meister, J. J.; Roy, A. K.; Hagnauer, G. L. *Macromolecules* **1987**, *20*, 910. (c) For a more general review of phosphazene chemistry, see: Allcock, H. R. *Chem. Eng. News* **1985**, *63*(11), 22.

(3) (a) Wettermark, U. G.; Wisian-Neilson, P.; Scheide, G. M.; Neilson, R. H. *Organometallics* **1987**, *6*, 959. (b) Roy, A. K.; Hani, R.; Neilson, R. H.; Wisian-Neilson, P. *Organometallics* **1987**, *6*, 378. (c) Roy, A. K.; Wettermark, U. G.; Scheide, G. M.; Wisian-Neilson, P.; Neilson, R. H. *Phosphorus Sulfur* **1987**, *33*, 147. (d) Wettermark, U. G.; Neilson, R. H. *Inorg. Chem.* **1987**, *26*, 929.

(4) (a) Wisian-Neilson, P.; Ford, R. R.; Neilson, R. H.; Roy, A. K. *Macromolecules* **1986**, *19*, 2089. (b) Wisian-Neilson, P.; Ford, R. R. *Organometallics* **1987**, *6*, 2258. (c) Wisian-Neilson, P.; Ford, R. R. *Macromolecules* **1989**, *22*, 2026. (d) Wisian-Neilson, P.; Schaefer, M. A. *Macromolecules* **1989**, *22*, 2003.

(5) Waters, K. R.; Neilson, R. H. *Phosphorus Sulfur* **1988**, *39*, 189.

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Table I. NMR Spectroscopic Data[a,b]

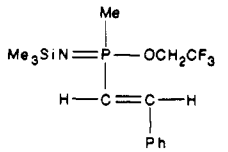
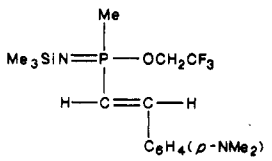
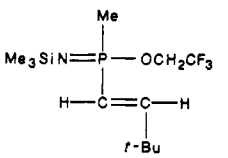
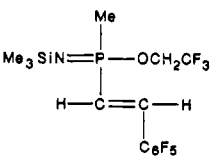
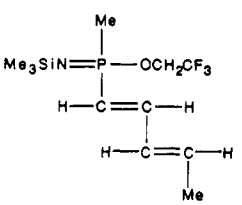
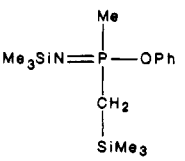
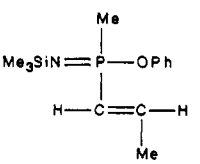
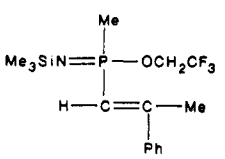
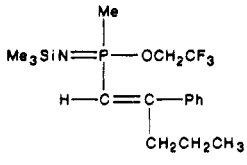
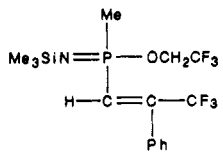
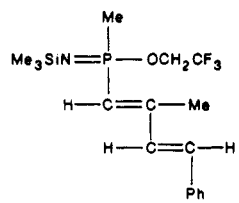
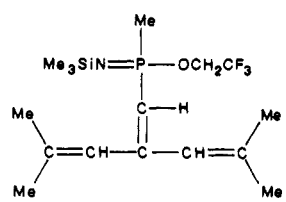
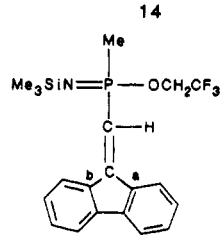
compd	signal	^{1}H NMR δ	^{1}H NMR J_{PH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{13}P NMR δ
 3	Me_3SiN	0.12		3.40	4.0	20.2
	Me_3SiN[c]	0.16		3.76	2.8	22.2[c]
	MeP	1.40	14.3	18.01	96.7	
	MeP[c]	1.60	14.3	18.37	96.9	
	P*CH*	6.39	21.9 {17.2}[d]	120.75	133.7	
	P*CH*[c]	6.33	21.9 {9.3}[d]	129.10	95.4	
	PCH=*CH*	5.98	14.6 {17.2}[d]	135.28	19.6	
	PCH=*CH*[c]	5.93	13.5 {9.2}[d]	147.00	5.4	
	Ph	7.3–7.6[e]		128–130[e]		
 4	Me_3SiN	0.07		3.82	3.4	21.0
	MeP	1.54	14.2	18.60	96.8	22.8[c]
	NMe_2	2.90		40.30		
	P*CH*	6.00	22.1 {17.1}[d]	114.15	136.8	
	PCH=*CH*	7.21	21.9 {17.1}[d]	147.36	5.9	
	Ph C^1			123.18	20.8	
	CH^2	6.6–6.7[e]		112.00		
	CH^3	7.3–7.4[e]		129.36		
	C^4			151.74		
 5	Me_3SiN	−0.05		3.69	3.5	24.0
	Me$_3$C	0.96		28.76		
	MeP	1.38	14.3	18.30	97.2	
	Me_3C			34.99	40.0	
	PCH	5.54	17.1 {16.3}[d]	118.55	130.2	
	PCH=*CH*	6.48	23.6 {17.1}[d]	160.88	2.9	
 6	Me_3SiN	0.03		3.48	3.3	19.6
	MeP	1.55	14.3	18.21	98.2	
	P*CH*	6.68	22.4 {17.6}[d]	130.71	128.1	
	PCH=*CH*	7.29	23.4 {17.6}[d]	130.50	4.5	
	C_6F_5 C^1			129.24	8.8	
	CF^{2-4}			136–147[e]		
 7	Me_3SiN	0.00		3.51	3.6	22.1
	Me_3SiN[c]	−0.01		3.69	3.6	23.5[c]
	MeP	1.43	14.3	18.37	97.0	
	MeP[c]	1.48	14.1	19.38	132.8	
	*Me*C	1.76	5.9	18.54		
	*Me*C[c]	1.78	6.1	18.50		
	PCH	5.34	18.4 {12.6}[d]	119.31	129.3	
	PCH[c]	5.56	23.1 {16.5}[d]	121.29	134.5	
	PCH=*CH*	6.6–7.0[e]		147.16	4.7	
	PCH=*CH*[c]	6.6–7.0[e]		146.95	27.5	
	MeC=*CH*	7.0–7.2[e]		128.33	9.7	
	MeC=*CH*[e]	5.9–6.1[e]		130.99	23.2	
	Me*CH*	5.8–6.0[e]		137.80		
	Me*CH*[c]	5.8–6.0[e]		138.74		
 8	Me_3SiN	−0.07		3.74	3.9	27.78
	Me_3SiC	0.21		0.42	2.6	
	PMe	1.55		20.17	87.4	
	PCH_2	1.2–1.4[e]		22.79	91.9	
	Ph C^1	7.0–7.4[e]		151.78	9.2	
	C^2			121.67	3.7	
	C^3			123.96		
	C^4			129.39		
 9	Me_3SiN	−0.04		3.68	3.8	17.5
	MeP	1.54	13.9	18.56	96.5	
	C*Me*	1.88	1.6 {6.6, 1.6}[d]	19.94	20.3	
	P*CH*	5.88	23.9 {16.8, 1.6}[d]	125.98	134.5	
	PCH=*CH*	6.64	21.3 {16.2, 6.6}[d]	145.93	5.0	
	Ph	7.1–7.3[e]		128–130[e]		
 10	Me_3SiN	0.04		3.53	4.1	22.4
	Me_3SiN[c]	0.10		3.56	3.8	23.5[c]
	MeP	1.02	14.3	19.67	91.0	
	MeP[c]	1.63	14.4	18.39	88.7	
	*Me*C	2.21		18.65	8.1	
	*Me*C[c]	2.49	2.6	28.74	18.9	
	P*CH*	5.85	13.1	122.96	133.4	
	P*CH*[c]	5.97	17.5	120.46	133.7	
	Ph	7.3–7.5[e]		128–130[e]		
	PCH=*C*			142.38	19.8	
	PCH=*C*[c]			140.96	8.1	

Table I (Continued)

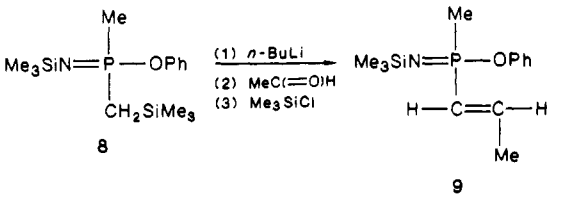
compd	signal	^{1}H NMR δ	^{1}H NMR J_{PH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
 11	Me_3SiN	0.05		3.56	4.0	21.0
	Me_3SiN[c]	0.10		3.61	3.9	23.9[c]
	CH_2CH_3	0.93	{7.3}[d]	13.76		
	CH_2CH_3[c]	0.91	{7.2}[d]	14.10		
	CH_2CH_3	1.4[d]		33.43		
	C—CH_2	2.42	3.0 {7.0}[d]	43.81		
	C—CH_2[c]	2.48	3.0 {7.0}[d]	44.04		
	MeP	1.62	13.8	19.98	94.6	
	MeP[c]	1.50	12.7	20.03	97.2	
	P*CH*	5.83	13.4	120.84	136.0	
	P*CH*[c]	5.79	18.7	122.32	132.2	
	PCH=*C*			141.86	19.8	
	PCH=*C*[c]			161.27	6.0	
	Ph	7.3–7.5[e]		127–129[e]		
 12	Me_3SiN	0.11		3.22	4.1	15.7
	MeP	1.74	15.0	19.64	103.2	
	OCH_2[b]	4.1–4.4[e]		59.60	5.0 {37.3}[f]	
	P*CH*	6.38	7.4	133.81	118.54	
	C—CF_3[b]			123.23	77.8 {277.0}[f]	
	Ph—*C*			143.42	{32.5}[f]	
	Ph	7.0–7.4[e]		128–130[e]		
	CH_2CF_3			123.74	8.5 {277.8}[f]	
 13	Me_3SiN	1.59		3.45	4.0	21.3
	Me_3SiN[c]	1.63		3.58	3.8	22.9[c]
	MeP	1.48	13.5	19.65	97.2	
	MeP[c]	1.61	14.4	19.80	95.2	
	*Me*C	2.14	1.8	14.92	6.6	
	*Me*C[c]	2.32	11.8	22.12	19.2	
	PCH	5.56	18.7	121.51	131.0	
	PCH[c]	5.75	18.4	123.41	135.3	
	HC=CHPh	6.81	{16.9}[d]	132.51	24.4	
	HC=CHPh[c]	6.92	{8.0}[d]	132.79	2.8	
	Ph—*CH*	7.55	{16.8}[d]	134.31	1.8	
	Ph—*CH*[c]	8.16	{8.1}[d]	136.40	1.8	
	PCH=*C*			128.59		
	PCH=*C*[c]			128.70		
	Ph	7.2–7.5[e]		126–128[e]		
 14	Me_3SiN	0.03		3.56	4.2	23.5
	MeP	1.76	13.1	19.16	96.4	
	CMe_2	1.77		19.84		
		1.65		19.96		
	PCH	5.37	18.0	121.42	130.2	
	PCH=*C*			123.29	8.3	
	HC=CMe_2	6.33	1.0	127.98		
	=*C*Me_2			152.96	5.5	
 15	Me_3SiN	0.09		3.32	3.9	18.6
	MeP	1.78	14.2	18.67	101.7	
	P*CH*	6.67	10.7	117.55	128.3	
	PCH=*C*			149.98	5.1	
	C[a]			138.80	18.9	
	C[b]			135.46	5.4	
	other[g]	7.2–8.6[e]		122–128[e]		

[a] Chemical shifts relative to Me_4Si for ^{1}H and ^{13}C spectra and to H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: $CDCl_3$ or CH_2Cl_2. [b] The ^{1}H and ^{13}C NMR spectral data for the P–OCH_2CF_3 group show very little variation throughout this series of compounds. The complete data are given for compound 12 as a representative example. [c] Resonances due to minor diasteromer. [d] J_{HH} values in braces. [e] Complex multiplet. [f] J_{FC} values in braces. [g] Aromatic ^{1}H and ^{13}C resonances.

were obtained in good yields (ca. 65–80%) as thermally stable, distillable liquids that were fully characterized by NMR spectroscopy (Table I) and elemental analyses (Table II).

These reactions generally occurred smoothly at low temperatures except when the hindered reagent trimethylacetaldehyde, *t*-BuC(=O)H, was used. In this case it was necessary to promote the reaction by adding TMEDA (tetramethylethylenediamine) prior to the addition of the aldehyde in order to obtain a high yield of the desired derivative **5**. The reactions usually afforded mixtures of cis and trans isomers with the trans product predominating, as evidenced by the large vinylic H–H coupling constants (Table I). With the more sterically hindered aldehydes [e.g., *t*-BuC(=O)H and C_6F_5C(=O)H], however, only the trans product was obtained.

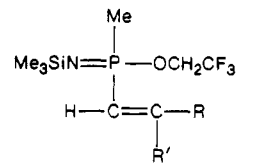
When the same reaction was attempted with acetaldehyde, it was not possible to completely separate the relatively volatile olefinic product from small amounts of unreacted starting material **2**. With this aldehyde, better success was achieved when the less volatile *P*-phenoxy analogue **8** was used as the starting material (eq 4). The

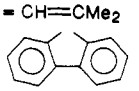


(4)

vinyl-substituted derivative **9** was then readily prepared and purified by fractional distillation. Since we have recently shown that *P-phenoxy*phosporanimines undergo the same type of condensation polymerization as do their *P-(trifluoroethoxy)*phosphoranimine counterparts,[2a,7] it is significant that they also exhibit similar derivative chemistry.

The overall scope of this synthetic method was next extended to the preparation of various *trisubstituted* olefinic products **10–15** by the use of ketones instead of aldehydes in the same process (i.e., eq 2 and 3). Compounds **10–15** were thus obtained in good yields as distillable liquids (Tables I and II).



10: R = Ph, R' = Me
11: R = Ph, R' = *n*-Pr
12: R = Ph, R' = CF_3
13: R = Me, R' = CH=CHPh
14: R = R' = $CH{=}CMe_2$
15: R, R' = 

When α,β-unsaturated carbonyl compounds were employed, the addition of the anion derivative of **2** occurred in a 1,2-manner to afford the conjugated dienes **7** and **13** (derived from crotonaldehyde and *trans*-4-phenyl-3-buten-2-one, respectively) and the cross-conjugated triene **14** (derived from phorone, 2,6-dimethyl-2,5-heptadien-4-one). Each of these products was obtained in a single isomeric form as indicated by the observation of only one peak in their ^{31}P NMR spectra and the appropriate number of signals in their ^{1}H and ^{13}C NMR spectra.

In addition to the development of a general synthesis of vinyl-substituted phosphazene precursors, one of the objectives of this work was to obtain detailed NMR spectroscopic characterization of the products. The availability of such data on these small molecule "monomers" should be very useful for the eventual characterization of their condensation polymers. Most of these compounds exhibit relatively complex NMR patterns (Table I), and, in many cases, there are two diastereomers present. In the case of the trifluoroacetophenone product **12**, the isomers were separated by vacuum distillation and the data for the major isomer, obtained in pure form, is given in Table I.

In some instances, two-dimensional NMR experiments (HOM2DJ and/or HETCOR) were conducted in order to distinguish various J_{HH} and J_{PH} couplings as well as to completely assign some of the ^{13}C NMR resonances. For example, a HETCOR ($^{1}H/^{13}C$ chemical shift correlation) experiment was performed on the *p*-(dimethylamino)-benzaldehyde product **4** in order to conclusively distinguish the signal of the β-vinyl carbon from resonances due to the aromatic ring carbons. Compound **4** was isolated in a 71% yield as predominantly the trans isomer. This was inferred from the large $^{3}J_{HH}$ coupling constant of ~17 Hz. Since the two vinyl protons are trans, this places the phosphorus in a trans relationship to the phenyl ring carbon (C^{1}), and, as a result, the $^{3}J_{PC}$ coupling (20.8 Hz) is greater than the $^{2}J_{PC}$ value (5.9 Hz). This is not an unusual observation in *P*-vinyl systems[5,8] that have trans *P*—CH=CH—*C* configurations, and, in fact, it can be used to determine which isomer is formed in a higher yield. Similar reasoning was applied in the interpretation of the ^{1}H and ^{13}C NMR spectra of the other compounds reported here.

Table II. Preparative and Analytical Data

compd	yield, %	bp, °C (*p*, mmHg)	anal.[a] C	anal.[a] H
3	65	92 (0.20)	51.01 (51.16)	6.33 (6.26)
4	71	85–108 (0.02)	50.65 (50.78)	7.10 (6.92)
5	76	80–85 (4.00)	46.12 (45.70)	8.41 (7.99)
6	73	83 (0.10)	39.90 (39.53)	3.95 (3.79)
7	64	40 (0.03)	43.78 (44.13)	7.19 (7.07)
8	79	60–71 (0.14)	53.85 (53.63)	8.87 (9.00)
9	72	84 (0.05)	58.00 (58.39)	8.36 (8.29)
10	67	80 (0.35)	51.29 (51.56)	6.65 (6.63)
11	58	92 (0.10)	53.86 (54.09)	7.28 (7.21)
12	87	66 (0.05)	44.24 (44.67)	5.13 (4.99)
13	74	125 (0.07)	54.75 (54.38)	6.88 (6.71)
14	71	104 (0.10)	51.80 (52.29)	7.81 (7.95)
15	81	143 (0.03)	58.85 (58.67)	6.03 (5.66)

[a] Calculated values in parentheses.

In summary, this investigation has resulted in the synthesis of several new vinyl-substituted phosphazene precursors by the Peterson olefination of the *C*-silyl reagents. Preliminary results[2a,7a] indicate that some of these products do, in fact, undergo smooth copolymerizations with precursors such as **1** to afford *soluble, uncross-linked* poly(alkyl/arylphosphazenes) containing a predetermined number of vinyl side groups. Details of these polymerizations and the characterization of the resulting polymers will be reported elsewhere.

Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without further purification: *n*-BuLi (hexane solution), 2,2,2-trifluoroacetophenone, phorone, *trans*-4-phenyl-3-buten-2-one, *p*-(dimethylamino)benzaldehyde, pentafluorobenzaldehyde, trimethylacetaldehyde, crotonaldehyde (predominantly trans), 9-fluoroenone, and chlorotrimethylsilane. Acetophenone, benzaldehyde, butyrophenone, and acetaldehyde were distilled prior to use. Ether, hexane, and TMEDA were distilled from calcium hydride prior to use. The starting phosphoranimine **3** was prepared according to the published procedure.[3a] The *P*-phenoxy analogue **8** was prepared in a similar fashion from the corresponding dimethylphosphoranimine $Me_3SiN{=}PMe_2(OPh)$.[7] Proton and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Varian XL-300 spectrometer; $^{31}P\{^{1}H\}$ NMR spectra were obtained on a JEOL FX-60 instrument. The HOM2DJ and HET-COR spectra were obtained by using standard parameters from revision 6.0 of the operating software supplied with the Varian instrument. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The following procedures are representative of those used for the synthesis of the new compounds prepared in this study. Tables

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I and II summarize the physical, analytical, and NMR spectroscopic data.

Preparation of Vinylphosphoranimines 3–15. In a typical experiment, a 250-mL, 3-necked flask, equipped with a magnetic stirrer, N_2 inlet, and a rubber septum, was charged with $Me_3SiN{=}P(OCH_2CF_3)(Me)(CH_2SiMe_3)$ (2) (12.8 g, 40 mmol) and Et_2O (100 mL). The solution was cooled to −78 °C and stirred for 30 min, and then *n*-BuLi (16.0 mL of 2.5 M hexane solution, 40 mmol) was added via syringe. After the mixture was stirred for 1 h, benzaldehyde (4.2 g, 40 mmol) was added via syringe and the mixture was stirred for ca. 3 h at −78 °C before being quenched with chlorotrimethylsilane (5.1 mL, 40 mmol). The solution was allowed to warm to room temperature, and the salts were allowed to settle. The supernatant solution was transferred by cannula to a 1-neck flask, and the salts were washed with hexane. The ether–hexane solvent mixture was removed under reduced pressure. Distillation through a 10-cm column afforded **3** as a colorless liquid (Tables I and II). Compounds **4–7** and **10–15** were prepared according to the same procedure by using the appropriate aldehyde or ketone in place of benzaldehyde. In the case of **9**, the *P*-phenoxyphosphoranimine **8** was used as the starting material.

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Registry No. **2**, 106821-78-7; (*E*)-**3**, 121231-24-1; (*Z*)-**3**, 121231-25-2; (*E*)-**4**, 121231-26-3; (*Z*)-**4**, 121231-27-4; **5**, 121231-28-5; **6**, 121231-29-6; (*E,E*)-**7**, 121231-30-9; (*Z,E*)-**7**, 121231-31-0; **8**, 121231-32-1; **9**, 121231-33-2; (*E*)-**10**, 121252-66-2; (*Z*)-**10**, 121252-67-3; (*E*)-**11**, 121231-34-3; (*Z*)-**11**, 121231-35-4; **12**, 121231-36-5; (*E,E*)-**13**, 121231-37-6; (*Z,E*)-**13**, 121231-38-7; **14**, 121231-39-8; **15**, 121231-40-1; PhC(=O)H, 100-52-7; Me_2N-*p*-$C_6H_4C(=O)H$, 100-10-7; *t*-BuC(=O)H, 630-19-3; $C_6F_5C(=O)H$, 653-37-2; MeCH=CHC(=O)H, 123-73-9; MeC(=O)H, 75-07-0; PhC(=O)Me, 98-86-2; PhC(=O)*n*-Pr, 495-40-9; $PhC(=O)CF_3$, 434-45-7; $Me_3SiN{=}PMe_2(OPh)$, 121231-41-2; *trans*-4-phenyl-3-buten-2-one, 1896-62-4; 2,6-dimethyl-2,5-heptadien-4-one, 504-20-1; 9*H*-fluoren-9-one, 486-25-9.

Chemistry of Metallacyclobutan-3-one (η^3-Oxodimethylenemethane) Complexes. 6.[1] The Synthesis, Structure, and Bonding in $Pt[\eta^3\text{-}CH_2C(O)CH_2](PPh_3)_2{\cdot}CH_2Cl_2$

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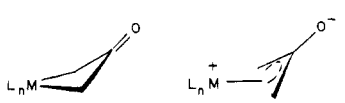
The synthesis of $Pt[\eta^3\text{-}CH_2C(O)CH_2](PPh_3)_2$ (**5**) was accomplished by the reaction of $Pt(\eta^2\text{-}trans\text{-}stilbene)(PPh_3)_2$ with an excess of 3-chloro-1-(trimethylsilyl)propan-2-one or by reaction of an excess of sodium amalgam with *cis*-$PtCl[CH_2C(O)CH_2Cl](PPh_3)_2$. The X-ray structure of **5**·CH_2Cl_2 is comparable to other oxodimethylenemethane–ML_2 complexes and bears a much closer resemblance to π-allyl complexes than to metallacyclobutanones. The crystal data were as follows: a = 13.835 (4) Å, b = 17.560 (9) Å, c = 15.42 (3) Å, β = 109.7 (1)°, monoclinic $P2_1/c$, Z = 4, R' = 0.0532. The geometry of $Pd[CH_2C(O)CH_2](PH_3)_2$ was optimized at the ab initio SCF level and found to be in good agreement with that of **5** and other complexes in this series. The computations reveal a low-energy reaction path for isomerization to a metallacyclobutanone. The energy difference between this optimized transition state and the ground state was found to be 7.9 kcal/mol at the MP(2) level. This is in moderately good agreement with the value of $\Delta G^{\ddagger}$ = 9.2 kcal/mol found for exchange of the syn and anti protons of **5** by ^1H NMR. The ring inversion process in oxodimethylenemethane complexes is compared to an analogous reaction observed for Cp_2M(butadiene) compounds.

Introduction

We have recently shown that a number of metallacyclobutan-3-one complexes contain highly puckered four membered rings[1-6] and bonding descriptions **1** and **2** have



1 **2**

been used to rationalize the structural features. These complexes, described hereafter as η^3-oxodimethylenemethane complexes, display a variation of ring puckering that depends upon the metal, auxiliary ligands, and the substituents on the ring carbons. As a continuation of these studies we wished to examine the parent, unsubstituted η^3-oxodimethylenemethane ligand. Mononuclear examples up to this time were unknown; however, a bridging η^4-oxodimethylenemethane complex has recently been described.[7] In view of our success with push–pull

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